

Degradation of 1,4-dioxane in water using TiO₂ based photocatalytic and H₂O₂/UV processes

H.M. Coleman*, V. Vimonses, G. Leslie, R. Amal

Particles and Catalysis Research Group, Australian Research Council Centre for Functional Nanomaterials, School of Chemical Sciences and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

Available online 20 April 2007

Abstract

1,4-dioxane is a synthetic compound found in industrial effluent and subsequently contaminates water bodies due to its high solubility and high volatility. It is of concern due to its toxic and hazardous nature and has been listed as a class 2B carcinogen. This study involved optimisation of the photocatalytic and H₂O₂/UVC processes for 1,4-dioxane removal. Different photocatalysts and loadings were investigated for the degradation of low concentrations of 1,4-dioxane in water including a commercial P25, a synthesised magnetic photocatalyst and an immobilised sol–gel system. A commercial catalyst (Degussa P25) was the most efficient. A lifetime study of the sol–gel reactor showed that the coating was stable over the time period studied. The optimum H₂O₂ concentration in the H₂O₂/UVC process was found to be 30 ppm. The addition of H₂O₂ to the photocatalytic process for 1,4-dioxane removal caused a decrease in rate for the commercial P25 photocatalyst and an increase in rate for the lab-made magnetic photocatalyst.

© 2007 Elsevier B.V. All rights reserved.

Keywords: 1,4-dioxane; Titanium dioxide photocatalysis; P25; Magnetic photocatalyst; Immobilised sol–gel system; H₂O₂/UV

1. Introduction

1,4-dioxane (1,4-diethylene dioxide) is a ring-structured chemical, C₄H₈O₂, used as an industrial solvent stabiliser that prevents the breakdown of chlorinated solvents during manufacturing processes. It has a propensity to enter the environment and contaminate water supplies because of its high solubility in water and high volatility. Industrial solvents are used in degreasing, electronics, metal finishing, fabric cleaning, pharmaceuticals, pesticides, antifreeze, membranes, paper manufacturing and many other applications. It is classified as a toxic chemical, hazardous pollutant and Class 2B carcinogen by the US Environmental Protection Agency [1]. Testicular tumours were seen in rats in a carcinogenicity study and evidence exists in rats that 1,4-dioxane has effects on certain sex hormones (i.e., is an endocrine disrupter) [2,3]. Similar observations have been made regarding human health effects. Effects included an increased incidence of miscarriages, premature births, maternal toxicosis and decreased birth weight [4]. It is thought to be the chief agent implicated in the cancers suffered by Vietnam military personnel (one of the

principal chemical components of Agent Orange) and is associated with increasing the chances of breast and endometrial cancer, stress-related illnesses and lower sperm counts [5]. 1,4-dioxane is resistant to biodegradation [6] and difficult to remove by conventional water treatment methods. Among the physical technologies capable of removing 1,4-dioxane, the most effective is distillation whereas carbon adsorption and air stripping are inadequate [7]. Due to the economic costs of distillation, chemical treatments have been considered as an alternative [8]. Nevertheless, the oxidation with chlorine or permanganate is ineffective, or could even lead to the formation of more toxic compounds [8–11].

Advanced oxidation technologies (AOTs) or processes (AOPs) are a group of related processes emerging to satisfy the demand for more effective and economical water and air remediation [12]. Various photochemical advanced oxidation processes have been suggested for the oxidation of organic compounds in water and wastewater. The most widely applicable ones are based on generation of hydroxyl radicals via photolysis of hydrogen peroxide, ozone and titanium dioxide [12]. Methods, which have been used in industry, include ultraviolet degradation, H₂O₂/UV and ozonation.

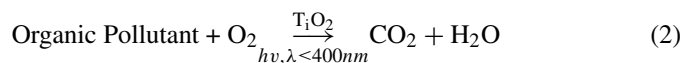
The mechanism most commonly accepted for the photolysis of H₂O₂ is the cleavage of the molecule into hydroxyl radicals

* Corresponding author. Tel.: +61 2 9385 6587; fax: +61 2 9385 5966.
E-mail address: h.coleman@unsw.edu.au (H.M. Coleman).

and other reactive species that attack the organic molecules [13].



