The degradation of microcystin-LR using doped visible light absorbing photocatalysts.

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Abstract

Microcystins are one of the primary hepatotoxic cyanotoxins released from cyanobacteria. The presence of these compounds in water has resulted in the death of both humans and domestic and wild animals. Although microcystins are chemically stable titanium dioxide photocatalysis has proven to be an effective process for the removal of these compounds in water. One problem with this process is that it requires UV light and therefore in order to develop effective commercial reactor units that could be powered by solar light it is necessary to utilize a photocatalyst that is active with visible light. In this paper we report on the application of four visible light absorbing photocatalysts for the destruction of microcystin-LR in water. The rhodium doped material proved to be the most effective material followed by a carbon modified titania. The commercially available materials were both relatively poor photocatalysts under visible radiation while the platinum doped catalyst also displayed a limited activity for toxin destruction.

1. Introduction

Cyanobacterial toxins produced and released by cyanobacteria in freshwater around the world are well documented (Carmichael, 1995; Sivonen, 1996). Microcystins are the most common of the cyanobacterial toxins found in water, as well as being the ones most often responsible for poisoning animals and humans who come into contact with toxic blooms and contaminated water (Codd et al., 1989; Dunn, 1996; Yu, 1994; Tsuji et al., 1995). The most important toxin is microcystin-LR which is a cyclic heptapeptide containing the amino acid 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (adda), with leucine and arginine in the variable positions. Microcystins are chemically very stable and conventional water treatment processes have so far proved relatively ineffective in removing them (Keijola et al., 1988, Lahti et al., 1989, Lawton and Robertson, 1999). The formation of chlorinated by-products of the microcystins has been reported by Merel et al. (2009). This group reported a detailed study of the use of chlorination as a treatment process for the removal of microcystins from water. Chlorination, this is only effective at relatively high doses with a sufficient contact time. Although chlorinated by-products have been characterised as yet the toxicity of these by-products is unknown. The biodegradation of microcystins -LR, -LF and the pentapeptide toxin nodularin in water has previously been studied (Edwards et al., 2008; Torunska et al.,

2008) who reported degradation half lives for the toxins of between 4 and 18 d. Moreover the use of methods such as granular carbon filtration and photochemical degradation have shown only limited efficacy (Kaya and Sano, 1998, Reynolds, 1987; Tsuji et al., 1994). Consequently there is a growing need for effective treatment technologies for removal of microcystins from water.

We have previously reported the effectiveness of TiO_2 photocatalysis for the removal of microcystins in water (Robertson et al., 1997; Robertson et al., 1998; Lawton and Robertson, 1999; Robertson et al., 1999; Lawton et al., 1999; Cornish et al., 2000, Liu et al., 2002; Liu et al., 2003). Although the process has been demonstrated to be extremely effective in removing the toxin a limitation of the process was the fact that the catalyst requires UV light. If a suitable visible light absorbing photocatalyst could be prepared the viability of the photocatalytic process would be significantly improved as there could even be the potential of operating the process using sun light. Choi et al. (2007) reported the use of a nitrogen doped TiO_2 catalyst for the destruction of microcystin under visible irradiation. Using this catalyst approximately 50% of a 5 μM solution of microcystin-LR was degraded in 30 min with virtually complete destruction being achieved in 2 h. Pelaez et al. (2009) studied the photocatalytic destruction of microcystin-LR using visible light absorbing N-F-

codoped TiO_2 nanoparticles. At pH 3 the toxin was completed degraded within 300 min when irradiated with light at 420 nm. It was proposed that under these conditions the electrostatic interaction between the toxin and photocatalyst favoured the decomposition process. The purpose of the research detailed in this paper was to look at the potential effectiveness of a number of visible absorbing photocatalysts for the destruction of microcystin-LR. The efficiency of these materials was also compared to the material that has been the subject of our previous work on photocatalytic destruction of microcystin, the UV light absorbing Degussa P25 TiO_2.

