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Effect of TiO_2 photocatalysis on the destruction of *Microcystis aeruginosa* cells and degradation of cyanotoxins microcystin-LR and cylindrospermopsin

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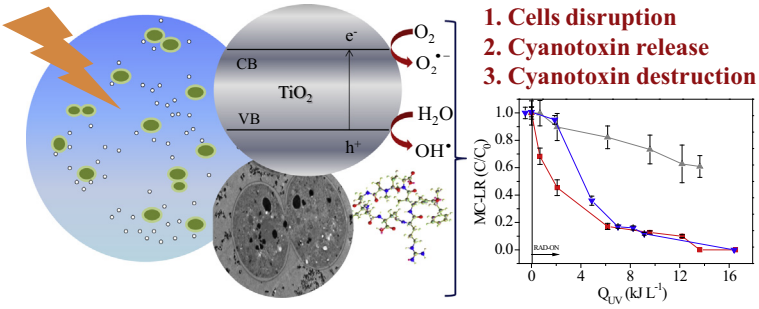
HIGHLIGHTS

- Destruction of the cyanobacterium *M. aeruginosa* by solar TiO_2 photocatalysis.
- TiO_2 nanoparticles aggregate in the exterior surface of the cell.
- Cell lysis is mainly associated with cell wall attack by the reactive oxygen species.
- Degradation of MC-LR and CYN cyanotoxins by solar TiO_2 photocatalysis.
- Treatment of water from a Portuguese river containing cyanobacterial blooms.

GRAPHICAL ABSTRACT



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ABSTRACT

This study assesses the effect of a solar driven TiO_2 photocatalytic process on the destruction of the cyanobacteria *Microcystis aeruginosa* with simultaneous removal of intracellular and extracellular microcystin-LR (MC-LR) due to cell lysis. Transmission electron microscopy (TEM) was used to study the interaction between TiO_2 nanoparticles and *M. aeruginosa* cells. Due to the cell size, TiO_2 nanoparticles aggregate on the exterior surface of the cell. Cell lysis is mainly associated with cell wall attack by the reactive species formed on the semiconductor surface, leading to the release of toxins to the liquid phase. The efficiency of the solar driven TiO_2 photocatalytic process was also evaluated in the treatment of natural water from a Portuguese river containing cyanobacterial blooms, in which prevails the genus *Microcystis*. The degradation of MC-LR, previously purified and spiked in distilled water, was assessed using a pilot scale solar photoreactor. Two degradation byproducts were identified and relative abundances were evaluated along the reaction time. The best results corresponding to the faster MC-LR and byproducts degradation were obtained with a catalyst concentration of 200 mg L^{-1}. The best catalyst concentration found to destroy MC-LR was also used in cylindrospermopsin (CYN) toxin degradation. CYN molecule showed higher recalcitrant character than MC-LR, requiring a higher solar exposure time to achieve similar degradation efficiencies.

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1. Introduction

Some cyanobacteria can produce a wide variety of toxins and additional molecules with unknown toxic potential (e.g. microviridins and aeruginosins) causing, therefore, incalculable difficulties in water treatment works, which depend on the raw surface water quality [1]. The presence of toxin-producing cyanobacteria in water for human consumption or recreational purposes poses a serious hazard to humans but has for too long been neglected or at most has been treated on a local level. Accumulation of toxin-producing cyanobacteria scum along the shores of ponds and lakes also present a hazard to wild and domestic animals. Providing the human population with safe drinking water is one of the most relevant issues in public health and will have more importance in this millennium [2].

The most common cyanobacterial toxins found in water are the hepatotoxins microcystins (MCs) [3,4]. The MC-LR is a heptapeptide cyclic compound with a ADDA group, containing leucine (L) and arginine (R) in variable positions (Fig. 1) [5]. MC-LR acts by inhibiting protein phosphatase which leads to hyperphosphorylation of cellular proteins such as cytokeratin 8 and 18 [6]. All protein phosphatase inhibitors are harmful to humans and warm-blooded animals [7]. Due to chronic effects, including the high risk of primary liver cancer, World Health Organization (WHO) has recommended a 1 $\mu g\ L^{-1}$ limit for MC-LR in drinking water [8].

CYN (Fig. 1) is an alkaloid structure that contains an uracil moiety attached to a sulphated guanidine moiety, suggesting that it may have carcinogenic activity [9]. CYN is resistant and stable at varying heat, light and pH conditions because of the presence of a tricyclic sulfated guanidine zwitterion group and uracil [9,10]. After 10 weeks at 50 °C only 57% CYN degradation was obtained, resulting in the appearance of an intermediate compound [9,10]. Additionally, boiling for 15 min does not cause a significant degradation of CYN [9,10].