Concerning the new oxidation methods under development heterogeneous photocatalysis appears very promising to destroy organic micropollutants, allowing them to reach very low concentrations. Photocatalysis, as the name suggests, involves light and a catalyst to bring about a chemical reaction. In titanium dioxide photocatalysis for water purification, the pollutants are usually organic compounds and, therefore, the overall process can be summarised by the following reaction equation [14,15].



Advanced oxidation processes (e.g. ozone, Fenton's reagent, H_2O_2 /ozone) have been evaluated for the degradation of 1,4-dioxane showing some degree of effectiveness [8]. Neither hydrogen peroxide nor ozone [10,11] alone readily oxidise 1,4-dioxane. Using Fenton's reagent the concentration of 1,4-dioxane and the related total organic carbon content was reduced within 10 h by 97 and 11%, respectively [9]. Ozonation and hydrogen peroxide combined are capable of disinfection but have been observed to form undesirable disinfection by-products [10]. We have previously investigated the use of the advanced oxidation technologies, titanium dioxide photocatalysis, photolysis and H_2O_2 /UVC, for the degradation of 1,4-dioxane in water [16,17]. The results showed that TiO_2 photocatalysis with both UVA and solar light is effective in degrading 1,4-dioxane and is much more efficient than the H_2O_2 /UVC process, UVA or UVC radiation alone. However, previous studies for photocatalysis of 1,4-dioxane in water have all involved a slurry TiO_2 reactor system [8,18–21]. The advantages of a slurry type reactor are the large surface area of catalyst and the intimate contact between the target compounds and the suspended particles, reducing mass transfer effects inherent in an immobilised system. The disadvantages are inhibition of light transmittance by the catalyst and the difficulties encountered when attempting to recover the particles from the treated effluent, due to the need for a solid–liquid separation process which is both time and energy consuming. A recently developed magnetic photocatalyst (MPC) [22], comprising of insulated magnetic core particles coated with a layer of photoactive TiO_2 , provides a solution to this problem. The magnetic core allows for increased ease of separation of the particles from the treated effluent whereby the particles can be easily recovered by the application of a magnetic field. Preparation of the MPC consists of coating colloidal magnetite particles with an initial layer of SiO_2 and a subsequent layer of TiO_2 . The insulative layer (SiO_2) is necessary to prevent interaction between the magnetic cores and the TiO_2 , as any interaction leads to the photodissolution of the cores during irradiation [22]. Immobilisation of TiO_2 on the reactor walls was also investigated in this work as a solution to the solid–liquid separation problem. Immobilisation of the titanium dioxide involved a sol–gel method based on a procedure by Hong [23]. From the point of view of water treatment applications, immobilised TiO_2 has the advantages of easy operation and energy saving, but has a reduced rate of reaction due to mass transfer effects. Currently

many water treatment plants employ the H_2O_2 /UVC process as a stage of treatment. Many research groups have investigated the effect of hydrogen peroxide on photocatalytic degradation of organic contaminants under the optimised catalyst loading conditions [24–26]. Poullos et al. [25] and Machado et al. [26] observed an enhancement whereas others have reported a negative effect of adding hydrogen peroxide for degradation of some organic pollutants [27,28]. This theory was investigated for the degradation of 1,4-dioxane using the P25 and MPC catalysts at varying concentrations of H_2O_2 .

Therefore, the main aim of this paper is to optimise the AOPs previously investigated (photocatalysis and H_2O_2 /UVC processes) for the removal of low concentrations of 1,4-dioxane in water. This involves investigating different photocatalysts (commercial Degussa P25 (P25), lab-made magnetic photocatalyst (MPC) and a sol–gel immobilised system) and loadings, a lifetime study of the immobilised sol–gel reactor, investigating the optimum concentration of H_2O_2 in the H_2O_2 /UVC process and the effect of the addition of H_2O_2 on the photocatalytic system.

