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The photocatalytic removal of bacterial pollutants from drinking water

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Abstract

Pathogens in drinking water supplies can be removed by sand filtration followed by chlorine or ozone disinfection. These processes reduce the possibility of any pathogens entering the drinking water distribution network. However, there is doubt about the ability of these methods to remove chlorine resistant microorganisms including protozoan oocysts. Concern has also been raised about the production of disinfection by-products following the chlorination process. Titanium dioxide (TiO_2) photocatalysis is a possible alternative/complementary drinking water treatment method.

TiO_2 electrodes were prepared by the electrophoretic immobilisation of TiO_2 powder (Aldrich and Degussa P25). These electrodes were tested for their photocatalytic bactericidal efficiency. *E. coli* K12 was used as a model test organism. The rate of disinfection was greater for the P25 electrode compared to the Aldrich electrode under open circuit conditions. The application of an electrical bias to the working electrode increased the rate of disinfection by ∼40% for the P25 electrode and ∼80% for the Aldrich electrode. The effect of applied potential was more pronounced under conditions of high initial bacterial cell loading and high light intensities. Bacterial recovery did not occur up to 48 h after disinfection.

Keywords: Titanium dioxide; Photocatalysis; *E. coli*; Photoelectrochemistry

1. Introduction

Alternative technologies are being investigated for the disinfection of water intended for human consumption, because commonly used potable water disinfection methods, e.g. chlorination and ozonation, are not efficient for the inactivation of some pathogens, e.g. *Cyptosporidium* [1]. There have been a number of outbreaks of cryptosporidiosis associated with the consumption of treated drinking water [2,3]. Concerns have also been raised about secondary pollution from disinfection by-products. Chlorination in the presence of organic material results in the production of chlorinated organic compounds, e.g. trihalomethanes (THMs) which are mutagenic [4].

Titanium dioxide (TiO_2) photocatalysis is a possible alternative or complementary technology to current drinking water treatment processes. TiO_2 photocatalysis does not require the addition of consumable chemicals and does not produce hazardous waste products. There have been many publications reporting the application of photocatalysis towards water remediation with recent review papers summarising the photocatalytic removal of organic, inorganic and microbial pollutants [5–7]. When TiO_2 particles are illuminated with near UV irradiation ($\lambda < 400$ nm), electron hole pairs are generated within the metal oxide semiconductor. The valence band hole has a very positive reduction potential and is capable of oxidising water, or hydroxide ions, to form hydroxyl radicals in water [7]. Hydroxyl radicals are known to be powerful, indiscriminate oxidising agents [8]. Mechanisms for the bactericidal action of TiO_2 photocatalysis have been proposed by a number of authors [9–13] and reviewed by Blake et al. [5]. Results from the above studies suggest that the cell membrane is the primary site of reactive oxygen species attack. Oxidative attack of the cell membrane leads to lipid peroxidation. The bacterial cell membrane provides an attachment site for cellular respiration and when damaged beyond repair respiration ceases [14]. The combination of cell membrane damage, and further oxidative attack of internal cellular components, ultimately results in cell death [5].

TiO_2 powder is commonly employed in the laboratory in the form of a slurry or suspension. This method yields a high catalyst surface area to volume ratio for pollutant hydroxyl radical interaction, but the catalyst must be removed by a post-treatment separation stage, which may not be cost effective on a large scale. Immobilisation of the catalyst removes the need for post-treatment separation. However,

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this method is associated with a decrease in surface area to volume ratio and decreased mass transfer resulting in a reduction in the pollutant degradation rate. The application of a small electrical bias to the immobilised film has been shown to increase the rate of degradation of both chemical [15–18] and microbial [19] pollutants. Kim and Anderson [15] reported the photoelectrocatalytic degradation of formic acid concluding that the application of 0 V vs. saturated calomel electrode (SCE) resulted in optimum degradation enhancement. The degradation of 4-chlorophenol was studied by Vindogopal and Kamat [17] who reported a 10-fold increase in the degradation rate, under anaerobic conditions and with the application of 0.83 V vs. SCE to the working electrode (WE). Rodriguez et al. [18] reported an increase in the degradation rate of 4-chlorophenol with applied potential using sputtered TiO_2 films. Butterfield et al. described the photoelectrochemical disinfection of *Escherichia coli* and *Clostridium perfringens*. An increase in the percentage disinfection was observed upon the application of an electrical bias [19].

The drinking water treatment industry uses a system of surrogate bacterial indicators in order to assess the efficiency of the disinfection process. *E. coli* is extensively used as a treatment efficiency indicator and if not detected the treated water is regarded as free from faecal contamination [20]. Photocatalytic inactivation studies using *E. coli* as a model bacterial pollutant have been previously carried out. Disinfection rates or inactivation times are usually not comparable from study to study due to a wide range of operational parameters and reactor configurations used in different laboratories. Reactor configurations range from small volume Pyrex beakers and Petri dishes, typically 1–10 cm^3, illuminated from the side or top by a tubular lamp [11,12,21,22] to the modification of commercial UV disinfection apparatus [23] and the design and construction of large volume immobilised flow through reactors [24].

This paper reports the disinfection of water containing *E. coli*, using immobilised commercially available TiO_2 powders, in order to assess the potential of photocatalytic and electrochemically assisted photocatalytic disinfection as an alternative to the conventional water treatment systems.