2. Materials and experimental methods

2.1. Materials

The two unmodified titania samples P25 (Degussa) and TH (Titanhydrat, Kerr-McGee) were commercially available, whereas the modified samples TiO_2-C (TiO_2-C1b: Sakthivel and Kisch, 2003), $\{[Ti]OPtCl_4L\}^{n-}$, L = H_2O, OH^-, n = 1, 2, (abbreviated as TiO_2-Pt(IV)) (Burgeth and Kisch, 2002), and $\{[TiO_2]\text{-}O\text{-}RhCl_3(H_2O)_2\}^-$ (abbreviated as TiO_2-Rh(III)) (5% $RhCl_3$/TH: Dai et al., 2008) were prepared according to the literature. P25 TiO_2 was used as a standard material for comparison on the relative effectiveness of the catalysts detailed above. This has previously been established as the most effective UV photocatalyst for the destruction of

115 cyanotoxins (Liu et al., 2009). Microcystin-LR was prepared as
116 previously reported (Edwards et al., 1996). The toxin was
117 resuspended in water prior to use.
118
119 *2.2 Photocatalysis*
120 The photocatalysis experiments were performed in 20 mL glass
121 vials under constant stirring at a distance of 30 cm from the front of
122 the light source (500 W Halogen, irradiation 393 μM^{-1}, Temp 306 K
123), as illustrated in Fig. 1. A 2% w/v sodium nitrite filter was used to
124 eliminate and UV photons generated by the halogen source entering
125 the reaction vessel. An IR filter was also used to minimise any
126 thermal effects on the process. 50 mg of the photocatalysts were
127 added to 5 mL of a 0.1 mg mL^{-1} microcystin-LR solution. The
128 photocatalysis was conducted in Milli-Q water (18.2 m Ω cm) and
129 the reaction pH was 4. After mixing for 5 min an initial sample was
130 removed to determine extent of dark adsorption. From previous
131 work it has been established that the dark adsorption process of
132 microcystins on titania photocatalysts is rapid and equilibrium is
133 established within the first five min (Robertson et al., 1997; Lawton
134 et al., 2003). The photocatalysis was then initiated and samples
135 were removed at 10 min intervals for the first 60 min after which
136 sampling was performed every 20 min to a maximum photocatalysis
137 period of 120 min.
138

139 *2.3 Analysis*

140 Treated samples were analysed by HPLC with photodiode array
141 detection as previously detailed (Lawton et al., 1994).

142

143 **3. Results and discussion**

144 In order to ensure that the visible activity of the photocatalysts
145 was being observed and there was no contribution to the process
146 from UV light, the process was initially examined using a standard
147 Degussa P25 material. On irradiating the suspension of P25 TiO_2
148 and microcystin with the halogen light filtered through 2% sodium
149 nitrite filter, no significant level of toxin degradation was observed
150 up to 120 min photocatalysis (Fig. 2a). The results of this initial
151 study confirmed that all residual UV light generated by the tungsten
152 halogen source had been removed, so only visible photons were
153 entering the reactor cell. Prior to using this filter set up a modest
154 destruction of microcystin-LR was achieved with unmodified
155 photocatalyst materials from the residual UV in the halogen source.
156 In order to determine the true level of visible activity of the
157 modified photocatalyst material, it was therefore necessary to utilise
158 this effective UV filter in order to eliminate any potential UV
159 activation of the materials.