2. Experimental

2.1. Reactor set-ups and analytical method

The reactors were constructed using borosilicate glass (or quartz) tubing of 6 mm outer diameter and 1 mm wall thickness and constructed as a spiral reactor. Photocatalysis experiments were carried out in a borosilicate glass reactor with the catalyst in suspension or immobilised. A black-light blue fluorescent lamp (NEC, 20W, $\lambda = 300\text{--}400\text{ nm}$, $\lambda_{\text{max}} = 350\text{ nm}$) was fitted through the centre of the coil. A similar set-up was used for the H_2O_2 /UVC experiments except the reactor was made from quartz and the light source was a slim line germicidal lamp (UV Air Pty Ltd, $\lambda = 254\text{ nm}$). Degussa P25 was employed as the commercial source of TiO_2 in suspension. Preparation of the MPC consists of coating colloidal magnetite particles with an initial layer of SiO_2 and a subsequent layer of TiO_2 , details of which are given in Beydoun et al. [22]. Immobilisation of the titanium dioxide involved a sol–gel method based on a procedure by Hong [23]. The reactor was connected to a peristaltic pump (Masterflex[®] Quick–Load) by Masterflex[®] flexible tubing to enable solution circulation through the reactor at a flow rate of 465 ml/min. A schematic of the reactor set-up can be found in a previous publication [17]. The mineralisation of 1,4-dioxane was monitored by measuring the amount of carbon dioxide generated during the reaction, which was detected by an online conductivity meter [29].

2.2. Experimental procedures

2.2.1. Photocatalysis

Fifty millilitres of photocatalyst suspension (or MilliQ water for the immobilised system) was first introduced into the photoreactor and the pH of the suspension was adjusted to a value of 3 by the addition of perchloric acid (70%, Ajax Chemicals). A pre-determined volume of the 1,4-dioxane (99%, Riedel-

de-Haen) to give a concentration of 0.36 ppm 1,4-dioxane (equivalent to 10 μg carbon) in the reactor, was then injected into the suspension followed by a 10 min mixing period without irradiation to allow dark adsorption of the organic molecules onto the photocatalyst surface. The solution was then irradiated with UV light and the rate of carbon dioxide generation was monitored by an online conductivity meter. This procedure was carried out in duplicate for photocatalysis of 1,4-dioxane in water (0.1 and 1 g/l of P25 and MPC and the sol–gel reactor). A lifetime study for the sol–gel reactor was carried out by repeating the same photocatalytic experiment over the period of time that the reactor was constantly used (three months). The effect of the addition of H_2O_2 (3, 5, 30 ppm) to the photocatalytic systems was also investigated.

2.2.2. $\text{H}_2\text{O}_2/\text{UVC}$

A pre-determined volume of H_2O_2 (to give a concentration of 3–100 ppm H_2O_2) and 1,4-dioxane to give an initial concentration of 0.36 ppm 1,4-dioxane was injected into the reactor containing 50 ml of MilliQ water followed by a 10 min mixing period without irradiation to allow equilibration. The solution was then irradiated with UVC light and the rate of carbon dioxide generation was monitored by an online conductivity meter.

3. Results and discussion

3.1. Effect of photocatalysts and their loadings

Fig. 1 shows the mineralisation curves for the degradation of 1,4-dioxane in water using the P25 catalyst and the MPC catalyst at two different loadings and the immobilised sol–gel reactor. The rates for 50% mineralisation were also calculated and are shown in Table 1.

Comparing photocatalysts, commercial P25 in suspension shows the best performance in degrading 1,4-dioxane which is over 13 times faster than the MPC at the 1 g/l loading and nine times faster at the 0.1 g/l loading (Table 1). The observed kinetic results can be explained by the lower photoactivity of the MPC as well as the differences in particle size and density of the catalysts (see Table 2). The MPC consists of an insulated magnetic core covered by TiO_2 resulting in a larger particle size and

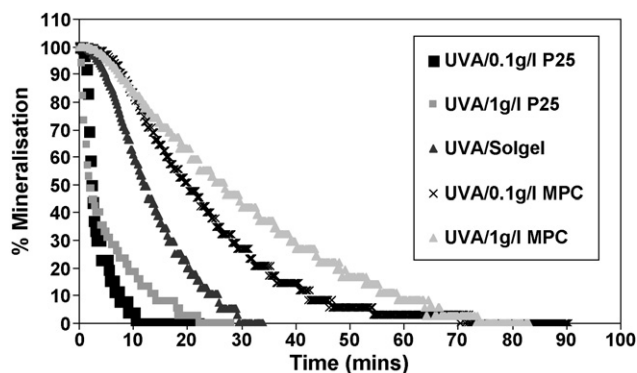


Fig. 1. Mineralisation curves for the degradation of 0.36 ppm 1,4-dioxane in water using different photocatalysts and loadings.

