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Remediation of a chlorinated aromatic hydrocarbon in water by photoelectrocatalysis

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Visible light-driven photoelectrocatalysis has potential as a remediation technology in wastewater treatment.

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ABSTRACT

Photoelectrocatalysis driven by visible light offers a new and potentially powerful technology for the remediation of water contaminated by organo-xenobiotics. In this study, the performance of a visible light-driven photoelectrocatalytic (PEC) batch reactor, applying a tungsten trioxide (WO_3) photoelectrode, to degrade the model pollutant 2,4-dichlorophenol (2,4-DCP) was monitored both by toxicological assessment (biosensing) and chemical analysis. The bacterial biosensor used to assess the presence of toxicity of the parent molecule and its breakdown products was a multicopy plasmid *lux*-marked *E. coli* HB101 pUCD607. The bacterial biosensor traced the removal of 2,4-DCP, and in some case, its toxicity response suggests the identification of transient toxic intermediates. The loss of the parent molecule, 2,4-DCP determined by HPLC, corresponded to the recorded photocurrents. Photoelectrocatalysis offers considerable potential for the remediation of chlorinated hydrocarbons, and that the biosensor based toxicity results identified likely compatibility of this technology with conventional, biological wastewater treatment.

1. Introduction

Chlorinated hydrocarbons, such as chlorophenols (CPs) are ubiquitous pollutants, which enter the environment as by-products of the manufacture of herbicides, preservatives and disinfectants (Pera-Titus et al., 2004). They are also commonly found in drinking water as disinfection by-products (DBPs) due to chlorination (Czaplicka, 2004; Peller et al., 2003). CPs possess endocrine disrupting properties (Yamasaki et al., 2005) and are also recognised by the International Agency for Research on Cancer (IARC) for their carcinogenic properties (Czaplicka, 2004; Wang et al., 1999). Moreover, many chlorinated hydrocarbons are extremely stable in the environment and prone to bioaccumulation (Wang et al., 1999; Mäkinen et al., 1993). These organo-xenobiotic pollutants usually degrade into long-living intermediates which, in some cases, are more toxic than the parent compound and, furthermore, accumulate to even higher concentrations in the environment (Peller et al., 2004). For many reasons, therefore, CPs are classified as priority pollutants by the US EPA (http://www.epa.gov/waterscience/standards/) and by the European Directive 2455/2001/EC (EC Decision 2455/2001/EC). For this study, 2,4-dichlorophenol (2,4-DCP) was chosen as a representative model for chlorinated hydrocarbons. The potential of heterogeneous photocatalysis for degradation of a wide range of organic compounds has been widely investigated (Bard, 1980; Hoffmann et al., 1995; Mills and LeHunte, 1997). Advanced oxidation processes (AOP) such as photocatalysis pose a valuable alternative to other remediation techniques. Besides being employable for the treatment of water and wastewater, they are suitable for the removal of organic and inorganic pollutants at low concentrations (Prevot and Pramauro, 1999). In comparison to conventional technologies (e.g. adsorption to granular activated carbon) that relocate the pollutant from an aqueous matrix into a solid matrix, photocatalysis requires no waste post-treatment.

To date, the most effective photocatalytic degradation of organic pollutants has been achieved with titanium dioxide (TiO_2) as a semiconductor and UV-A as light source (Herrmann, 1999). However, the use of UV-light may have limitations, due to slightly higher operating cost for the wastewater treatment process. Most photocatalytic applications use slurries of catalysts, which need to

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be separated at the end of the treatment of the contaminated water. The development of a range of immobilised catalysts has widened the field of the application of photocatalysis in the treatment of organic pollutants. In comparison to TiO_2 slurries, immobilised photoelectrodes are stable in aqueous solution, non-toxic and use O_2 derived from air for photocatalytic degradation (Herrmann, 1999).