160

161 The photocatalytic activity of the five catalysts for the
162 destruction of microcystin-LR was subsequently assessed in the

same experimental setup. On adding the photocatalyst to the microcystin solution it was initially clear that each of the materials displayed varying levels of initial dark adsorption of the toxin. This dark adsorption of the toxins on TiO_2 photocatalysts has been previously reported and is believed to be due to a combination of the surface charge of the photocatalysts material and the hydrophobicity of the toxin (Lawton et al., 2003). Table 1 summarises for each of the photocatalysts the amount of microcystin remaining in solution after dark adsorption and after 60 min of irradiation time. The photocatalytic destruction of the microcystin over 120 min irradiation time for both modified and unmodified materials under visible light irradiation is detailed in Fig. 2b. At the high photocatalyst concentration employed (10 g L^{-1}) the amount of absorbed light should be about the same in each experiment and reaction rates are therefore comparable. Unlike the two unmodified titania samples, which do not absorb visible light, all modified photocatalysts efficiently decomposed the toxin, with TiO_2-C and TiO_2-Rh(III) having the highest activity. In the latter system half of the toxin present in solution was degraded after 10 min whereas TiO_2-C needed 30 min to induce the same amount of destruction. As can be recognized, only the TiO_2-Rh(III) sample enabled complete toxin degradation after 60 min.

186 Scheme 1 summarizes the positions of band edge and
187 absorption onset of the various photocatalysts. It is rather unlikely
188 that the small changes in the redox potentials of the light-generated
189 electron and holes are responsible for the different degradation
190 activities. It is more likely that the different chemical nature of the
191 reactive holes seems to be decisive. It was proposed that in the
192 case of the Rh(III) modified material the hole is a Rh(IV) species
193 (Eq. 1, Dai et al., 2008), whereas in TiO_2-C and related carbon-
194 modified titania it may be a radical or radical cation of a condensed
195 aromatic compound (Neumann et al., 2005; Zabek et al., 2009 and
196 references cited therein). It appears very probable that such
197 different species oxidize microcystin with different reaction rates. It
198 is known that the interfacial electron transfer from the conduction
199 band to oxygen (Eq. 2) is the rate-determining step of most
200 semiconductor catalyzed photooxidation reactions (Gerischer and
201 Heller, 1991; Schwitzgebel et al., 1995). If this would be the case,
202 then TiO_2-C should react faster than TiO_2-Rh(III) since the driving
203 force is lower for the latter due to the corresponding flatband
204 positions of –0.48 V (Sakthivel and Kisch, 2003) and -0.34 V (Dai
205 et al., 2008) for the carbon- and rhodium-modified material,
206 respectively. However, it cannot be excluded that charge
207 generation in TiO_2-Rh(III) is more efficient resulting in a higher
208 electron concentration and therefore in faster oxygen reduction (Eq.
209 2). As a result of this also the concentration of the hydroxyl radical,

the other strongly oxidizing intermediate generated through reaction steps according to Eq. 3-6, are expected to be higher than in TiO_2-C.

$$[TiO_2]O\text{-}Rh^{3+} + h\nu \rightarrow [TiO_2]O\text{-}Rh^{4+} + e^-_{CB} \quad (1)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{-\bullet} \quad (2)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^{\bullet} + OH^- + O_2 \quad (5)$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\bullet} + OH^- \quad (6)$$

The observation that TiO_2-Pt(IV) is much less active than the rhodium and carbon modified samples suggests that the adsorbed chlorine radical (representing the reactive hole) generated through a homolytic Pt-Cl bond cleavage (Burgeth and Kisch, 2002) can induce only an inefficient microcystin oxidation. TiO_2-Pt(IV) exhibits the strongest dark adsorption of 84%. A light-induced desorption of microcystin may be responsible for the small concentration increase found for P25.