Although cylindrospermopsin cyanotoxin has been detected in different natural waters around the world [8,11–13], few studies report the application of water treatment technologies to destroy this toxin [14], mainly due to the high costs associated with the purification process [15,16].

In contrast to microcystin (MC), a toxin that is released from the cells when their rupture occurs, high concentrations of CYN can be found in the water throughout the bloom development, when the cells are still viable [17]. This cytotoxin has been associated with liver and kidney damage using mouse bioassays, with symptoms that clearly can be distinguished from those caused by other cyanobacterial hepatotoxins including MCs [18].

The control of cyanobacterial toxins in drinking water is a hard task and research has been focused on the upgrade of water treatment plants with technologies able to eliminate those toxins. Pantelić et al. [19] reported that the elimination of cyanobacterial toxins in drinking water can be achieved through: (i) methods able to remove intracellular toxin, such as coagulation, dissolved air flotation, sand filtration and membrane processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis); (ii) methods able to remove extracellular toxin, such as chlorination, activated carbon adsorption, reverse osmosis, advanced oxidation technologies (permanganate oxidation, ozonation, UV photolysis, TiO_2 photocatalysis, Fenton, photo-Fenton, sonolysis) and biological oxidation.

Special attention has been given to TiO_2 photocatalysis, in which powerful reactive oxygen species (ROS), such as hydroxyl radicals ($OH^{\cdot}$), are responsible for the degradation of the cyanotoxin molecules into biodegradable compounds or the mineralization into CO_2, H_2O and inorganic ions [3,20–31].

However, there is a lack of information on the removal of cyanobacterial cells [32], such as *Microcystis aeruginosa*, using photocatalytic processes, regarding the elimination of intracellular and extracellular toxin, especially using real waters. In addition, the mechanism of cell destruction by TiO_2 photocatalysis is not completely known as well as the interaction of the nanoparticles with the cells.

The main goal of this study was to assess the performance of a solar driven TiO_2 photocatalytic process on the destruction of *M. aeruginosa* cells and simultaneous removal of intracellular and extracellular cyanotoxin MC-LR, using synthetic solutions and natural water from a Portuguese river containing cyanobacterial blooms. The interaction of TiO_2 nanoparticles with *M. aeruginosa* cells was evaluated by transmission electron microcopy (TEM). The degradation of purified MC-LR cyanotoxin spiked in distilled water was assessed using a pilot scale solar photoreactor with different TiO_2 concentrations, and the main degradation byproducts were identified. The best photocatalyst concentration was used in the photocatalytic degradation process of CYN toxin using a lab scale photoreactor.

2. Experimental

2.1. Cyanobacteria culture conditions, MC-LR and CYN purification

Stock cultures of cyanobacteria *M. aeruginosa* strain Laboratory of ecotoxicology, genomics and evolution – LEGE 91094 (IZANCY-A2) and *Cylindrospermopsis raciborskii* LEGE 97047, were separately inoculated in Z8 medium [33]. The cultures were kept at 25 ± 1 °C under fluorescent light (light/dark cycle of 14/10 h), for approximately 30 days. MC-LR was purified from the *M. aeruginosa* culture using the procedure previously described by Ramanan et al. [34]. All solvents used in HPLC analyses were high-purity chromatography grade (LiChrosolv, Merck). Aqueous solutions were prepared

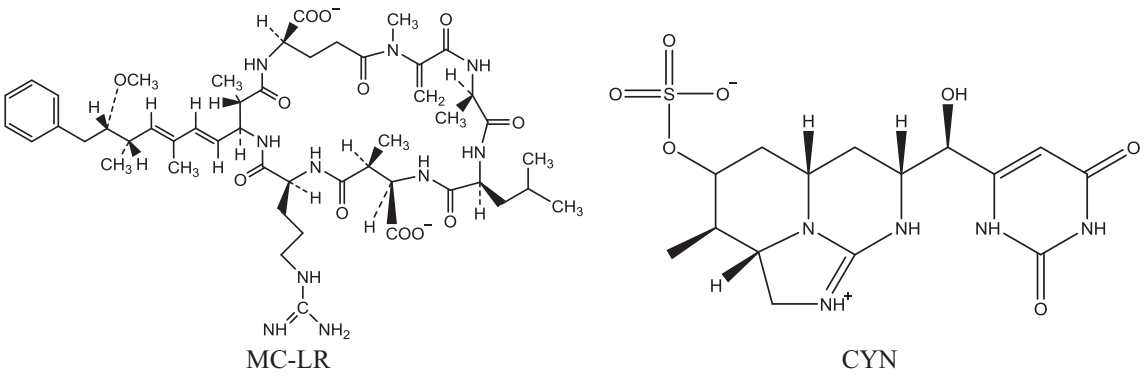

Fig. 1. MC-LR and CYN molecular structures (pH = 7.0).