This study reports the use of immobilised tungsten trioxide (WO_3) as catalyst in a photoelectrocatalytic (PEC) batch reactor driven by a visible light source. WO_3 has proven to be an efficient photocatalyst for a range of chemicals (Solarska et al., 2005), and is also resistant against photocorrosion (Santato et al., 2001a). Furthermore, such working electrodes are suitable for the treatment of aqueous solutions with a low load of organic pollutants. To our knowledge, it is the first time that a PEC batch reactor with a WO_3 catalyst, driven by visible light, has been employed to degrade organo-xenobiotics and an electrical current generated.

The simple monitoring of the disappearance of the model pollutant by chemical analytical tools such as HPLC is not sufficient, because no information about intermediates is obtained, particularly in relation to their bioavailability and potential toxicity. Therefore validation of the performance of the PEC batch reactor was achieved in this study by a combination of chemical analysis and toxicological assessment. *Lux*-marked, metabolic, bacterial biosensors have proven to be a useful tool for the rapid screening of contaminated water (Boyd et al., 1997; Shaw et al., 1999; Amin-Hanjani et al., 1993; Meighen, 1991). These biosensors are environmental bacteria into which luminescence (*lux*) reporter genes have been inserted (Shaw et al., 1999; Amin-Hanjani et al., 1993). Luminescence output of the biosensors reports on their metabolic activity, and therefore allows conclusions to be drawn about bioavailability and toxicity of the pollutant(s) present (Shaw et al., 1999; Dawson et al., 2006; Paton et al., 1995a,b). Bacterial biosensors therefore offer an extremely useful tool to assess the photoelectrocatalytical degradation of a single parent compound, and identify potential toxicity of breakdown products, in a multicomponent system.

The aims of this study were: firstly, to verify that visible light-driven photoelectrocatalysis offers a potentially important remediation technology for chlorinated hydrocarbons; secondly, to use biological toxicity assessment and chemical analysis as a combined approach for the validation of the overall performance of the photoelectrocatalytical degradation of the model pollutant 2,4-DCP; finally, to monitor possible toxic intermediates in the PEC batch reactor by use of bacterial biosensors.

2. Materials

All 2,4-DCP solutions were diluted down from a 160 ppm 2,4-DCP stock, 99%, GC grade (Sigma) for each set of experimental conditions.

2.1. Photoelectrocatalytic batch reactor (PEC)

The PEC batch reactor applied in this study can be defined as a three-compartment batch reactor, comprising two main compartments, the anode (and its associated analyte) and the cathode (containing distilled water), separated from each other by a third compartment and glass frits (Fig. 1). The latter compartment was filled with a 4% agar gel in 3 M KCl. This agar-salt bridge maintains the electrical conductivity between the anode and cathode compartment (Mbindyo et al., 1997), and also prevents the mixing of analyte and the water of the cathode. The tungsten trioxide (WO_3) thin film catalyst was prepared, following the method of Augustynski et al. (Solarska et al., 2005; Santato et al., 2001a,b). Briefly, a WO_3 sol was spread onto glass substrates which had an F-doped SnO_2 electrically conducting overlayer (Solaronix, Switzerland), with a sheet resistance of 8 $\Omega\,sq^{-1}$. The film was annealed at 550 °C for 30 min. The illumination of the WO_3 electrode was conducted with a commercially available 35 W quartz-halogen bulb from a distance of 10 mm from the side of the anode compartment. This form of light source only provides light in the visible range of the spectrum (450–650 nm) with a minimal UV irradiation. A platinum-black counter electrode (double-layered Pt mesh) was placed in the dH_2O of the cathode compartment with air directed through it. The potential of the WO_3 electrode was assessed against a saturated calomel reference electrode (SCE) placed in the solution of the anode compartment. During photoelectrocatalytic degradation, photocurrents were continuously recorded by an ADC16 data logger (Pico Technology Limited).