2. Materials and methods

2.1. TiO_2 electrode preparation

TiO_2 powders Degussa P25 (70% anatase, 30% rutile) and Aldrich (99.9% anatase) were electrophoretically immobilised onto titanium foil by a method previously described [25]. The coated substrate area was ~1.35 cm^2 with a catalysis loading of ~0.8 mg cm^{-2}. Electrical contact to the conducting support was made by the attachment of a copper wire using silver loaded conducting epoxy (Circuitworks).

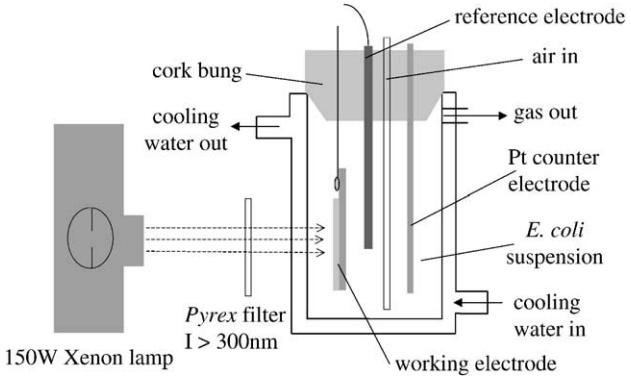

Fig. 1. Quartz water jacketed photocatalytic reactor.

The contact and any uncoated substrate were insulated using a layer of negative photoresist (Casio Chemicals).

2.2. Photocatalytic reactor configuration

A 150 W xenon arc lamp (Applied Photophysics) was used as the illumination source, with a borosilicate glass filter to remove wavelengths below 300 nm. Ferioxalate actinometry was used to measure the light intensity incident on the electrode using a UG11 300–400 nm band pass filter (Speirs Robertson) [26]. TiO_2/Ti electrodes were positioned in a quartz water-jacketed reactor 6 cm from the lamp, see Fig. 1. The reactor was thermostatically controlled at $20 \pm 2\,^{\circ}C$ and the solution was stirred using a small magnetic flea. The solution was air sparged, using an aquarium pump, at flow rate of 900 $cm^3\,min^{-1}$. For deoxygenated conditions, the solution was sparged with oxygen-free nitrogen (OFN) at 900 $cm^{-3}\,min^{-1}$.

Experiments were carried out using both Degussa P25- and Aldrich-coated electrodes. Quarter strength Ringers solution (Oxoid) was used as the bacterial suspension medium, consisting of 2.25×10^3 mg dm^{-3} NaCl, 1.05×10^2 mg dm^{-3} KCl, 1.2×10^2 mg dm^{-3} $CaCl_2$ and 50 mg dm^{-3} $NaHCO_3$ in distilled water.

In a typical experiment, 10 cm^3 of bacterial suspension in Ringers solution was placed in the reactor in the dark for 10 min with air sparging. At time zero, a 10 μl sample was removed and the electrode illuminated; further samples were removed at 10 min intervals.

2.3. Electrochemically assisted photocatalysis (EAP)

The quartz cell was used as a one-compartment photoelectrochemical cell to investigate the effect of EAP. The TiO_2/Ti foil electrode acted as the WE. The counter-electrode (CE) was a platinum wire and the reference electrode (RE), a saturated calomel electrode (Thermo Russell). Potentiostatic control was effected by using a potentiostat with PC control (Sycopel AEW2). A fixed potential of +1000 mV vs. SCE was applied to the WE. The photocurrent was recorded against time for the duration of the experiment.

2.4. Bacterial growth and detection

E. coli K12 was aerobically subcultured overnight from stock suspension in Luria Bertani (LB) medium. Components of LB medium included sodium chloride (Sigma) 10.0 g, tryptone (Difco) 10.0 g and yeast extract (Difco) 5.0 g in 1 dm^3 distilled water, corrected to pH 7 and autoclaved at 121 °C for 20 min. The culture absorbance at 520 nm was used as an index of cell density allowing prediction of the initial bacterial cell loading. The cells were harvested by centrifugation (at 5000 rpm for 10 min) and washed three times in 1/4 strength Ringers solution before resuspension in Ringers solution at an initial cell count of approximately 5×10^5 cells cm^{-3}. Samples removed from the photocatalytic reactor were diluted appropriately in Ringers solution and plated onto LB agar, LB meduim supplemented with 20 g dm^{-3} bactoagar (Difco) [27]. Plates were incubated for 24 ± 4 h at 37 °C and colony-forming units (CFUs) were visually identified and reported as average CFU cm^{-3}.