In the work performed by Choi et al. (2007) using a nitrogen doped titania sample 50% toxin destruction was achieved in around 30 min with complete decomposition reported within 2 h visible light photocatalysis. It is not possible to directly compare the results of

234 this study with those obtained in the work of Choi et al. (2007) as
235 the experimental conditions such as the initial toxin concentration
236 and light intensity were not the same.
237
238 In order to assess the relative efficiency of the visible light
239 photocatalytic process to the UV absorbing titania, the degradation
240 of microcystin-LR was examined using both a standard Degussa P25
241 material and a modified P25 catalyst TiO_2-Pt(IV) under UV
242 irradiation. For both materials the microcystin was decomposed
243 within 10 min of photocatalysis (Fig. 2c) as compared to about 20
244 min for the best visible light photocatalyst TiO_2-Rh(III). This
245 unexpected result can be rationalized by assuming that holes
246 generated below the valence band edge ("hot carriers") rather
247 oxidize microcystin than relax to the conduction band edge level.
248 The opposite behaviour may be responsible for the lower activity of
249 TiO_2-Rh(III).
250
251 The use of artificial UV light sources for photocatalytic water
252 treatment represents one of the most significant costs of the
253 process. Consequently there has been significant interest in utilizing
254 sunlight as the energy source for large scale photocatalytic water
255 treatment (Bahnemann, 2004). Unfortunately UV light represents
256 approximately 5% of the energy in solar light, while 45% is in the
257 visible region. Therefore at the planet's surface, the typical UV-flux

of 20 to 30 W m^{-2}, the sun generates 0.2 to 0.3 mol photons m^{-2} h^{-1} between 300-400 nm for potential utilisation by photocatalytic reactors (Bahnemann, 1994). If visible light absorbing catalysts were to be utilised potentially up to nine times this energy could be available, depending on the band gap of the catalyst being utilized. Consequently, although it would appear in this study that the TiO_2/UV process is more efficient than the TiO_2/Visible process, the advantages of being able to utilise visible light far outweigh the relatively poorer photocatalytic efficiency particularly for any large scale application. There may be potential toxicity risks associated with using metal doped titania materials. This risk would depend on the potential leaching of the dopant metals from the titania material into the water. In any commercial application it would be necessary to assess the risk of such a leaching process occurring and this would need to be a subject of more in depth future work.

4. Conclusions

The photocatalytic degradation of the cyanotoxin, microcystin-LR has been achieved using visible light absorbing photocatalysts. The process was demonstrated to be particularly efficient for the TiO_2-Rh(III) material with 90% of the toxin being destroyed in 20 min irradiation. Although the TiO_2/UV process was still relatively more efficient, the advantages of being able to use visible light to drive this process significantly outweigh the marginally faster

kinetics under UV irradiation. These visible light absorbing materials could therefore significantly improve the viability of semiconductor photocatalysis as a practical water treatment process for removal of microcystins from potable water supplies.

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409 activity in carbon-modified titania. Photoch. Photobio. Sci. 8,
410 264–269.
411

