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Technical Note

Photocatalytic degradation of microcystin-LR in aqueous solutions

Loraine C.V. Jacobs [a], Patricio Peralta-Zamora [a,*], Francinete Ramos Campos [b], Roberto Pontarolo [b]

[a] Departamento de Química, Universidade Federal do Paraná, CP 19081, CEP 81531-980 Curitiba, PR, Brazil
[b] Departamento de Farmácia, Universidade Federal do Paraná, Avenida Prefeito Lothário Meissner, 632, CEP 80210-170 Curitiba, PR, Brazil

HIGHLIGHTS

- Heterogeneous photocatalytic degradation of microcystin-LR.
- High degradation capacity of bench and continuous TiO_2-based process.
- Residual microcystin-LR concentrations lower than 1 μg L^{-1}.
- Multiple hydroxylations followed by elimination of labile peptide residues of the molecule.

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ABSTRACT

In this work, the photocatalytic degradation of aqueous microcystin-LR was studied using TiO_2 and ZnO as photocatalysts. The process was optimised and characterised at the bench scale (200 mL); both semiconductors exhibited a high degradation capacity at reaction times of 1 min (degradation greater than 95%). The transient species that were observed indicate that the degradation occurs via the multiple hydroxylation and elimination of the labile peptide residues of the molecule. When photocatalysis was applied in a continuous treatment system (20–50 L), the photocatalytic process exhibited a high degradation efficiency, which resulted in residual microcystin-LR concentrations that were less than 1 μg L^{-1} (C_0 = 5 μg L^{-1}).

1. Introduction

Eutrophication is promoted by a variety of human activities, particularly the disposal of untreated sewage, and is a growing threat to aquatic ecosystems throughout the world (Sotero-Santos et al., 2008; Iberlings and Chorus, 2007). Eutrophication has numerous negative consequences, including the proliferation of cyanobacteria or blue–green algae (Mwaura et al., 2004; Molica et al., 2005). The propagation of these organisms has aesthetic, ecological, economic and public health consequences, the latter of which are mainly associated with the production of cyanotoxins (Sivonen and Jones, 1999; Soares et al., 2007).

Research into toxic blooms of cyanobacteria has revealed that they primarily produce microcystins (Mackintosh et al., 1990), which are cyclic heptapeptides that have significant hepatotoxic effects (Mackintosh et al., 1990; Sivonen and Jones, 1999). microcystin-LR is an environmentally relevant hepatotoxin, and its mechanism of action involves the inhibition of phosphatases, which are responsible for several metabolic functions (Dawson and Holmes, 1999).

Between 1991 and 2001, toxic cyanobacteria blooms were identified in several Brazilian states (PR, RJ, SP, P, RS, Ba and DF) and microcystins were predominant (FUNASA, 2003). In accordance with the recommendations of the World Health Organisation, the Brazilian Ministry of Health has established 1 μg L^{-1} as the maximum acceptable concentration of microcystin-LR in drinking water (Brazil, 2004).

Microcystins have a cyclic peptide structure that makes them highly stable and resistant to chemical hydrolysis; they can retain their toxicity even after boiling. Moreover, home filtration systems have a relatively low removal capacity (below 50%), even when they include activated carbon and ion-exchange-resin filtration systems (Lawton et al., 1998).

In general, procedures that are based on ultra- and nano-filtration can remove microcystins at rates greater than 95%, which makes them a good option for the treatment of small-to-medium volumes of water (Gijsbertsen-Abrahamse et al., 2006). Alternatively, chemical processes that use oxidising agents such as ozone (Brooke et al., 2006), potassium permanganate (Rodríguez et al., 2007) and chlorine (Rodríguez et al., 2008) can completely remove microcystins after relatively short reaction times. However, the low selectivity and mineralisation capacity of these chemicals can lead

* Corresponding author. Tel.: +55 41 33613297; fax: +55 41 33613186.
E-mail address: zamora@ufpr.br (P. Peralta-Zamora).