2.5. Bacterial regrowth study

In order to assess the ability of bacteria to undergo repair and regrow after photocatalytic disinfection, experiments were set up using a Degussa foil electrode under standard conditions, light intensity 2.8×10^{-8} Einsteins cm^{-2} s^{-1}, initial bacterial cell loading $\sim 5 \times 10^5$ CFU cm^{-3}. The photocatalytic inactivation of the bacterial cells was assessed by removing samples every 15 min for 120 min and plating onto LB agar as before. After 120 min treatment, the contents of the photocatalytic reactor were aseptically removed to a sterile vessel. The disinfected sample was kept in dark at room temperature to allow bacterial repair to occur. 100 μl aliquots were withdrawn and plated onto LB agar at intervals between 10 min and 48 h after disinfection. In order to ensure detection of any recovered cells, samples were transferred to LB medium to allow reproduction to larger numbers. 1 cm^3 aliquots were aseptically removed from the sterile vessel and transferred to 15 cm^3 of LB medium at 12, 24, 36 and 48 h after disinfection. Control experiments were carried out with the addition of 1 cm^3 of sterile distilled water (negative control) and 1 cm^3 of untreated bacterial suspension (positive control) to LB medium. All samples were incubated for 24 h at 37 °C. The absorbance at 520 nm was followed during the incubation of the LB medium samples, as an indicator of bacterial growth. After 24 h incubation, 100 μl samples were plated onto LB agar to confirm *E. coli* regrowth. The experiment was repeated in triplicate.

3. Results

3.1. Photocatalytic disinfection of E. coli cells

The percentage survival of *E. coli* cells vs. time for the open circuit electrodes is shown in Fig. 2. Following an initial lag phase, in the first 20 min, the rate of disinfection followed zero order kinetics. Disinfection rates were calculated using the data points between 20 and 60 min. In the absence of TiO_2 and/or UVA, disinfection was not observed. Bacterial inactivation occurred at a faster rate on the Degussa film.

3.2. Control experiments

Fig. 3 shows the results of the control experiments. No significant bacterial inactivation was observed in the pres-

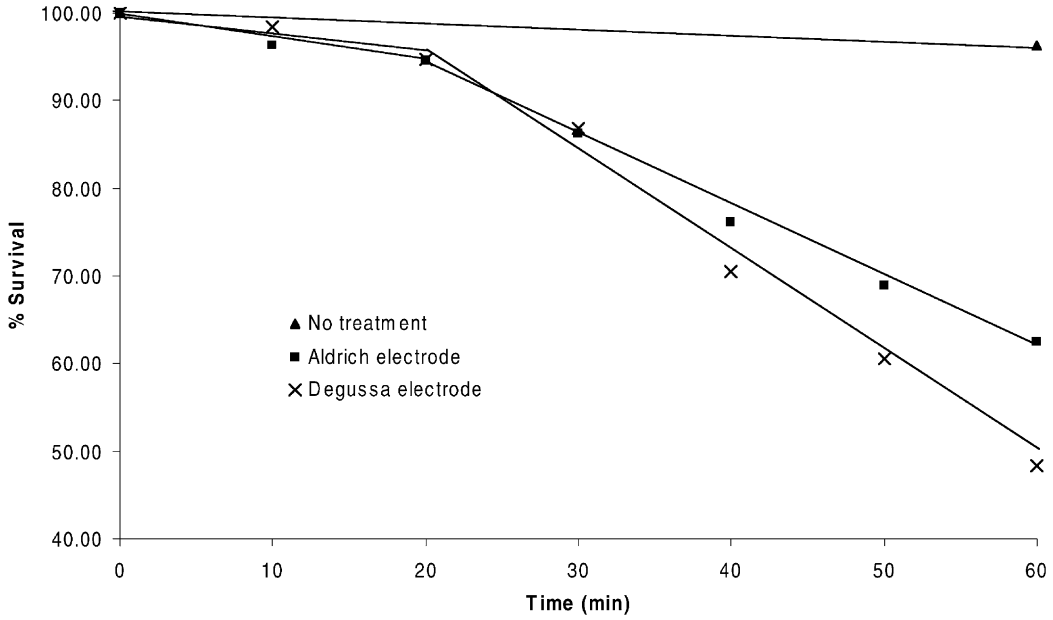

Fig. 2. Photocatalytic inactivation of *E. coli* using Degussa and Aldrich TiO_2 electrodes. Percentage bacterial survival is plotted against disinfection time.

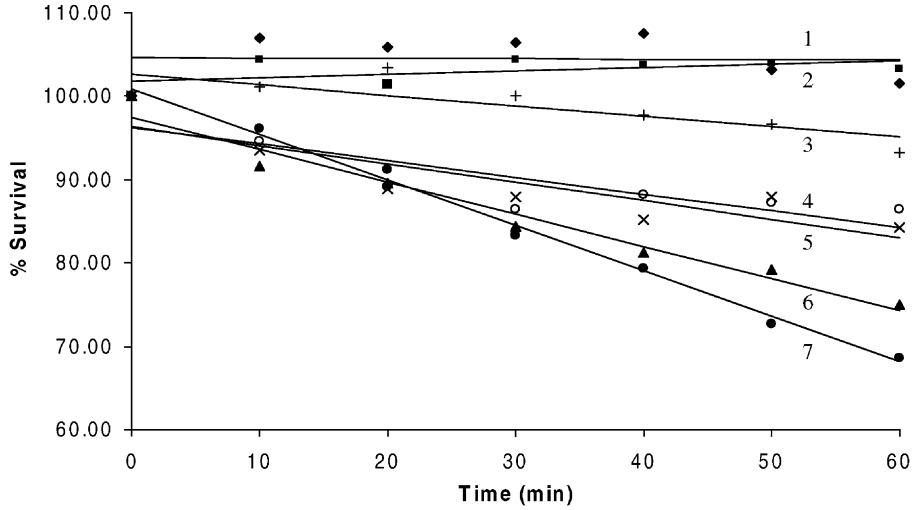

Fig. 3. Control experimentation. Percentage survival plotted against disinfection time. (1) No treatment, (2) TiO_2 alone, (3) TiO_2 + UVA + OFN sparging, (4) TiO_2 + air sparging, (5) air sparging only, (6) UVA only, (7) UVA + air sparging.

ence of TiO_2 in the dark. Disinfection occurred under UVA illumination without TiO_2, in both aerobic and anaerobic conditions.