Table 1

Mineralisation rates for 1,4-dioxane for photocatalytic processes investigated

Photocatalytic process	Rate, ($\mu\text{gC}/\text{min}$) \pm standard error
1 g/l commercial P25 photocatalyst	2.42 ± 0.14
0.1 g/l commercial P25 photocatalyst	2.23 ± 0.05
Immobilised (sol–gel)	0.40 ± 0.02
0.1 g/l magnetic photocatalyst	0.24 ± 0.01
1 g/l magnetic photocatalyst	0.18 ± 0.02

density, which gives a lower available particle surface per unit mass for reaction [30]. Similar results have also been shown in previous studies for photocatalytic degradation of sucrose [31] and *Escherichia coli* (*E. coli*) [30,32] in water.

Comparing loadings for each catalyst, 1 g/l was found to be slightly more active than 0.1 g/l for P25 photocatalyst, giving rates of 2.4 and 2.2 $\mu\text{gC}/\text{min}$ for the 50% mineralisation rate, respectively (Table 1). It is well known that 1 g/l of commercial P25 TiO_2 is the optimum loading for the degradation of a wide range of organic substances in water [30,34]. Mehrvar et al. [21] investigated the effect of P25 catalyst loading for 1,4-dioxane degradation and found 1.5 g/l to be the optimum loading, followed closely by 1 g/l. However, this was for much higher concentrations of 1,4-dioxane (27.8 ppm). In this work, the opposite trend was found for the MPC where 0.1 g/l loading showed a small increase in degradation rate, giving a rate of 0.24 $\mu\text{gC}/\text{min}$ compared to 0.18 $\mu\text{gC}/\text{min}$ for 1 g/l (Table 1). It is important to note that the difference in rate between the two loadings for both photocatalysts is not that significant which may be due to the low concentration of 1,4-dioxane under study. It is expected that the amount of holes (h^+) and highly reactive hydroxyl radical (OH^\bullet) generated by 0.1 g/l photocatalyst is sufficient to oxidise and mineralise this low amount of organic pollutant. Also, light scattering by the particles can reduce the amount of light transmitted. The considerably larger MPC particles would therefore give different light scattering properties to P25 particles, thus resulting in a different optimum catalyst loading.

Photocatalysis using the sol–gel reactor was slower compared to that obtained in the P25 suspension reactor (the rate is six times more for the suspension reactor, Table 1). This result is as expected, due to the mass transfer limitation of an immobilised system. The mineralisation rate obtained in the immobilised sol–gel reactor is twice the rate of MPC and when compared with previous reported work [17]; it is 2.5 times faster than the 3 ppm $\text{H}_2\text{O}_2/\text{UVC}$ system and six times faster than UVC alone. It is therefore much more attractive to use an immobilised system for practical and commercial applications, as lengthy and

Table 2

Particle characteristics for the commercial (Degussa P25) and synthesised magnetic TiO_2 photocatalysts [30]

Sample	TiO_2 crystal phase	Particle diameter in suspension (nm)
P25	79% anatase, 21% rutile [33]	200
Magnetic photocatalyst	Anatase (coating)	1060

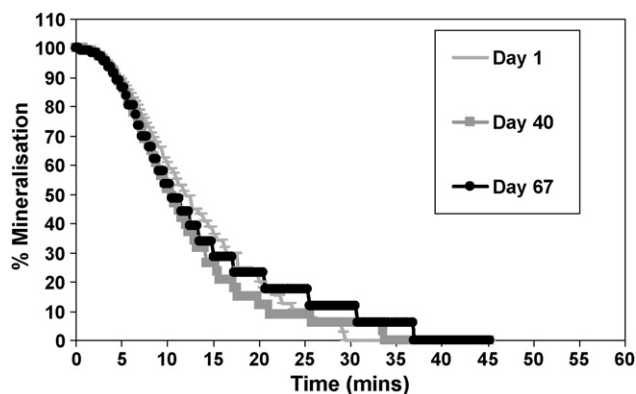


Fig. 2. Mineralisation curves for 0.36 ppm 1,4-dioxane degradation for the lifetime study of the sol-gel reactor.

Table 3

Rates for 0.36 ppm 1,4-dioxane degradation for the lifetime study of the sol-gel reactor

Day	Rate, ($\mu\text{gC}/\text{min}$) \pm standard error
1	0.421 ± 0.002
40	0.480 ± 0.004
67	0.487 ± 0.003

expensive separation steps are eliminated along with the high energy costs required for high energy UVC lamps. This reactor was further studied by conducting a lifetime durability study to determine the effectiveness of the coating.