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to the formation of degradation intermediates, which creates biologically unstable environments in water supply systems.

Because of the disadvantages of conventional treatment systems, advanced oxidation processes have been investigated; these studies have focused on the use of heterogeneous photocatalysis that is mediated by titanium dioxide (Lawton et al., 2003; Choi et al., 2007; Antoniou et al., 2008). These studies have shown that aqueous microcystin degrades rapidly in the presence of an immobilised and suspended photocatalyst.

Even the degradation of microcystin by ZnO-mediated photocatalytic processes has not been found in the recent literature, several studies have demonstrated the high photocatalytic efficiency of this semiconductor toward many substrates of environmental relevance (Xie et al., 2011), in many cases showing results that are similar than that shown by TiO_2 (Kandavelu et al., 2004). Furthermore, ZnO can absorb a larger fraction of the solar spectrum than TiO_2, a fact that implies a better suitability for photocatalytic degradation in presence of sunlight (Elmolla and Chaudhuri, 2010).

The goal of this study is to verify of the ability of heterogeneous photocatalysis (UV/TiO_2 and UV/ZnO) to degrade aqueous microcystin-LR. According to our research, there are currently no reports in the literature that address the photocatalytic degradation of microcystin using the ZnO/UV system.

2. Experimental

2.1. Chemicals

Aqueous microcystin-LR (Abraxis, 95% purity) was used at concentrations that ranged from 1000 μg L^{-1} to 5 μg L^{-1}. Degussa P-25 titanium dioxide (75% anatase/25% rutile, BET 50 $m^2 g^{-1}$) and Merck zinc oxide (wurtzite, BET 4 $m^2 g^{-1}$) were used in the heterogeneous photocatalysis process.

HPLC-grade formic acid, methanol and acetonitrile (JT Baker) were used in the chromatographic analyses. All of the other reagents were of analytical grade.

2.2. Photocatalytic treatment

The degradation of aqueous microcystin-LR was studied in a 250-mL batch photochemical reactor that was equipped with a water cooling system (25 ± 2 °C) and a magnetic stirrer. The sample was radiated using a mercury vapour lamp at 125 W (without the original glass bulb) that was inserted into the solution through a quartz (UV-C) or Pyrex (UV-A) bulb. In this reactor, TiO_2 or ZnO (250 mg L^{-1}) was added to the aqueous microcystin-LR (200 mL, pH 6), and the solution was treated up to 10 min. Aliquots were collected at regular intervals (typically 1, 3, 5 and 10 min) and submitted to analytical control. To evaluate the adsorption of microcystin into the photocatalyst surface, experiments were carried out in the absence of radiation. To assess the effect of photolysis, experiments were carried out in the presence of UV-C and UV-A radiation, but in the absence of photocatalyst.

The degradation of the sample was also studied in a continuous treatment system (Fig. 1) that was constructed from four PVC tubular reactors that each had a 2.6 L capacity. Mercury vapour lamps (125 W) were placed on top of each reactor and protected with a Pyrex glass bulb. The residue was fed upstream at a flow rate of approximately 1 L min^{-1} using a peristaltic pump. In this reactor, TiO_2 or ZnO (250 mg L^{-1}) was added to the aqueous microcystin-LR (pH 6), and the solution was treated up to 10 min. Aliquots were collected at regular intervals and submitted to analytical control.

2.3. Analytical control

The microcystins were quantified using an Enzyme-Linked Immunoabsorbent Assay (ELISA); the tests were performed using ENVIROLOGIX (EP 022, Portland, USA) or Abraxis (PN 522015, Philadelphia, USA) kits. ELISA is based on the reaction between microcystin and specific monoclonal antibodies. All of the tests were conducted according to the manufacturer's recommended procedure.