3.3. Electrochemically assisted photocatalysis

Fig. 4 compares the rate of disinfection with the application of 1000 mV (SCE) to the working electrode in comparison to that of open circuit conditions. A significant increase in the disinfection rate of both films was observed. The rate increased with EAP by ∼40% for Degussa electrode and ∼80% for Aldrich electrode.

3.4. Effect of initial cell loading

Fig. 5 shows the effect of initial cell loading on the rate of disinfection for the Degussa electrode. As the initial cell loading increases the rate of disinfection increases. The effect of EAP was more pronounced at higher initial bacterial cell loading.

3.5. The effect of light intensity

The effect of light intensity on the rate of disinfection was studied at incident light intensities between 1.5×10^{-8} and

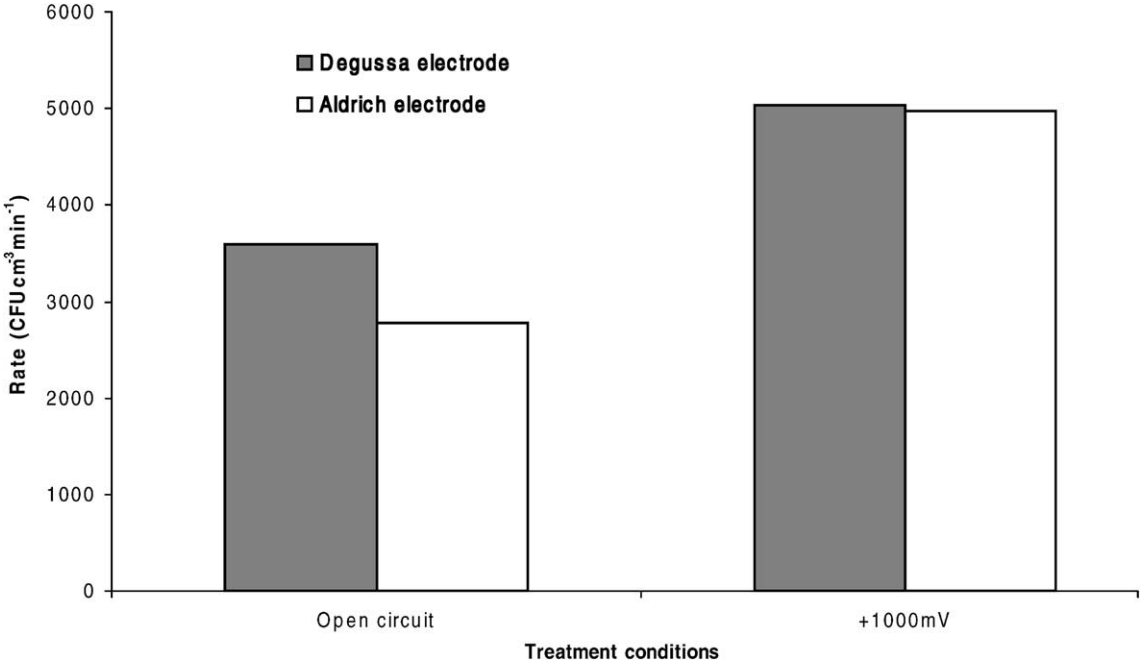

Fig. 4. Disinfection rates during photocatalytic and electrochemically assisted photocatalytic disinfection of *E. coli* on Degussa and Aldrich TiO_2 electrodes.

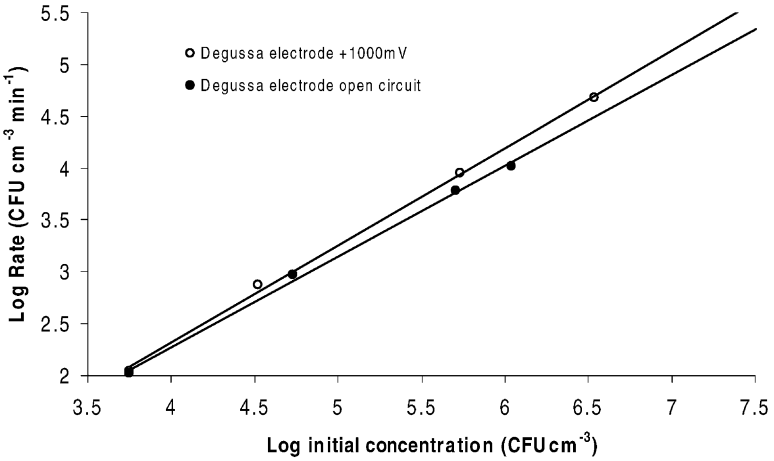

Fig. 5. Double log plot of rate of disinfection vs. initial bacterial cell loading during photocatalytic and electrochemically assisted photocatalytic experimentation.