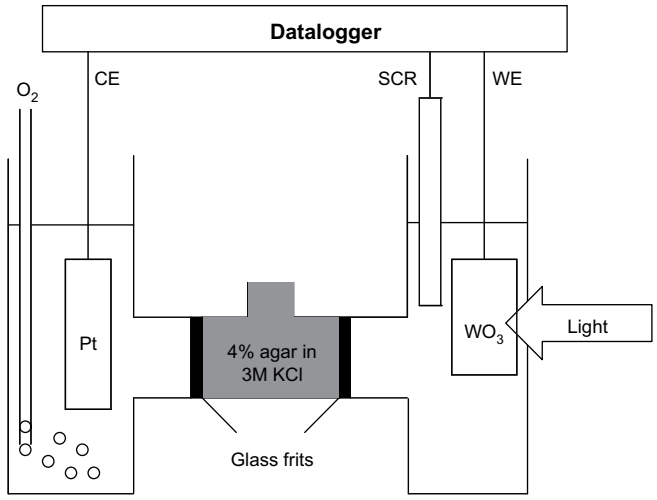

Fig. 1. Schematic diagram of the photoelectrocatalytic batch reactor (PEC). WE – WO_3 working electrode; SCE – saturated calomel reference electrode; CE – Pt gauze counter electrode. ADC16 Data logger connected to a computer.

2.2. Photoelectrocatalytic degradation

To minimise loss of chemical compound due to evaporation, the PEC batch reactor was set up in a cold room (4 °C). The anode compartment contained 60 ml 40 ppm 2,4-DCP and was sealed with a tightly fitting silicone plug that, as well as holding the WO_3 electrode and the reference electrode, also included a silicone septum as sample port. The cathode compartment held the same volume of distilled water. The PEC batch reactor was allowed to equilibrate for 30 min before the first sample was retrieved. For the chemical analysis, 500 μl of analyte was directly mixed in an HPLC vial with 500 μl methanol and stored at 4 °C. For the toxicity assessment, 1800 μl was withdrawn from the solution of the anode compartment and stored at 4 °C. Degradation experiments were executed for 48 h.

2.3. Negative control experiments

A set of negative control experiments was defined to verify the results obtained from the degradation experiments. The first negative control was set up according to the above procedure, with illuminated anode compartment but without catalyst. In the second experiment, the PEC batch reactor (including catalyst) was employed but without illumination. For this, the anode compartment was wrapped in tin foil to protect it from scattered light entering the photoreactor.

2.4. Biological analysis

Freeze-dried cells of the metabolic biosensor *E. coli* HB101 pUCD607 were resuscitated in 10 ml 0.1 M KCl, followed by incubation for 1 h at 25 °C on an orbital shaker at 200 rpm (Rattray et al., 1990; Bundy et al., 1997). Aliquots of 100 μl bacterial suspension were added to 900 μl test solution (analyte of the PEC batch reactor and 2,4-DCP standard solutions). Bioluminescence in relative light units (RLU) was measured after an incubation time of 15 min, 30 min and 60 min using a Jade bench-top luminometer (Labtech International).

The effective concentrations that caused a 20% and 50% decline in the bioluminescence response of *E. coli* HB101 pUCD607 to 2,4-DCP were determined. Concentrations of 2,4-DCP in distilled water, ranging from 0 mM up to 5 mM, were tested for their toxicity. All measurements were carried out in triplicate and followed the above procedure.

The analyte in the PEC was monitored for toxicity at certain time intervals. Each toxicity measurement was performed with at least two replicates and luminescence was recorded after incubation.

2.5. Chemical analysis

Sample analyses of the analyte solution were carried out in a Thermo Separation Products HPLC with a P2000 pump unit, AS3000 autosampler and UV1000 detection HPLC. Prior to analysis, all samples were mixed 1:1 (v/v) with methanol (HPLC grade). An Interpak ODS2 column (15 cm × 4.6 mm × 5 μm) was used with a mobile phase of 80% methanol and 20% double-deionised water and a flow of 1 ml per

minute. The UV detector was set at 230 nm and a running time of 6 min per sample was established. Samples were injected between standards.