3.2. Lifetime study of the sol-gel reactor

Fig. 2 shows the mineralisation profiles for the lifetime study of the sol-gel reactor over the time period when it was constantly used for experiments (67 days) and Table 3 shows the rates of reaction. It can be seen clearly that there is no significant difference in degradation rates over time, indicating that the sol-gel reactor is stable under the studied conditions.

3.3. Effect of H_2O_2 concentration in the $\text{H}_2\text{O}_2/\text{UVC}$ process

Fig. 3 shows the effect of H_2O_2 concentration in the $\text{H}_2\text{O}_2/\text{UVC}$ process in the concentration range 3–100 ppm

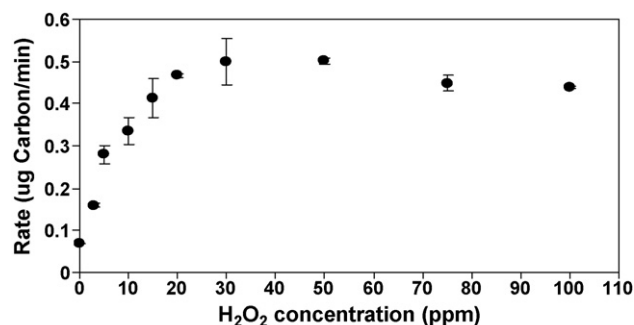


Fig. 3. Mineralisation rates for the effect of H_2O_2 concentration in the $\text{H}_2\text{O}_2/\text{UVC}$ process for the degradation of 0.36 ppm 1,4-dioxane in water.

H_2O_2 . Results are shown as rate of mineralisation at each concentration studied.

The mineralisation rate of 1,4-dioxane increases as the concentration of H_2O_2 increases up to 30 ppm H_2O_2 , which gives the highest mineralisation rate of $0.5 \mu\text{gC}/\text{min}$ (Fig. 3). The concentration beyond this point shows no enhancement to the degradation process and actually starts to decrease when the H_2O_2 concentration is increased beyond 60 ppm. This could be due to an excess of H_2O_2 in the system that can act as a hydroxyl radical scavenger resulting in a decrease in the mineralisation rate [35]. If an excess of H_2O_2 is used, HO^\bullet radicals will produce hydroperoxyl radicals, HOO^\bullet , which are much less reactive [12]. It has also been reported that the optimum concentration of H_2O_2 is dependant on the $\text{H}_2\text{O}_2/\text{contaminant}$ molar ratio [36], therefore the optimum concentration of H_2O_2 will always be dependent on pollutant concentration. Radical-radical recombination as a competitive reaction must also be taken into account:



The optimum rate is comparable with the rate for photocatalysis using the sol-gel reactor ($0.4 \mu\text{gC}/\text{min}$) but is still much less than the P25 suspension reactor ($2.4 \mu\text{gC}/\text{min}$) (4.8 times slower).

3.4. Effect of the addition of H_2O_2 on the photocatalytic process

The results of the effect of the addition of H_2O_2 on the photocatalytic oxidation of dioxane using P25 and MPC systems are shown as rate of mineralisation in Fig. 4.

It can be seen that the addition of 3 ppm H_2O_2 to the P25/UVA system increases the rate slightly. It is known that H_2O_2 can enhance the reaction by providing additional hydroxyl radicals either through trapping of photogenerated electrons (Eqs. (4) and (5)) [23] and/or photolysis of H_2O_2 (Eq. (6)).

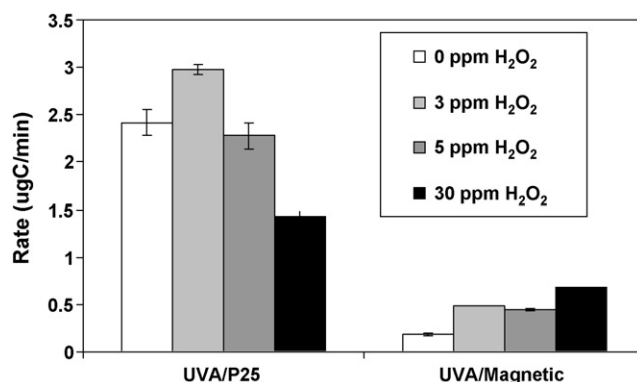
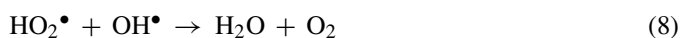
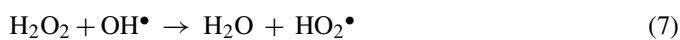


Fig. 4. Rates of mineralisation for photocatalytic processes with H_2O_2 addition.