Chromatographic analysis was performed on an Agilent chromatographic system, which consists of a quaternary pump and autosampler coupled to a mass spectrometer (Applied Biosystems); the mass spectrometer is a triple-quadrupole API 3200 that uses positive electrospray ionisation. A C_{18} silica column (Waters 150 × 3 mm) with a pore size of 3 μm was used (Phenomenex, Torrance, CA). A gradient elution was employed; the eluent consisted of a mixture of 0.1% formic acid in water (phase A) and 0.1% formic acid in acetonitrile (phase B). The mobile phase initially contained a 70/30 ratio of A/B, and this ratio was adjusted to 30/70 A/B over 25 min. The flow rate of the eluent was 0.20 mL min^{-1}, and the injection volume was 20 μL.

3. Results and discussion

3.1. Photocatalytic degradation of microcystin-LR

The impact of the experimental variables (pH and mass of the photocatalyst) on the degradation efficiency was investigated

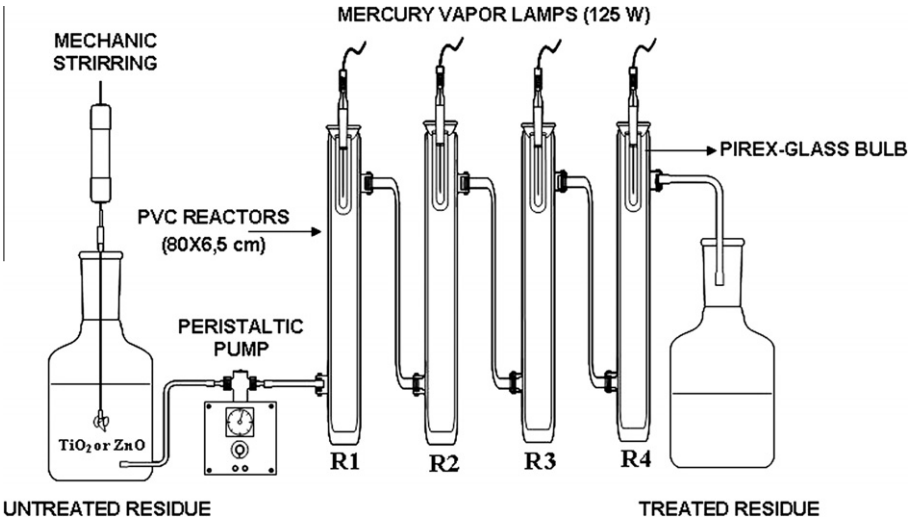

Fig. 1. A schematic of the continuous photochemical reactor used to study the photocatalytic degradation of microcystin-LR.

using a factorial design system. Each variable was studied at two values (pH levels of 4 and 8 and photocatalyst masses of 50 and 150 mg), which created a 2^2 complete factorial design around a central point (pH: 6, photocatalyst mass: 100 mg) performed in triplicate. A preliminary experiment was performed at low microcystin concentrations (5–15 μg L^{-1}), and both photocatalysts exhibited significant adsorption. The concentration of the model substrate was consequently increased to 50 μg L^{-1}.

Measurements of the amount of microcystin that had been removed after a reaction time of 1 min (monitored by ELISA) allowed determining a negligible influence of the mass of the semiconductor on the degradation capacity of the photocatalytic system (Fig. 2). However, the pH has a slightly negative effect (−5) on the degradation capacity of TiO_2 and a positive effect (3.5) on the degradation capacity of ZnO. The pH can influence a photocatalytic process by modifying the semiconductor surface or the chemical nature of the target compound (Hoffman et al., 1995; Domènech et al., 2001). Therefore, the TiO_2-mediated photocatalysis is, in general, more efficient at a pH level between 3 and 5, whereas the ZnO-mediated process is more efficient at a pH between 6 and 8 (Domènech et al., 2001).

Even though certain pH values led to higher degradation efficiencies, the differences between the degradation efficiencies were relatively small. Therefore, a pH of approximately 6 (which corresponds to the natural pH of aqueous microcystin) and a semiconductor mass of 50 mg were used in all subsequent experiments.