2.6. Statistical analysis

Analysis of variance (ANOVA) was carried out using the statistical software Minitab 14.12 (Minitab Inc.). Least significance difference (LSD) values with a 95% confidence interval were calculated.

The effective concentrations, EC_{20} and EC_{50}, for *E. coli* HB101 pUCD607 to 2,4-DCP were determined. A four parameter logistic curve was fitted to data plots using SigmaPlot 10.0 (SYSTAT Software Inc.). The mean and standard error of the EC values were calculated from triplicate values obtained from the dose–response curve.

3. Results and discussion

The results of a trial application of a new, visible light-driven PEC batch reactor are presented. The aim was to assess, using toxicological and chemical validation, the potential of this advanced oxidation technology for the remediation of water contaminated with organo-xenobiotic compounds, using 2,4-DCP as a model pollutant.

Dose–response curves and calculated EC values were used to confirm the suitability of *lux*-marked, bacterial toxicity biosensors as a screening tool to address the efficacy of the PEC batch reactor in degrading the model organo-xenobiotic 2,4-DCP. This approach included the monitoring of the possible occurrence of toxic degradation products.

The toxicity of different 2,4-DCP concentrations, using the bacterial biosensor *E. coli* HB101 pUCD607, was assessed. All concentrations were measured at an identical pH (pH 6.0). The dose–response curve (Fig. 2) demonstrated a marked decrease in bioluminescence with increasing concentration of 2,4-DCP and identified through the calculated EC values (Table 1) the strong toxicity of this pollutant. Similar results have been reported (e.g. Tiensing et al., 2002; Choi and Gu, 2002), and the toxicity of 2,4-DCP on bacterial cells can be explained by its mode of action. The compound directly impacts on the energy-transducing membranes of cells (Heipieper et al., 1991; Shaw et al., 2000). Furthermore, 2,4-DCP acts as an uncoupler because of changes between the molecule's dissociated and undissociated state (Lewis et al., 1994), closely associated with the ambient pH (Pera-Titus et al., 2004; Shaw et al., 2000).

The primary validation of the efficacy of remediative technologies such as PEC batch reactor under test tends to be analytical to ensure that performance criteria in terms of degradation kinetics are met. On the contrary, in this study a linkage between toxicity testing using bacterial biosensors and chemical analysis was aimed for. Testing with bacterial biosensors enables both the toxicity of contaminants such as DCP to be assessed, and also the occurrence of toxic intermediates in the course of degradation to be identified. It therefore facilitates assessment of the compatibility of this advanced oxidation technology with conventional biological wastewater treatment. It is essential, then, that the pattern of the toxicity response during the PEC treatment is to be related to the loss of the parent molecule, detected by analytical chemistry.

Table 1
EC values of 2,4-DCP (mM) for *E. coli* HB101 pUCD607 after 15 min, 30 min and 60 min incubation. s.e. – standard error of triplicate measurements

	15 min	s.e.	30 min	s.e.	60 min	s.e.
EC_{20}	0.131[a]	0.003	0.147[a]	0.003	0.155[a]	0.006
EC_{50}	0.193[b]	0.004	0.221[c]	0.004	0.237[c]	0.003
EC_{80}	0.341[d]	0.004	0.402[e]	0.007	0.432[f]	0.004

Values followed by the same letter were not significantly different ($P \leq 0.05$).

The results of the toxicity assessment using *E. coli* HB101 pUCD607 during three independent degradation experiments in the PEC batch reactor are presented in Fig. 3. Different bars for each sample display three incubation times at which the toxicity response of the bacterial biosensor was recorded. The first sample, dH_2O (pH 5.5) served as a control to monitor the biosensor response to a non-toxic solution, and bioluminescence values are also recorded as a percentage of this control. A pH of 5.5 represents an established value for ecological toxicity testing (Sinclair et al., 1999). Five time points were sampled during the degradation experiment after 0, 8, 24, 32, and 48 h, named t0, t8, t24, t32, and t48, respectively. The overall pattern of toxicity response over time was a steady increase in bioluminescence (i.e. a decrease in toxicity of up to three times for an incubation of 15 min). However, a slight decrease, followed by an increase in bioluminescent response of the bacterial biosensor was observed at t24 and t32. This pattern may indicate the formation of more and/or less toxic intermediates derived from the parent compound, 2,4-DCP, and therefore turning the single-compound solution into a multi-component system in the PEC batch reactor.