However, it is interesting to note that the addition of 5 ppm H_2O_2 actually decreases the rate slightly. This may be due to a slight excess of hydroxyl radicals at this concentration, which will cause hydroperoxyl radicals to be formed (HOO^\bullet) and are much less reactive. As mentioned earlier, it has been shown previously that the optimum concentration of H_2O_2 is dependent on the H_2O_2 /contaminant molar ratio [35] indicating that 3 ppm H_2O_2 may be the optimum concentration to be added to the photocatalytic system for the degradation of 0.36 ppm 1,4-dioxane using P25 and anything higher than this will cause a decrease in reaction rate. Furthermore, the addition of 30 ppm H_2O_2 to the P25 photocatalytic system decreases the rate substantially (1.7 times). The decrease may be a combination of formation of less reactive hydroperoxyl radicals (Eq. (7)) and also due to competition of hydrogen peroxide with the contaminants for conduction band electrons [23]. Hydrogen peroxide has been found to consume hydroxyl radicals according to the following equations [37]:



Radical–radical recombination also needs to be taken into account (see Eq. (3) above).

The effect of the addition of H_2O_2 to the MPC system is quite different. Even a small amount (3 or 5 ppm) of H_2O_2 causes an increase in rate of 2.5 times and the addition of 30 ppm H_2O_2 increases the rate by 3.8 times. These results are probably due to the low activity of the MPC compared to P25 in generating hydroxyl radicals, which means that addition of H_2O_2 will cause the rates to increase due to the increased number of hydroxyl radicals present for reaction. As reported, hydroxyl radicals can be generated when H_2O_2 traps photogenerated electrons (Eq. (5) above) [38]. This trapping would also help suppress recombination of electron-hole pairs produced at the activated catalyst surface [23]. It is also interesting to note that previous studies of degradation of pulp and paper mill effluents suggested that the common explanation that H_2O_2 acted simply as an alternate electron acceptor could not be sustained in some cases. It appears that H_2O_2 plays a role in initiation of radical chain reactions that persist after the initial dose of H_2O_2 has been consumed [39].

In general, the role of H_2O_2 in the photocatalytic degradation of organic contaminants is still unclear and has been reported to have either positive or negative effects depending on the radiation properties (i.e. wavelength, intensity), solution pH, physiochemical properties of the contaminant, type of catalyst and the oxidant to contaminant ratio [23]. It is therefore necessary to consider all these parameters within a H_2O_2 /UV/photocatalyst system.

4. Conclusions

TiO_2 photocatalysis completely mineralises 1,4-dioxane to CO_2 in P25 suspension, MPC suspension and sol–gel reactors as does the H_2O_2 /UVC process. Commercial P25 photocatalyst with UVA radiation shows the best performance in degrading 0.36 ppm 1,4-dioxane in water. One gram per litre TiO_2 loading

is the optimum loading for the P25 photocatalyst although 0.1 g/l also gives a very similar rate, which may be due to the low concentrations of 1,4-dioxane studied. However, the opposite trend was noted for the MPC with 0.1 g/l being the optimum loading. The differing trend was attributed to the particle size and the light scattering characteristics of the photocatalysts. The sol–gel TiO_2 immobilised reactor shows promise from an industrial point of view with the sol–gel coating remaining stable over the time period studied. The optimum H_2O_2 concentration giving the highest degradation rate in the H_2O_2 /UVC process in the system studied was 30 ppm, giving a rate comparable to the photocatalytic sol–gel system. The addition of H_2O_2 to the photocatalytic system generally decreased the rate for the P25 reactor, but increased the rate for the MPC. The observations were attributed to a combination of photocatalyst activity, hydroxyl radical formation from hydrogen peroxide trapping electrons, formation of HOO^\bullet radicals, radical–radical recombination and optimum H_2O_2 /contaminant molar ratios.

Advanced oxidation technologies such as photocatalysis and H_2O_2 /UVC show considerable promise for the complete mineralisation of micropollutants such as 1,4-dioxane in water. It is highly encouraging that these processes are effective for complete removal of such harmful substances in our water supplies where other more conventional treatments have failed. It is imperative that research into these processes for these applications are continued in order to optimise the systems studied particularly from an industrial application point of view. The successful and efficient degradation of these compounds will potentially provide cheaper and cleaner means of removing them from groundwater, wastewaters and drinking water.