4×10^{-8} Einsteins $cm^{-2}\ s^{-1}$ (Fig. 6). The rate of disinfection increased with increasing light intensity. EAP increased the rate of disinfection compared to the open circuit electrode at all light intensities studied. The effect of EAP was more pronounced at higher light intensities.

3.6. Bacterial recovery

After 120 min illumination, 99.996% of the initial bacterial cells had been inactivated. Bacterial growth was not detected by the absorbance or plating methods from any of the samples, with the exception of the positive control.

3.7. Photocurrent response of TiO_2 electrodes

Table 1 shows the steady-state photocurrent measured during the short circuit and fixed potential experiments. The illumination of the TiO_2-coated electrodes resulted in the production of anodic photocurrent. Photocurrents were higher for the Degussa electrodes when compared to the Aldrich electrodes.

Table 1
Effect of illumination on the steady-state photocurrent[a]

	Degussa foil electrode photocurrent (μA)	Aldrich foil electrode photocurrent (μA)
Dark	0	0
Light SC[b]	14	NM[c]
Light + 1000 mV	151	57

[a] Conditions: bacterial cell loading $\sim 5 \times 10^5$ CFU cm^{-3}, light intensity 2.8×10^{-8} Einsteins $cm^{-2}\ s^{-1}$.
[b] Short circuit conditions.
[c] Not measured.

Table 2 shows the steady-state photocurrent of the Degussa electrode in solutions with different initial bacterial cell loading. The photocurrent response was unaffected by the initial bacterial cell concentration.

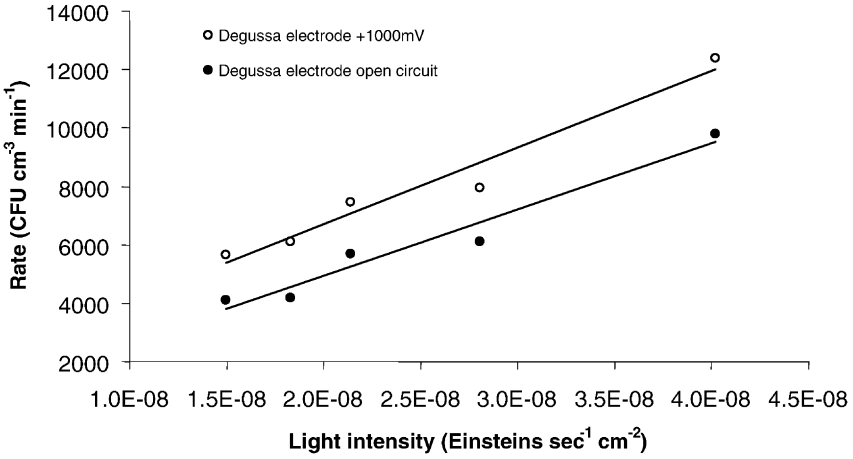

Fig. 6. Disinfection rate vs. incident light intensity during photocatalytic and electrochemically assisted photocatalytic experimentation.

Table 2
Effect of initial bacterial cell concentration on the steady-state photocurrent[a]

Initial cell concentration (CFU cm^{-3})[b]	Photocurrent (μA)
4.80×10^2	128
5.60×10^3	137
3.30×10^4	135
5.40×10^5	134
3.45×10^6	132

[a] Conditions: Degussa electrode, light intensity 2.8×10^{-8} Einsteins cm^{-2} s^{-1}, +1000 mV bias.
[b] Colony forming units per cubic centimetre.

Table 3
Effect of incident light intensity on the steady-state photocurrent[a]

Light intensity (einstein cm^{-2} s^{-1})	Photocurrent (μA)
4.02×10^{-8}	172
2.80×10^{-8}	154
2.14×10^{-8}	131
1.83×10^{-8}	106
1.50×10^{-8}	103

[a] Conditions: Degussa electrode, cell loading $\sim 5 \times 10^5$ CFU cm^{-3}, +1000 mV bias.

Table 3 shows the steady-state photocurrent response of a Degussa electrode measured at different light intensities. The increase in the photocurrent was directly proportional to the light intensity.

4. Discussion

4.1. Disinfection kinetics

The bactericidal activity of TiO_2 photocatalysis towards *E. coli* cells has previously been reported by a number of authors [5,11–13,22,24,28–33]. Fig. 2 shows the disinfection results obtained in this study and confirms the findings of the above authors, however, only Zheng et al. [12] report an initial lag period. Ringers solution was chosen as the electrolyte for our disinfection experiments as it provided a more challenging test solution than distilled water, i.e. Ringers solution is also known to increase bacterial stability due to its isotonic properties. In distilled water the leakage of calcium and magnesium ions from the cell wall surface is believed to reduce the bacterial stability [5]. In Ringers solution the bacterial cells, being more stable than cells in distilled water, require a larger number of reactive oxygen species attacks therefore resulting in a more prolonged initial disinfection time.

The detrimental effects of anions on the photocatalytic degradation of organic compounds were reported by Abdullah et al. [34]. The anion content of Ringers solution could reduce the initial bactericidal activity due to competitive adsorption onto the TiO_2 film. Chloride ions may be oxidised to chlorine and hypochlorite. Additional experiments were carried out in distilled water, under open circuit conditions to assess the efficiency of disinfection in the absence of anions. The rate of disinfection in distilled water was greater than that in Ringers solution and therefore the presence of inorganic ions in the Ringers solution inhibited the photocatalytic disinfection process. The production of chlorine, from the oxidation of chlorides, did not increase the rate of disinfection.