The significant change in pH of the analyte from 5.5 for t0 to 3.5 for t48 observed during the degradation experiments in the PEC batch reactor did not occur in the negative controls. The pH change is unlikely to be responsible for the measured toxicity response of

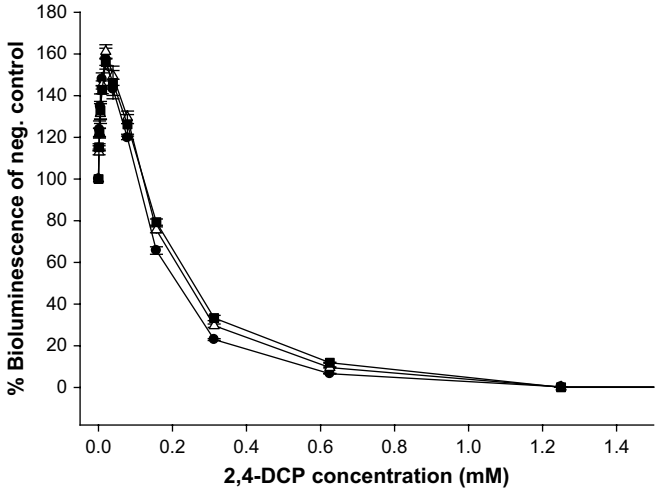

Fig. 2. Dose–response curve of 2,4-DCP obtained with the *lux*-marked bacterial biosensor *E. coli* HB101 pUCD607. ● 15 min incubation, △ 30 min incubation, and ■ 60 min incubation. Bars represent standard errors of triplicate measurements.

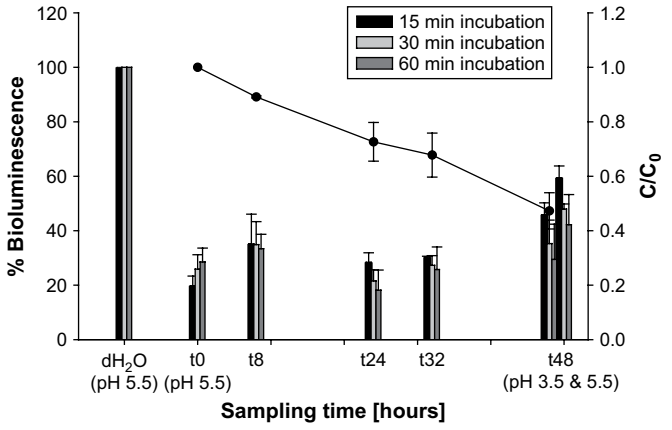

Fig. 3. 2,4-DCP degradation in the PEC batch reactor (●). Concentrations of 2,4-DCP determined by HPLC. Data presented as means of three independent experiments. Error bars represent standard errors of the mean of three independent measurements. Toxicity assays using *E. coli* HB101 pUCD607 for three, independent 2,4-DCP degradation experiments in the PEC batch reactor, comparing three different incubation times at 15 min, 30 min, and 60 min (vertical bars). For t48 bioluminescence values for the original sample pH 3.5 and for an adjusted pH 5.5 are shown. Error bars represent standard errors of the mean of three independent toxicity measurements.

the biosensor *E. coli* HB101 pUCD607. The expected percentage bioluminescence for a 2,4-DCP solution with an assumed pH of 3.5 should be close to zero (Sinclair et al., 1999). A combination of a loss of 2,4-DCP and the formation of less toxic intermediates is likely to explain the observed decrease in overall toxicity response of the biosensor to the analyte.