Acknowledgements

Australian Research Council Linkage project, National Water Research Institute, USA, Orange County Water District, USA and CH2M Hill, Australia for funding.

References

- [1] M. Sittig (Ed.), Handbook of Toxic and Hazardous Chemicals and Carcinogens, Noyes Publishers, NJ, 1991.
- [2] M.G. Stepanov, A.V. Arutyunyan, Impaired central regulation of reproductive function due to unfavorable environmental factors, *Vopr. Med. Khim.* 41 (5) (1995) 33–35 (in Russian).
- [3] NICNAS (National Industrial Chemicals Notification and Assessment Scheme), 1,4-Dioxane, Priority Existing Chemical No.7, Full public Report, June 1998.
- [4] E.K. Ailamazian, Effect of ecological factors on the course of pregnancy, *Vestn. Akad. Med. Nauk.* 7 (1990) 23–25 (Russian).
- [5] J. Shaw, Common Sense Nutrition, <http://www.common-sense-nutrition.com/dioxane.htm>, accessed 6/11/06.
- [6] P.H. Howard, Solvents, in: P.H. Howard (Ed.), Handbook of Environmental Fate and Exposure Data For Organic Chemicals, Lewis Publishers, Michigan, USA, 1990, pp. 216–221.
- [7] G.W. Ware (Ed.), p-Dioxane in Reviews of Environmental Contamination and Technology, vol. 106, Springer Verlag, New York, 1988, pp. 113–121.
- [8] V. Maurino, P. Calza, C. Minero, E. Pelizzetti, E.M. Vincenti, Light-assisted 1,4-dioxane degradation, *Chemosphere* 35 (11) (1997) 2675–2688.
- [9] G.M. Klecka, S.J. Gonsoir, Removal of 1,4-dioxane from wastewater, *J. Hazard. Mater.* 13 (1986) 161–168.

