Destruction of cyanobacterial toxins by semiconductor photocatalysis

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The rapid destruction of microcystin, a cyanobacterial toxin, using a titanium dioxide photocatalyst is observed; the process is extremely efficient with high concentrations of toxin completely undetectable within 10–40 min, depending on the initial concentration.

Cyanobacterial (blue-green algal) toxins are extremely toxic naturally occurring substances which display hepato- and neuro-toxic behaviour.[1,2] Several genera of freshwater cyanobacteria including *Microcystis*, *Oscillatoria*, *Anabaena* and *Aphanizomenon* produce a range of potent natural toxins. These toxins can be classified in two general categories, neurotoxins [*e.g.* anatoxin-a, anatoxin-a(s) and saxitoxins] and hepatotoxins, namely microcystins which are the subject of this investigation. The heptapeptide microcystins are a family of *ca.* 50 congeners which exhibit potent inhibition of protein phosphatase 1 and 2A resulting in a range of clinical symptoms. Acute doses of microcystin, such as that recently experienced by patients undergoing dialysis, results in death due to hepatic failure.[3] Longer-term exposure to sub-lethal levels, however, is suspected of promoting primary liver cancer. The incidence of cyanobacterial blooms in freshwaters, including drinking water reservoirs, appears to have increased over the past few decades due to rising nutrient levels caused by intensive farming practices, sewage generation and detergent usage.[4] Microcystins are chemically very stable[5] and conventional water treatment processes fail to remove them, furthermore the use of more advanced methods such as granular carbon filtration and photochemical degradation have shown only limited efficacy.[6,7] The use of semiconductor photocatalysis for destruction of environmental pollutants is a well established technique with the mineralisation of a wide range of materials being reported.[8] When semiconductors are illuminated with light of an appropriate wavelength, electrons are promoted from the occupied valence band (producing oxidising sites) to the unoccupied conductance band (producing reducing sites). It is believed that hydroxyl radicals are generated at the valence band which promote the mineralisation of the pollutants.[9]

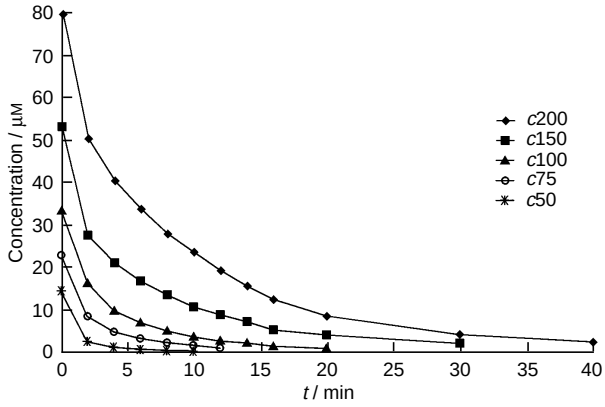

Fig. 1 The destruction of a range of concentrations of microcystin-LR using a titanium dioxide photocatalyst. Samples were quantified by HPLC using the previously described method of Lawton *et al.* (ref. 11).

Table 1 Rates of decomposition of microcystin-LR in the presence of TiO_2 photocatalyst

Initial toxin concentration/μm	Initial rate/ μm min^{-1}	Specific activity/ μm min^{-1} cm^{-2} ($\times 10^{-6}$)[a]	Specific rate/ μm cm^{-2} min^{-1} μm $photon^{-1}$ ($\times 10^{-3}$)[b]
50	5.95	108.3	33.4
75	7.20	130.8	40.4
100	9.51	155.1	47.9
150	12.22	233.2	72.1
200	14.60	265.5	82.0

[a] The specific activity represents the rate of destruction per unit area of catalyst assuming a catalyst surface area of 50 m^2 g^{-1}. [b] The specific rate represents the rate of destruction per unit area of catalyst per photon absorbed assuming the number of photons absorbed by the reactor as 1×10^{-4} photons min^{-1} determined using potassium ferrioxalate actinometry (ref. 19).

We have discovered that this technique is extremely effective in the destruction of microcystin-LR (molecular weight 994)[2] one of the most commonly occurring cyanobacterial toxins. This toxin, a heptapeptide with the generic structure of a microcystin and leucine (L) and arginine (A) in the variable positions, was purified from a natural sample of *Microcystis aeruginosa*.[10] Aqueous solutions of microcystin-LR (pH 4, 306 K) were illuminated in the presence of air and a TiO_2 catalyst (1% m/v solution of TiO_2 Degussa P-25) using a xenon UV lamp (280 W UVASpot 400 Lamp, Uvalight Technology Ltd, spectral output 330–450 nm). The investigation was performed on a series of solutions containing varying concentration of microcystin-LR. The concentrations (μm) used to evaluate the photocatalytic destruction of microcystin-LR greatly exceeded that which occurs naturally (nm–pm). This, however, enabled us to directly quantify the toxin by HPLC (as described elsewhere[11]) without multi-step processing which is necessary to quantify the much lower levels found in the environment. Very rapid destruction of microcystin-LR was observed for all concentrations (Fig. 1) even at the highest level tested (200 μm) with the toxin virtually undetectable after 40 min. It was found that the initial rate of decomposition was influenced by the initial toxin concentration (Table 1). In fact, at concentrations below those shown the rate of destruction was so rapid that microcystin-LR was undetectable by the first sampling point (2 min). These data suggest that the much lower concentrations which can be present in drinking water will be rapidly removed by this technique. The samples that were illuminated without TiO_2 displayed no degradation. As was observed with the initial rates of destruction, the specific rates and specific activities for the process were also reduced with increasing toxin concentration.

