Chemical Engineering Journal 330 (2017) 355–371

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Mechanisms underlying degradation pathways of microcystin-LR with doped TiO_2 photocatalysis

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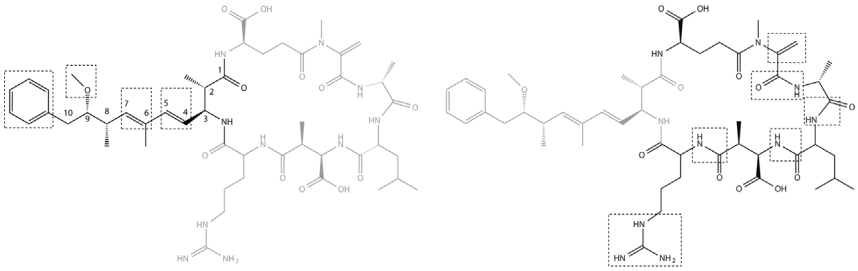
GRAPHICAL ABSTRACT



(A) Attack of the Adda side chain of microcystin-LR

(B) Attack of the cyclic structure of microcystin-LR

ARTICLE INFO

Keywords:
Titanium dioxide
Microcystin-LR
Water treatment
Photodegradation
Intermediates

ABSTRACT

The presence of cyanotoxins in different water sources, originating from cyanobacterial algal blooms, is a ubiquitous, global concern. Microcystins (MCs) are the most commonly occurring class of cyanbacterial toxin, and are characterized as cyclic heptapeptides containing five D-amino acids and two variable L-amino acids. Over 100 MC variants exist, and microcystin-LR (MC-LR) is one of the most hazardous and prevalent. Removing MC-LR from aqueous solutions by titanium dioxide (TiO_2) photocatalysis has been proposed as a possible solution for this. Both metal and non-metal doped TiO_2 photocatalysts have been investigated over recent decades for their MC-LR photocatalytic degradation properties under visible light. This review provides an overview of visible light-activated TiO_2 synthesis technologies, and structural and electronical properties. The photocatalytic behavior of visible light-activated TiO_2 for the photodegradation of MC-LR is discussed. The structural elucidation of reaction intermediates of the degradation pathways, and the mechanisms of MC-LR degradation by visible-light activated TiO_2 in comparison with conventional UV-activated TiO_2, is given particular emphasis. We also aimed to identify research gaps and uncertainties that exist for the use of visible light-activated TiO_2 in photocatalysis. Additional research requirements for visible light-activated TiO_2 photocatalysts and potential areas for future applications of doped TiO_2 photocatalysts under visible light are also proposed.

1. Introduction

Cyanobacterial blooms pose a significant threat to public health and the environment, as they can produce and release a variety of cyanotoxins into fresh and marine water systems [1–3]. Humans are exposed to cyanobacterial toxins through several avenues, including drinking

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http://dx.doi.org/10.1016/j.cej.2017.07.161
Received 1 May 2017; Received in revised form 9 July 2017; Accepted 27 July 2017
Available online 29 July 2017
1385-8947/

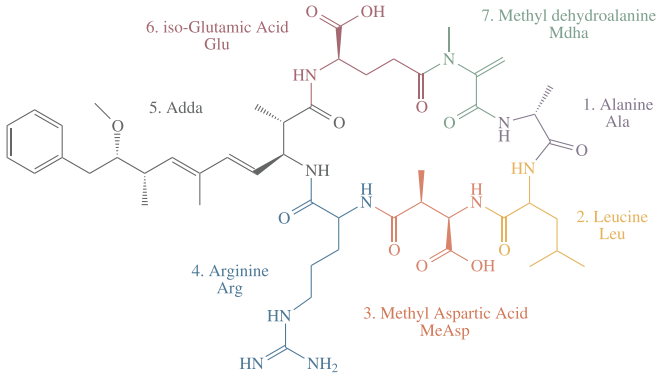

Fig. 1. Chemical structure of MC-LR.