- [10] C.D. Adams, P.A. Scanlan, N.D. Secrist, Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone, *Environ. Sci. Technol.* 28 (1994) 1812–1818.
- [11] J. Hoigne, H. Bader, Rate constants of reaction of ozone with organic and inorganic compounds in water I. Non dissociating organic compounds, *Water Res.* 17 (1983) 173–183.
- [12] J. Prousek, Advanced oxidation processes for water treatment. Photochemical processes, *Chem. Listy* 90 (5) (1996) 307–315.
- [13] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [14] A. Mills, R.H. Davies, D. Worsley, Water purification by semiconductor photocatalysis, *Chem. Soc. Rev.* 22 (1993) 417–425.
- [15] A. Wold, Photocatalytic properties of TiO₂, *Chem. Mater.* 5 (1993) 280–283.
- [16] H.M. Coleman, H. Hon, R. Amal, G. Leslie, M. Wehner, S. Fitzsimmons, Removal of oestrogenic and carcinogenic substances from water using alternative water treatment methods, in: *Proceedings of AWA Conference on Contaminants of Concern*, Canberra, Australia 22nd–23rd June, 2005.
- [17] H.M. Coleman, V. Vimonses, G. Leslie, R. Amal, Removal of contaminants of concern in water using advanced oxidation techniques, *Water Sci. Technol.*, 2006, in press.
- [18] R.R. Hill, G.E. Jeffs, D.R. Roberts, Photocatalytic degradation of 1,4-dioxane in aqueous solution, *J. Photochem. Photobiol., A* 108 (1997) 55–58.
- [19] M. Mehrvar, W.A. Anderson, M. Moo-Young, Photocatalytic degradation of aqueous tetrahydrofuran, 1,4-dioxane and their mixture with TiO₂, *Int. J. Photoenergy* 2 (2000) 67–80.
- [20] M. Mehrvar, W.A. Anderson, M. Moo-Young, Photocatalytic degradation of aqueous organic solvents in the presence of hydroxyl radical scavengers, *Int. J. Photoenergy* 3 (2001) 188–191.
- [21] M. Mehrvar, W.A. Anderson, M. Moo-Young, Comparison of the photoactivities of two commercial titanium dioxide powders in the degradation of 1,4-dioxane, *Int. J. Photoenergy* 4 (2002) 142–146.
- [22] D. Beydoun, R. Amal, G.K.–C. Low, S. McEvoy, Novel photocatalyst: titania-coated magnetite. Activity and photodissolution, *J. Phys. Chem. B* 104 (18) (2000) 4387–4396.
- [23] Y.J. Hong, Preparation and characterization of sol–gel derived peroxo titania and its application for nano-crystalline dye sensitized solar cell, Ph.D. thesis, University of New South Wales, Sydney, Australia, 2002.
- [24] M.F. Kabir, E. Vaisman, C.H. Langford, A. Kantzas, Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification, *Chem. Eng. J.* 118 (2006) 207–212.
- [25] I. Poullos, E. Micropoulou, R. Panou, E. Kostopoulou, Photooxidation of eosin Y in the presence of semiconducting oxides, *Appl. Catal., B* 41 (2003) 345–355.
- [26] A.E.H. Machado, J.A. de Miranda, R.F. de Freitas, E.T.F.M. Duarte, L.F. Ferreira, Y.D.T. Albuquerque, R. Rugeiro, C. Sattler, L. de Oliveria, Destruction of the organic matter present in effluent from a cellulose and paper industry using photocatalysis, *J. Photochem. Photobiol., A* 155 (2003) 231–241.
- [27] H.D. Chun, J.K. Park, Photocatalytic oxidation of chlorinated organic compounds over TiO₂ membrane coated on glass tube, *Hazard. Waste Hazard. Mater.* 11 (1994) 501–510.
- [28] R. Dillert, I. Fonefett, U. Siebers, D. Bahnemann, Photocatalytic degradation of trinitrotoluene and trinitrobenzene: influence of hydrogen peroxide, *J. Photochem. Photobiol., A* 94 (1996) 231–236.
- [29] R.W. Matthews, Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide, *J. Catal.* 111 (1988) 264–272.
- [30] H.M. Coleman, C.P. Marquis, J.A. Scott, S.S. Chin, R. Amal, Bactericidal effects of titanium dioxide-based photocatalysts, *Chem. Eng. J.* 113 (2005) 55–63.
- [31] S. Watson, D. Beydoun, R. Amal, Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO₂ crystals onto a magnetic core, *J. Photochem. Photobiol., A* 148 (1–3) (2002) 303–313.
- [32] H.M. Coleman, R. Amal, C.M. Marquis, Photocatalysis for the removal of contaminants of concern – endocrine disrupters and pathogens, in: *Proceedings of EPSRC International Conference on Developments in Water Treatment and Supply*, York, UK 5th–6th July 2005c, 2005.
- [33] K. Chiang, R. Amal, T. Tran, Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide, *Adv. Environ. Res.* 6 (4) (2002) 471–485.
- [34] C. Tang, V. Chen, The photocatalytic degradation of reactive black 5 using TiO₂/UV in an annular photoreactor, *Water Res.* 38 (2004) 2775–2781.
- [35] E. Evgenidou, K. Fytianos, I. Poullos, Photocatalytic oxidation of dimethoate in aqueous solutions, *J. Photochem. Photobiol., A* 175 (2005) 29–38.
- [36] S. Malato, J. Blanco, M.I. Maldonado, P. Fernandez-Ibanez, A. Campos, Optimising solar photocatalytic mineralisation of pesticides by adding inorganic oxidising species; application to the recycling of pesticide containers, *Appl. Catal., B* 28 (2000) 163–174.
- [37] H. Yang, K. Zhang, R. Shi, X. Li, X. Dong, Y. Yu, Sol–gel synthesis of TiO₂ nanoparticles and photocatalytic degradation of methyl orange in aqueous TiO₂ suspensions, *J. Alloys Compd.* 413 (2006) 302–306.
- [38] F. Haque, E. Vaisman, C.H. Langford, A. Kantzas, Preparation and performance of integrated photocatalyst adsorbent (IPCA) employed to degrade model organic compounds in synthetic wastewater, *J. Photochem. Photobiol., A* 169 (2005) 21–27.
- [39] E. Vaisman, A. Starosud, C.H. Langford, Application of photocatalysis for oxidation of organics and decolourization of pulp mill effluents, in: *Proceedings of Sustainable Forest Management Network Conference Science and Practice: Sustaining the Boreal Forest*, Edmonton, Alberta, February 14–17, 1999, pp. 301–306.