The degradation of aqueous microcystin (50 μg L^{-1}) was assessed for reaction times up to 10 min, and the results are shown in Fig. 3. In the TiO_2-mediated process (Fig. 3a), the substrate was gradually adsorbed; a maximum removal of approximately 50% was achieved after a contact time of 10 min. In the ZnO-mediated process (Fig. 3b), the adsorption was less efficient; 20% removal was achieved in the same reaction time.

The substrate was rapidly degraded by photolysis with UV-C radiation (Fig. 3a and b); it was almost completely removed after a reaction time of 5 min. According to previous studies (Tsuji et al., 1995), high-energy radiation induces a structural change in the microcystin-LR molecule; conformational isomers such as 6(*Z*)-Adda-microcystin-LR are typically formed. These isomers are not usually detected by ELISA. Even though these conformational changes only involve the rotation of the functional groups at carbon 8 of the Adda group, these isomeric forms do not exhibit mutagenic or carcinogenic properties (Tsuji et al., 1995) .

In the photocatalytic process, the microcystin-LR degrades quickly; a nearly complete removal was achieved after a treatment time of approximately 3 min (Fig. 3a and b).

Because of the strong effect of ultraviolet radiation (UV-C), further degradation studies were performed using lower-energy radiation. In these experiments, the mercury vapour lamp was protected by a Pyrex glass bulb, which only allows radiation with wavelengths that exceed 320 nm (UV-A) to pass. Under these conditions (Fig. 3c and d), the photolysis is less efficient (the microcystin completely degrades after 10 min of treatment), but the photocatalysis maintains its high degradation efficiency; a nearly complete removal of the substrate was achieved in approximately 10 min.

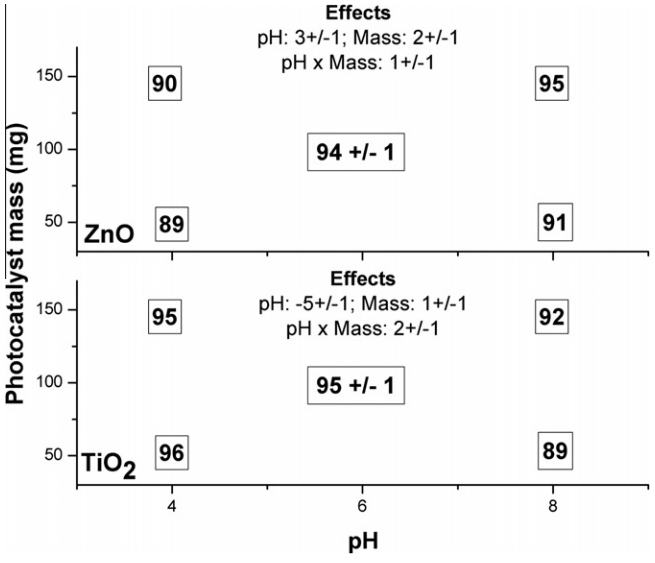

Fig. 2. A geometric representation of the 2^2 factorial design used to evaluate the effects of pH and semiconductor mass on the degradation efficiency of the photocatalytic process (Microcystin: 50 μg L^{-1}; volume: 200 mL; reaction time: 1 min; analytical control: ELISA). The numbers in boxes represent the degradation (%) of microcystin at a reaction time of 1 min.

3.2. Identification of the intermediates

Liquid chromatography coupled with mass spectrometry (HPLC–MS) was used to identify the main photolysis and photocatalysis intermediates. Because the ion analyser (quadrupole) has a relatively low sensitivity to microcystin-LR, the working concentration was raised to 1 mg L^{-1}.

The chromatographic pattern of microcystin-LR was recorded (Fig. 4); the pattern exhibited an average retention time of 3.91 min and a *m/z* ratio of 995.2, which is consistent with that of the *quasi* molecular ion $(M + H)^+$ reported in the literature (Antoniou et al., 2008).