The degradation of 2,4-DCP in the PEC batch reactor assessed by HPLC analysis, achieved a loss of 53% in 48 h (Fig. 3). Although the PEC batch reactor is not sufficiently defined to conclusively characterise the kinetics of the degradation, from the observations made, the process approximates first order kinetics. This agrees with the findings of Pandiyan et al. (2006) and Herrmann (1999). Negative controls confirmed that, in the absence of the catalyst, illumination of a 2,4-DCP solution with light in the visible range did not lead to a significant loss of the analyte. Without illumination and the working electrode present, no major loss in 2,4-DCP concentration due to adsorption was observed. In general, the rate of adsorption of 2,4-DCP on to experimental equipment is regarded as low (Peller et al., 2003). Statistical analysis confirmed that the results of the degradation experiments and the negative controls were significantly different ($P = 0.001$). Furthermore, as mentioned above, a significant change in pH of the analyte during the running time of the degradation experiment was recorded (Fig. 3). This decrease in pH was expected due to the breakdown of 2,4-DCP. However, no change of pH was observed in the negative controls. The low pH in the analyte might have prevented higher degradation rates (Pera-Titus et al., 2004) and led to a slowing down of the degradation due to changes in the surface charge of the semiconductor (Pandiyan et al., 2006). Moreover, at a low pH, chloride anions are drawn to the positive surface of the catalyst, reducing electrochemical reactions and therefore leading to lower degradation rates (Dalrymple et al., 2007).

Under illumination of the semiconductor, a photocurrent of 7.5 μA was observed in the PEC batch reactor (data not shown). Currents recorded in absence of light were displayed as a steep decrease in photocurrents to a value of 0 μA (i.e. no illumination of the catalyst). After the light was switched back on, the photocurrent returned to the reproducible value that was measured before the illumination was interrupted. This light intermittence also served as a control to establish that the photocatalyst was still functioning in the correct mode. The presence of a marked photocurrent provides direct evidence that "fuel" is being degraded, and its observed decline over the length of the experiment ($\sim$7.5 μA to $\sim$5 μA) can be directly related to loss of the parent molecule. However, changes in photocurrent are also observed in unbuffered solutions and in samples with low pH in the analyte (Vinodgopal et al., 1994). The characteristics (dynamic pattern) of the monitored photocurrent will be most simple when no intermediates are formed during degradation.

The *lux*-marked bacterial biosensor *E. coli* HB101 pUCD607 proved to be a suitable tool for monitoring PEC-mediated degradation of 2,4-DCP (Beaton et al., 1999) and to complement chemical analysis (Dawson et al., 2006). Chemical analysis alone is not sufficient to assess the degradation of pollutants because heterogeneous photocatalysis can lead to a set of chemical compounds whose toxicity may have synergistic, additive or antagonistic effects. These effects on the toxicity response of bacterial biosensors were reported by Tiensing et al. (2002). On the other hand, the ecologically relevant assessment of the degraded pollutant enabled the bioavailability (Shaw et al., 2000), toxicity (Svenson and Hynning, 1997) and formation of recalcitrant compounds (Grabner et al., 1994) to be assessed and related to the success of future biodegradation. As well as reducing the toxicity of organo-xenobiotic substances, photocatalytic treatment can also enhance their biodegradability (Adams et al., 1997). Although not investigated in this study, even a partial treatment with AOP may be sufficient to allow the re-introduction of the photocatalytically treated water back into the main stream wastewater treatment plant to reduce the risk of toxic shock to the biological treatment step.

In this study, the combined use of chemical analysis and biological toxicity assessment proved a highly useful approach to assess the capacity of a novel, visible light-driven PEC batch reactor to degrade the model pollutant 2,4-DCP, and identify the possible appearance of toxic intermediates. Despite the slow degradation rates associated with the small active catalyst surface area and sub-optimal flow characteristics of this trial reactor, successful remediation of the DCP was observed. This identifies the considerable potential of this advanced oxidative process for the remediation of water contaminated with organo-xenobiotics.

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