A third factor involved in the kinetics observed during the disinfection could be the ability of the bacteria to recover from the inflicted oxidative damage during the initial stages of treatment. In order to detect bacterial regrowth, and therefore accurately monitor disinfection experimentation, a non-selective growth agar should be used. Selective agars, commonly used for the detection of waterborne-microorganisms, contain components that inhibit or promote the growth of specific bacterial species, or groups of organisms. The absence of some basic microbial metabolites from selective agars can prevent bacterial injury repair and regrowth [35,36]. Within the disinfection experiments, Ringers solution was used as both the experimental medium and the dilution buffer before plating onto non-selective LB agar providing suitable conditions for bacterial repair and recovery [12,37,38]. The samples removed from the reactor during the early stages of disinfection could have undergone only cell wall damage, subsequent injury repair and regrown during incubation on LB agar plates therefore demonstrating that disinfection had not occurred. If a selective agar had been used as the detection media the lag phase would not have been observed [39].

The theory of bacterial recovery, due to cell wall damage occurring during the initial stages of the disinfection was reported by Zheng et al. [12]. In that work the process of bacterial inactivation was studied using $\sim 10^6$ *E. coli* cells cm^{-3} in a TiO_2 slurry reactor. Bacterial viability was followed using LB agar with the disinfection kinetics showing a lag phase over the first 15 min of the experiment. An *o*-nitrophenol β-D-galactopyranoside (ONPG) probe was used to assess the level of cellular damage during the photocatalytic process. This approach demonstrated that cell membrane damage did not take place during the initial stages of the reaction but occurred approximately 15–20 min after the treatment. The decrease in cell viability followed the same trend, a lag period over the first 15 min of reaction followed by a linear decline in viable cell numbers. Cell membrane damage is known to result in cell death, however mechanisms to repair cell wall damage do exist and therefore bacterial cell wall damage alone will not cause bacterial inactivation.

In summary, the combination of increased initial bacterial stability towards disinfection, anion concentration decreasing the efficiency of the photocatalytic mechanism, and the provision of conditions favourable for bacterial repair and recovery, could be responsible for the lag period observed during the first 20 min of the experiments.

4.2. Control experiments

Fig. 3 shows that bacterial inactivation was possible in the absence of the photocatalyst. UVA or air sparging alone showed some bactericidal effect, however when combined the effect was synergistic with a marked increase in the disinfection rate. Oxygen is thought to have a direct effect on microorganisms.

Sunlight has been used as a method of water disinfection [40] where in addition to the heating effect the mechanism of treatment has been attributed to the production of reactive oxygen species by the UVA photosensitization of oxygen within the water sample [41–45]. Therefore the inactivation of *E. coli* in this study by combination of UVA and air sparging is consistent with previous reports.

4.3. The effect of catalyst source on photocatalytic disinfection of E. coli

Fig. 4 compares the rate of disinfection for Degussa and Aldrich electrodes. The Degussa electrode showed better photocatalytic efficiency than the Aldrich electrode under open circuit conditions. This may be attributed to differences in crystal structure and particle size of Degussa and Aldrich powders.

Degussa P25 is comprised of a 70:30 anatase–rutile mixture, average particle size 30 nm, with Aldrich being predominantly anatase with a larger particle size of $\sim$1 μm [46]. Degussa P25 is reported to have a high photoreactivity due to slow electron hole recombination [47]. This has been attributed to efficient charge separation as a result of defects in the crystal structure and surface morphology caused by TiO_2 preparation method [48]. The particle size of Aldrich TiO_2 is such that when the immobilised catalyst is heat-treated the resulting film will have less efficient charge transfer characteristics due to larger inter-particle boundaries than those found within Degussa films. Electron transfer to molecular oxygen has been reported to be less efficient in large TiO_2 particles than within small TiO_2 particles [49]. In this work, poor electron transfer from the Aldrich films to oxygen, leading to electron hole recombination, or lower effective catalyst surface area available for reaction could be reasons for the decreased disinfection observed on Aldrich films during photocatalytic disinfection.

4.4. Electrochemically assisted photocatalytic disinfection of E. coli

The rate of disinfection for both Degussa and Aldrich electrodes was increased with the application of a positive potential (Fig. 4). The increase in rate can be attributed to a reduction in photogenerated charge carrier recombination within, and at the surface of the semiconductor film [50]. The application of a positive potential lowers the Fermi energy level of the supporting substrate resulting in more efficient electron transfer from the particulate film to the supporting substrate [51]. EAP also increases mass transfer of negatively charged bacterial species [52,53] towards the positive TiO_2 anode via electromigration. This helps reduce mass transfer limitations imposed by the reduction of catalyst surface area to volume ratio encountered when using an immobilised catalyst.

Under applied potential, the rate of disinfection of both Degussa and Aldrich electrodes were similar (Fig. 4). The larger increase in disinfection rate observed with the Aldrich electrode under EAP compared to open circuit is probably due to a reduction in charge carrier recombination rates within the particulate films. Electron trapping is known to occur in both anatase and rutile forms of TiO_2 [54] and could play a significant role in the interfacial diffusion of electrons. The rutile component of Degussa TiO_2 could influence the diffusion rate acting as an electron sink thus preventing the Degussa films taking advantage of the modified-diffusion gradient created by the application of a potential bias to the same extent as a purely anatase Aldrich film.