To study the photolysis process, the sample was submitted to UV-C and UV-A radiation for up to 3 min (Fig. 4). When high-energy radiation (UV-C) was applied, the intensity of the main peak was constant; however, the profile changed, suggesting that three species co-eluted with a retention time between 4.0 and 4.2 min. In the mass spectrometric analysis, a similar molecular ion signal (*m/z* 995.3–995.5) and fragmentation profile were observed; only the intensities and relative abundances of the profiles varied. These observations suggest the co-elution of highly similar compounds; this conclusion is supported by the results of previous investigations into the isomerisation of microcystin-LR when it is submitted to high-intensity radiation (Tsuji et al., 1995).

A similar experiment was conducted using lower-energy radiation (UV-A). In this case, the intensities and the profiles of the chromatographic peaks remained the same, suggesting that the compound retained its original structure (*m/z* 995.2). This result is consistent with previous studies (Welker and Steinberg, 1999), reporting that microcystin-LR is resistant to lower-energy radiation (solar).

Preliminary experiments confirmed the high degradation efficiency of heterogeneous photocatalysis. This high efficiency makes detection of the degradation intermediates of either photocatalyst difficult. Therefore, the treatment conditions were relaxed so that the degradation intermediates could be observed; the concentrations of the photocatalyst (250 mg L^{-1}) and microcystin-LR (1 mg L^{-1}) were maintained, but the radiation exposure was changed. The UV-C radiation was provided by a mercury vapour lamp (125 W) that was placed at a distance of 15 cm from the surface of the solution.

After treatment with ZnO for 1 min, two degradation intermediates were observed. Previous research (Antoniou et al., 2008) indicates that the first intermediate (t_r: 4.25 min, *m/z* 1017.3) may arise from the incorporation of three hydroxyl groups into the Adda residue and the removal of CO from the arginine group. The second transient species (t_r: 1.80 min, *m/z* 825.8) may have arisen