412 **List of Captions for Figures.**

413
414 **Fig. 1.** Experimental set up for Photocatalysis Studies.
415
416 **Fig. 2.** a) Degradation of microcystin-LR in the presence of P25
417 with no illumination. b) Degradation of microcystin-LR using
418 different photocatalyst materials. TH ▲, P25 ■, TiO_2-C ♦, TiO_2-
419 Pt(IV)□ and TiO_2-Rh(III)◇. c) Degradation of microcystin-LR in the
420 presence of modified P25 TiO_2-Pt(IV) ■ and P25 ♦ under UV
421 illumination using a deuterium light source.
422
423 **Scheme 1**. Band edge positions and onset of absorption (---)
424 of various photocatalysts. Lengths of arrows correspond to energy
425 of exciting light ($\lambda \geq 400$ nm). (Sakthivel and Kisch, 2003; Burgeth
426 and Kisch, 2002; Dai et al., 2008.)
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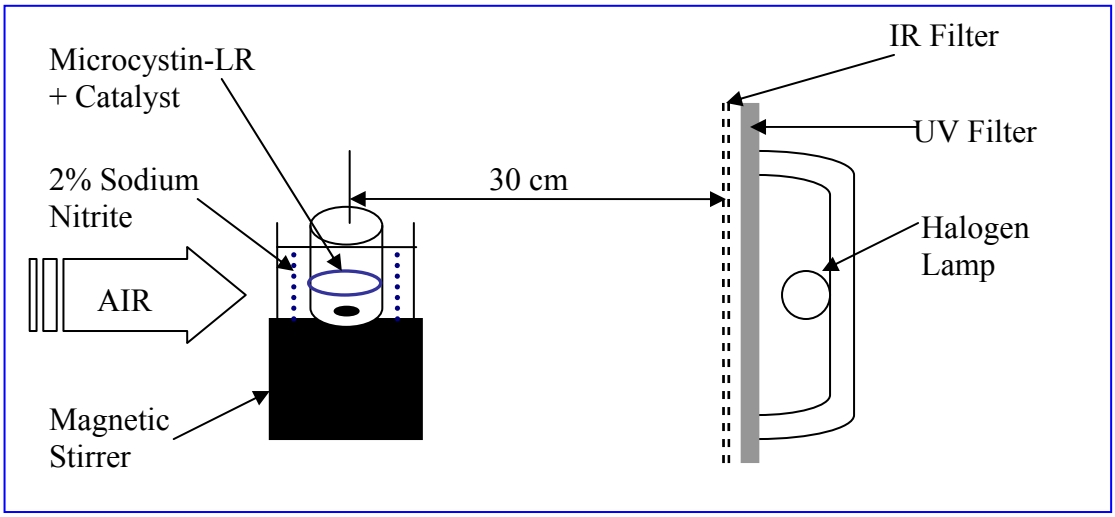
Microcystin-LR
+ Catalyst
2% Sodium
Nitrite
AIR
Magnetic
Stirrer
30 cm
IR Filter
UV Filter
Halogen
Lamp

Fig. 1

447 **Table 1.** Percentage of Microcystin-LR in solution after
448 equilibration in the dark (a) and after 60 min of visible light
449 irradiation (b).
450

Photocatalyst	% Microcystin-LR remaining in solution	
	t = 0	T = 60 min
P25	57	60
TH	80	70
TiO_2-Pt(IV)	16	10
TiO_2-C	68	20
TiO_2-Rh(III)	40	0

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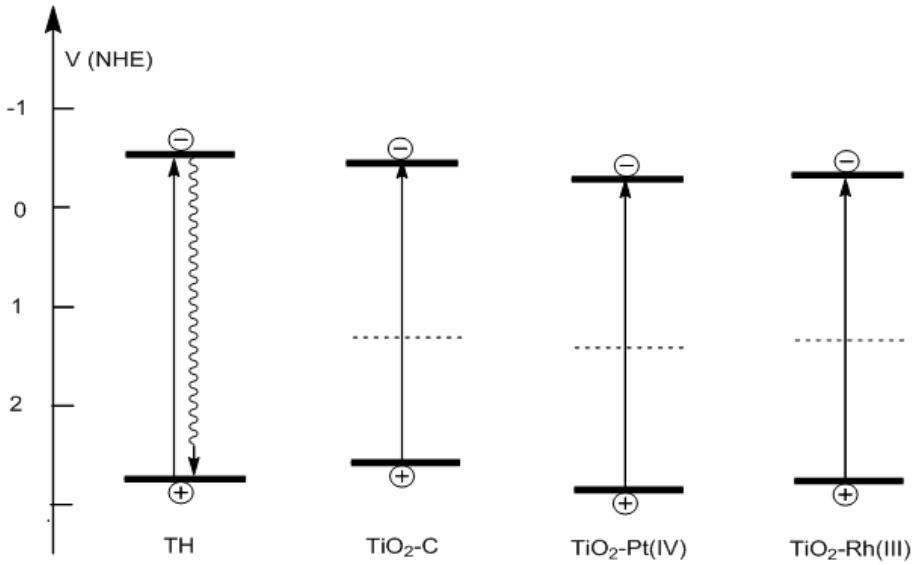

Scheme 1.