The Langmuir–Hinshelwood kinetic rate model has been widely applied to the initial rate of the photocatalytic destruction of a wide series of compounds.[12] Eqn. (1) displays the Langmuir–Hinshelwood kinetic rate law where r_0 is the initial rate of disappearance of the substrate and C_0 is the initial

substrate concentration, k is the rate constant of the reaction and K is the Langmuir adsorption constant.

$$r_0 = \frac{kKC_0}{1 + kKC_0} \quad (1)$$

The constants k and K may be determined from a plot of $1/r_0$ *vs*. $1/C_0$. If the system obeys the Langmuir–Hinshelwood model this plot should be linear. The intercept of the line provides us with $1/k$ while the slope is equal to $1/kK$. We examined the suitability of applying this model to our system. The reciprocal of initial rate *vs*. initial concentration values for the microcystin decomposition reactions were plotted (Fig. 2) and a linear relationship was observed, confirming that our system does indeed follow the Langmuir–Hinshelwood model. From the graph we determined that k and K for the destruction of microcystin were 19.23 μm min^{-1} and 2.9×10^{-2} dm^3 μmol^{-1} respectively. Rate and adsorption constants reported for the photocatalytic destruction for other organic compounds are comparable with those reported here.[8,13–15] Examples include 4-chlorophenol (k = 79.3 μm min^{-1}, K = 4.88×10^{-3} dm^3 μmol^{-1}),[13] benzene (k = 39 μm min^{-1}, K = 1.8×10^{-2} dm^3 μmol^{-1})[14] perchloroethylene (k = 34 μm min^{-1}, K = 8.6×10^{-3} dm^3 μmol^{-1})[14] and phenol (k = 12.9 μm min^{-1}, K = 2.19×10^{-2} dm^3 μmol^{-1}).[15]

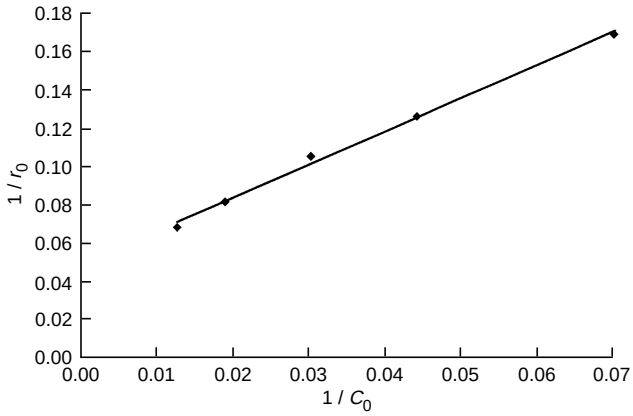

Fig. 2 Plot of the reciprocal of the initial rate ($1/r_0$) *vs*. the reciprocal of the initial concentration ($1/C_0$)

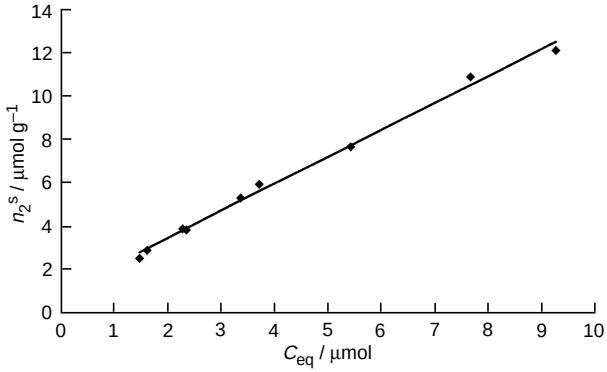

Fig. 3 Dark adsorption isotherm of microcystin-LR on TiO_2. The number of moles of microcystin-LR attached per gram of TiO_2 is n_2^S while C_{eq} represents the equilibrium concentration of microcystin after 24 h.

Dark adsorption isotherms, for the adsorption of microcystin on TiO_2, were prepared in order to compare the value of the Langmuir adsorption constant determined by this method with that of the constant determined using the initial rates method for the photocatalytic model. Universal bottles containing the toxin solution plus TiO_2 were shaken at room temperature in the dark using a flask shaker for 24 h. The dissolved microcystin-LR was separated from the catalyst and quantified by HPLC. The dark adsorption isotherm for microcystin-LR was plotted (Fig. 3) and the K value was found to be 2.9×10^{-4} dm^3 μmol^{-1}. This is 100 times lower than the value obtained using the initial rates method. Similar differences have been observed by other workers.[16,17] It has been proposed that this may be due to photoadsorption reactions at the TiO_2 surface or that decomposition of the substrate may not occur exclusively at the catalyst surface but may be promoted by hydroxyl radicals released from the catalyst surface.[16,17]

Preliminary results from our laboratory have shown that this system can also be successfully applied to the destruction of other classes of cyanobacterial toxins.[18] The efficient removal of microcystins and the benefits of the reported removal of other organic contaminants, indicates that photocatalysis is an extremely attractive treatment method for potable water supplies.

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