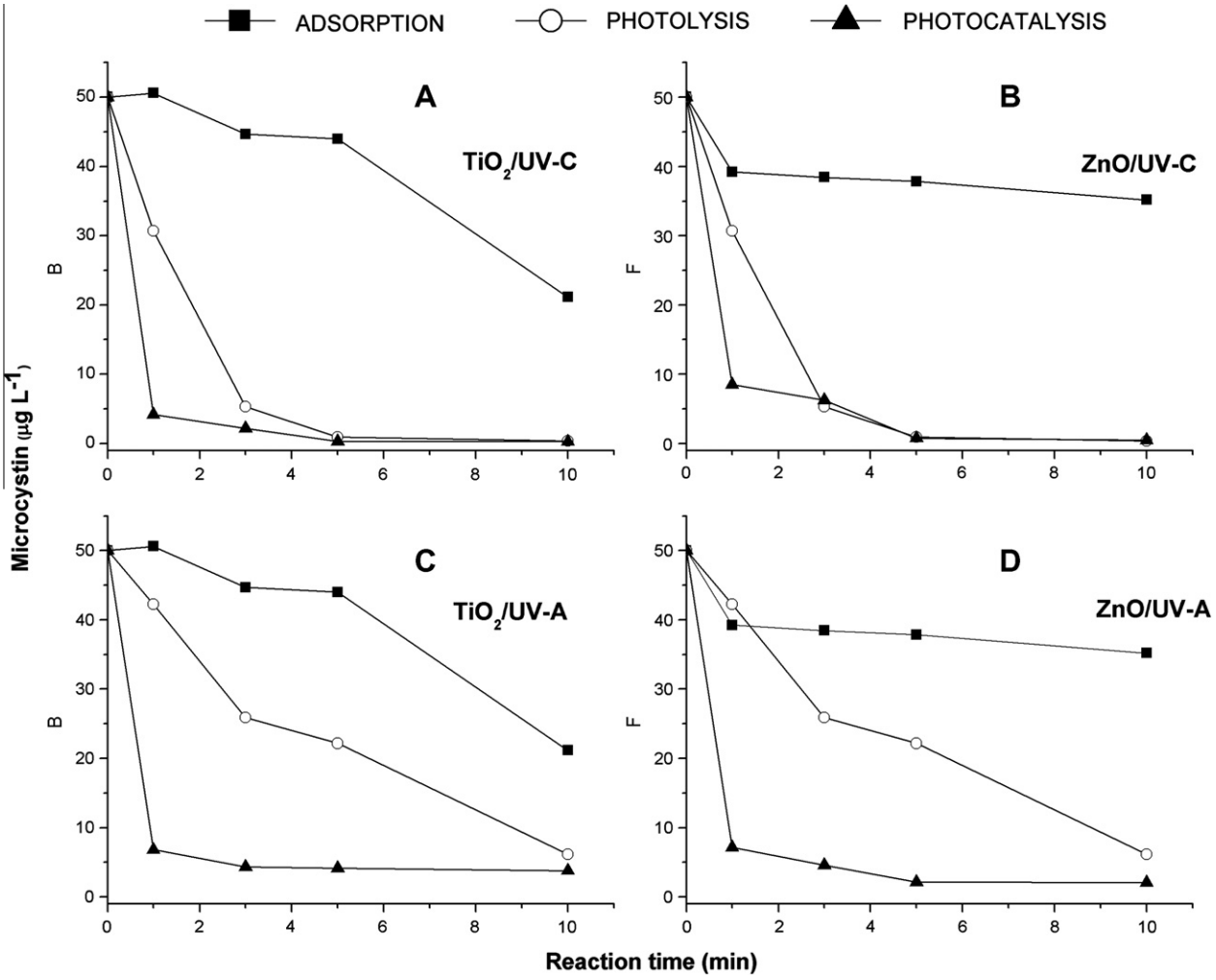

Fig. 3. Changes in the concentration of microcystin-LR during TiO_2- and ZnO-photocatalysis assisted by UV-C (A and B) and UV-A (C and D) radiation.

from the fragmentation of the Adda residue at the C8-C9 bond (Fig. 4).

Unfortunately, the literature contains no reports that pertain to the photocatalytic degradation of microcystin-LR by ZnO. However, the TiO_2/UV studies indicate that at least 14 degradation products are formed and that these products have *m/z* ratios between 1071.5 and 783.4 (Antoniou et al., 2008). In general, fragments with $m/z > 1000$ are formed from the hydroxyl addition or substitution at unsaturated MC-LR bonds, especially those in Adda or Mdha residues (Antoniou et al., 2008).

In the TiO_2 experiments, only one transient species was observed. It had a t_r of 1.8 min and a *m/z* ratio of 804.7, suggesting that this fragment was formed from the loss of leucine and Adda residues from the trihydroxide microcystin-LR molecule.

Because of the complexity of the microcystin-LR molecule and the photocatalytic degradation process, it is difficult to propose a degradation mechanism. According to the literature (Antoniou et al., 2008), most of the degradation intermediates appear in the first 2 min of treatment and are completely eliminated after approximately 120 min. Polyhydroxylated intermediates are initially formed ($m/z > 1000$) by hydroxyl addition or substitution at the unsaturated groups of the Mdha and Adda residues. The labile C8–C9 bond of the Adda residue can then be easily broken, which results in the formation of fragments with a *m/z* ratio of approximately 850. As more labile peptide residues are eliminated, intramolecular cyclisation can occur, which forms cycles with a lower mass (*m/z* of 700).

Fig. 4 illustrates the previously described reactions. This degradation process is supported by the observations of this study and those that have been reported in the literature (Antoniou et al., 2008).