Butterfield et al. [19] previously described photoelectrochemical disinfection of *E. coli*; however sufficient details of the photoelectrochemical methods were not given to allow comparison with this work.

4.5. The effect of initial bacterial concentration

Increased initial cell loading raises the probability of interaction between the catalyst film and the pollutant. This reduces the overall mass transfer limitations and results in an increase in disinfection rate with increased initial bacterial loading. Pham et al. [55] observed a similar trend during the inactivation of *Bacillus pumilus* spores in a slurry reactor. The effect was attributed to the increased probability of collision between hydroxyl radicals and bacterial spores. The same workers later published a mathematical model explaining their findings [56]. At high initial bacterial cell loading the effect of applied potential was more pronounced. Increased electron transfer efficiency, under bias conditions, results in the transfer of holes becoming the rate limiting step in the reaction, therefore raising the concentration of bacterial pollutant will increase the rate of disinfection.

4.6. The effect of incident light intensity

A linear increase in both the disinfection rate and the photocurrent response was observed with increasing light intensity, Fig. 6 and Table 3. For the open circuit electrode under the higher light intensities charge carrier recombination becomes a rate determining factor. The application of an applied potential serves to remove CB e^-'s, which reduces the number of charge carrier recombinations, resulting in more efficient disinfection.

4.7. Bacterial recovery

In this work the number of colony forming units was reduced by 99.996% after 120 min photocatalytic treatment. Bacterial cells were allowed up to 48 h to recover from disinfection. Following the recovery period, the number of CFUs remained below detectable limits showing that photocatalytic disinfection had caused irreversible damage to the bacterial cells. Previous research has suggested that bacterial cells can enter a viable but non-culturable (VBNC) state when exposed to oxidative stress [57]. Bacterial cells are undetectable by traditional methods when in a VBNC state [58]. If conditions become favourable the cells have the ability to return to their viable state and are therefore able to cause disease [58]. Further work is required to determine if photocatalytic disinfection can enter a VBNC state.

5. Conclusion

Photocatalysis has been used to disinfect water containing *E. coli*. Under open circuit conditions, bacterial inactivation occurred at a faster rate using Degussa electrodes compared to the Aldrich electrodes. Under EAP the rate of disinfection on both Degussa and Aldrich films was similar. The effect of applied potential was more pronounced under conditions of high initial bacterial cell loading and high incident light intensity. Preliminary investigations suggest that bacterial recovery does not occur after photocatalytic disinfection. Further work is required to determine if photocatalytic disinfection can enter a VBNC state.