3.3. Studies of degradation in a continuous reactor

Finally, the degradation of microcystin-LR in a continuous photochemical reactor (Fig. 1) was investigated. These experiments were conducted using 5 μg L^{-1} microcystin-LR solution at its natural pH (approximately 6), 12.5 g of photocatalyst (250 mg L^{-1}) and a flow rate of 1 L min^{-1}. Aliquots were collected at regular intervals from each of the four reactors, and ELISA was used to determine the residual microcystin content in each sample.

When TiO_2 was used (Fig. 5a), the continuous photocatalytic system exhibited a high degradation capacity, and residual microcystin concentrations below the WHO-recommended limit (1 μg L^{-1}) were achieved by all of the reactors at all times. In reactor 4, which had the longest retention time (approximately 10 min), the concentrations were below the quantification limit (0.1 μg L^{-1}).

The degradation efficiency was significantly lower in the case of ZnO (Fig. 5b). In reactors 1, 2 and 3, the residual microcystin concentrations were greater than 1.0 μg L^{-1}. In reactor 4, however, the degradation reached approximately 80%, which resulted in residual concentrations that approached the recommended WHO limit (1 μg L^{-1}).

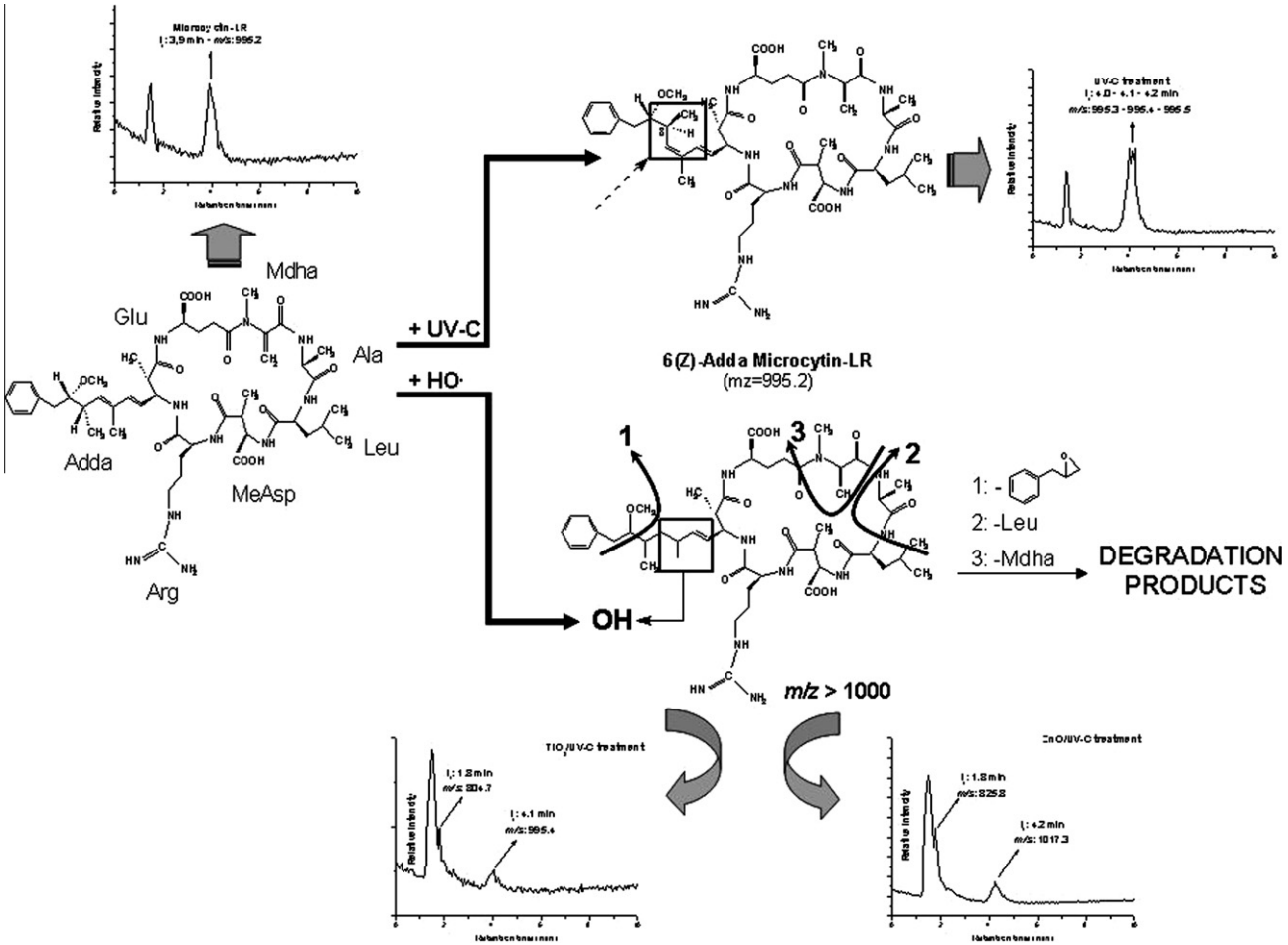

Fig. 4. The chromatographic identification of the reaction intermediates of the photolytic and photocatalytic degradation of microcystin-LR.

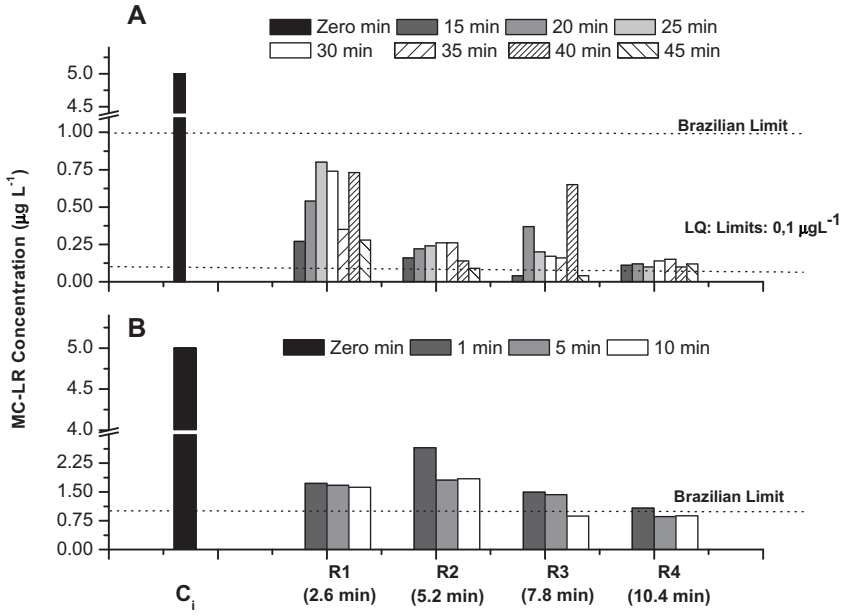

Fig. 5. The residual concentration of microcystin-LR during photocatalytic treatment with TiO_2 (A) and ZnO (B).

Differences between ZnO and TiO_2 were expected because previous studies report that TiO_2 is more efficient than ZnO for inducing mineralisation in organic matter (Yeber et al., 1999).

4. Conclusions

Aqueous microcystins are rapidly degraded by heterogeneous photocatalysis; they are almost completely removed at reaction times of less than 5 min. When applied in continuous mode, the photocatalytic process maintains its high degradation capacity, which results in residual microcystin concentrations that are below the recommended limit of the World Health Organisation ($1\ \mu g\ L^{-1}$).

Because microcystin-LR has a high photosensitivity, it is significantly degraded by photolysis under UV-C radiation. However, photolysis usually only causes small conformational changes in the functional groups that are located on the Adda residue. Photocatalysis, however, induces higher degrees of degradation. This process involves multiple hydroxylations that are followed by the elimination of the labile peptides.

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