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References

[1] U. Szewzyk, R. Szewzyk, W. Manz, K.H. Schleifer, Ann. Rev. Microbiol. 54 (2000) 81–127.
[2] G.R. Finch, M. Belosevic, Can. J. Civ. Eng. 28 (2001) 67–80.
[3] H.V. Smith, J.B. Rose, Parasitol. Today 14 (1998) 14–22.
[4] Water Chlorination: Chemistry, Environmental Impact and Health Effects, Lewis Publishers, Inc., Chelsea, MI, 1985.
[5] D.M. Blake, P.C. Maness, Z. Huang, E.J. Wolfrum, J. Huang, W.A. Jacoby, Sep. Purif. Meth. 28 (1999) 1–50.
[6] D. Blake, NREL Report, Golden, CO, 1999.
[7] A. Mills, S. LeHunte, J. Photochem. Photobiol. A 108 (1997) 1–35.
[8] L.M. Dorfman, G.E. Adams, NSRDS-NBS 46 (1973) 1–72.
[9] T. Matsunaga, R. Tomoda, T. Nakajima, H. Wake, FEMS Microbiol. Lett. 29 (1985) 211–214.
[10] T. Saito, T. Iwase, J. Horie, T. Morioka, J. Photochem. Photobiol. B 14 (1992) 369–379.
[11] P.C. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, Appl. Environ. Microbiol. 65 (1999) 4094–4098.
[12] H. Zheng, P.C. Maness, D.M. Blake, E.J. Wolfrum, S.L. Smolinski, W.A. Jacoby, J. Photochem. Photobiol. A 130 (2000) 163–170.
[13] K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Environ. Sci. Technol. 32 (1998) 726–728.
[14] J. Gutteridge, Lipid Peroxidation, Some Problems and Concepts, Federation of American Societies for Experimental Biology, Augusta, MI, 1988.
[15] D.H. Kim, M.A. Anderson, Environ. Sci. Technol. 28 (1994) 479–483.
[16] K. Vinodgopal, S. Hotchandani, P.V. Kamat, J. Phys. Chem. 97 (1993) 9040–9044.
[17] K. Vinodgopal, P.V. Kamat, Sol. Energy Mater. Sol. Cells 38 (1995) 401–410.
[18] J. Rodriguez, M. Gomez, S.E. Lindquist, C.G. Granqvist, Thin Solid Films 360 (2000) 250–255.
[19] I.M. Butterfield, P.A. Christensen, T.P. Curtis, J. Gunlazuardi, Water Res. 31 (1997) 675–677.
[20] K.H. Baker, D.S. Herson, Water Environ. Res. 71 (1999) 530–551.
[21] N. Kashige, Y. Kakita, Y. Nakashima, F. Miake, K. Watanabe, Curr. Microbiol. 42 (2001) 184–189.
[22] M. Bekbolet, C.V. Araz, Chemosphere 32 (1996) 959–965.
[23] W.S. Kuo, Y.T. Lin, J. Environ. Sci. Health A 35 (2000) 671–680.
[24] J.C. Ireland, P. Klostermann, E.W. Rice, R.M. Clark, Appl. Environ. Microbiol. 59 (1993) 1668–1670.
[25] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, Appl. Catal. B 17 (1998) 25–36.
[26] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1973.
[27] R. Atlas, Handbook of Microbial Media, CRC Press, Boca Raton, FL, 1993.
[28] T. Matsunaga, M. Okochi, Environ. Sci. Technol. 29 (1995) 501–505.
[29] Y. Horie, M. Taya, S. Tone, J. Chem. Eng. Jpn. 31 (1998) 577–584.
[30] L. Belhacova, J. Krysa, J. Geryk, J. Jirkovsky, J. Chem. Technol. Biotechnol. 74 (1999) 149–154.
[31] N.P. Huang, Z.D. Xiao, D. Huang, C.W. Yuan, Supramol. Sci. 5 (1998) 559–564.
[32] C. Wei, W.Y. Lin, Z. Zainal, N.E. Williams, K. Zhu, A.P. Kruzic, R.L. Smith, K. Rajeshwar, Environ. Sci. Technol. 28 (1994) 934–938.
[33] R.J. Watts, S.H. Kong, M.P. Orr, G.C. Miller, B.E. Henry, Water Res. 29 (1995) 95–100.
[34] M. Abdullah, G.K.C. Low, R.W. Matthews, J. Phys. Chem. 94 (1990) 6820–6825.
[35] R.G. Qualls, J.C.H. Chang, S.F. Ossoff, J.D. Johnson, Appl. Environ. Microbiol. 48 (1984) 699–701.
[36] S.K. Shah, E.A. McBean, W.A. Anderson, Can. J. Civ. Eng. 23 (1996) 373–380.
[37] K. Tosa, T. Hirata, K. Taguchi, Water Sci. Technol. 35 (1997) 71–76.
[38] T. Jouenne, L. Bertin, G. Charriere, G.A. Junter, Water Res. 25 (1991) 829–833.
[39] P.S.M. Dunlop, Unpublished results, University of Ulster, Newtownabbey, 2001.
[40] A. Downes, T. Blunt, Proc. Roy. Soc. 28 (1877) 488.
[41] R.M. Conroy, M. Elmore-Meegan, T. Joyce, K.G. McGuigan, J. Barnes, Lancet 348 (1996) 1695–1697.
[42] S.C. Kehoe, T.M. Joyce, P. Ibrahim, J.B. Gillespie, R.A. Shahar, K.G. McGuigan, Water Res. 35 (2001) 1061–1065.
[43] K.G. McGuigan, T.M. Joyce, R.M. Conroy, J.B. Gillespie, M. Elmore-Meegan, J. Appl. Microbiol. 84 (1998) 1138–1148.
[44] K.G. McGuigan, T.M. Joyce, R.M. Conroy, J. Med. Microbiol. 48 (1999) 785–787.
[45] R.J. Smith, S.C. Kehoe, K.G. McGuigan, M.R. Barer, Lett. Appl. Microbiol. 31 (2000) 284–288.
[46] J.A. Byrne, Titanium dioxide photocatalysis for the treatment of polluted water, DPhil Thesis, University of Ulster, 1997.
[47] S.T. Martin, H. Herrmann, M.R. Hoffmann, J. Chem. Soc., Faraday Trans. 90 (1994) 3323–3330.

[48] R.I. Bickley, T. Gonzalezcarreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, J. Solid State Chem. 92 (1991) 178–190.
[49] H. Gerischer, Electrochim. Acta 38 (1993) 3–9.
[50] H. Gerischer, A. Heller, J. Electrochem. Soc. 139 (1992) 113–118.
[51] J.A. Byrne, B.R. Eggins, J. Electroanal. Chem. 457 (1998) 61–72.
[52] P. Gilbert, D.J. Evans, E. Evans, I.G. Duguid, M.R.W. Brown, J. Appl. Bacteriol. 71 (1991) 72–77.
[53] W.W. Wilson, M.M. Wade, S.C. Holman, F.R. Champlin, J. Microbiol. Meth. 43 (2001) 153–164.
[54] S. Leytner, J.T. Hupp, Chem. Phys. Lett. 330 (2000) 231–236.
[55] H.N. Pham, T. McDowell, E. Wilkins, J. Environ. Sci. Health A 30 (1995) 627–636.
[56] H.N. Pham, E. Wilkins, K.S. Heger, D. Kauffman, J. Environ. Sci. Health A 32 (1997) 153–163.
[57] S.B. Farr, T. Kogoma, Microbiol. Rev. 55 (1991) 561–585.
[58] D. McDougald, S.A. Rice, S. Kjelleberg, Biologia 54 (1999) 617–623.