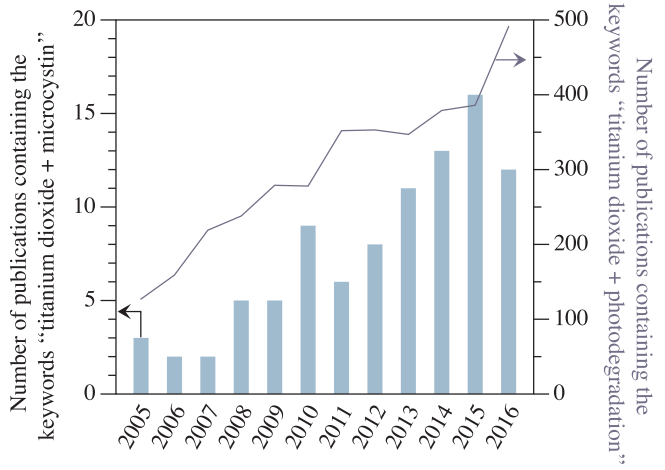

Fig. 2. Evolution of the number of publications in indexed journals containing the keywords "titanium dioxide + photodegradation" and "titanium dioxide + microcystins" between 2005 and 2016.

water, recreational contact, and the food chain [4–7]. Monocyclic heptapeptides, i.e., microcystins (MCs), is the most well-understood cyanotoxin family [8] with over 100 recognized members [9]. They have strong hepatotoxicity and can cause serious health problems in humans, including nausea, skin dermatitis, and liver damage [10–13]. It is also believed that they are responsible for the high levels of primary liver cancer in China [14,15]. Microcystin-LR (MC-LR) is the most frequently reported MC, and is also the most harmful. The L and R in this MC represent the amino acids leucine and arginine at the variable 2- and 4-positions, respectively. Fig. 1 illustrates the chemical structure of MC-LR, including its cyclic structure and the presence of the amino acid Adda, which renders MCs resistant to heat, hydrolysis, and oxidation.

The biological and chemical inertness, non-toxicity, and long-term stability of titanium dioxide (TiO_2) photocatalysis has led many to investigate its potential for application in antimicrobial, deodorization, and air and water purification. It has been shown that cyanotoxins, as well as off-odor compounds in aqueous solutions, can effectively be degraded through TiO_2 photocatalysis [16–24]. While the procedure has been determined as highly effective in the removal of cyanotoxins, a wide band gap of approximately 3.2 eV for anatase and 3.0 eV for rutile (the main polymorphs used in TiO_2 photocatalysis) indicates that the irradiation of conventional TiO_2 by a photocatalytic reaction can only occur using UV light ($\lambda < 387$ nm). Furthermore, quantum efficiency is greatly reduced by the rapid recombination of photo-induced electrons and holes [25,26], therefore, improving the generation and separation of photo-induced electron-hole pairs in TiO_2 is of particular importance for further applications involving the removal of organic pollutants, such as cyanotoxins, from water.

Several strategies, including structural and chemical modifications, have been adopted to increase the photoactivity of TiO_2. Doping with metal and/or non-metal is considered to be a potential method for enhancing the photocatalytic efficiency of TiO_2, as this may impede electron–hole recombination and improve its visible light harvesting capacity. This is significant because visible light constitutes more than 40% of solar photons, in comparison with the 4–5% coming from the UV portion of the solar spectrum [27].

Publications that included the keywords "titanium dioxide + photodegradation", and "titanium dioxide + microcystins" as topics in indexed journals (according to ISI Web of Science™ from 2005 to 2016) have been steadily increasing (Fig. 2), suggesting that TiO_2-based photodegradation of cyanotoxins is gaining scientific interest.

This review aims to analyze the most recent work on the use of doped-TiO_2 for the removal of MC-LR from aquatic systems. This review (1) describes the principles of TiO_2 towards the development of visible light activated-TiO_2 as a photocatalyst for removing MC-LR from aqueous solutions, and (2) outlines the photodegradation pathway of MC-LR under visible light activated-TiO_2. This review also highlights further research required for doped-TiO_2 removal of MC-LR.

2. Principles and mechanisms of TiO_2 photocatalysis

The photocatalytic machinery of TiO_2 is activated by the absorption of a photon *hv* with energy equal to, or greater than, the band gap of TiO_2. This results in an electron–hole pair on the surface of the TiO_2 nanoparticle, as depicted in Fig. 3 [28–32].

Different methodologies have been assessed for synthesizing metal and non-metal doped TiO_2, generating various structural and optical properties (see Supplementary Information) that aim to overcome some of the drawbacks mentioned above, in particular the band gap energy and recombination rate. Several mechanisms have been proposed after incorporating these impurities into the crystalline structure of titanium dioxide. The mechanisms of metal-doped TiO_2 photocatalysis are shown in Fig. 4(A): (1) band gap narrowing [33,34], (2) retardation of electron–hole recombination [35–37], (3) enhancing the adsorption of contaminants [38–41] and (4) enhancing the conductivity of TiO_2, so that electrons can be more effectively transferred from the majority of the TiO_2 structure to the surface area [42].

The mechanisms of non-metal-doped TiO_2 photocatalysis are shown in Fig. 4(B): (1) band gap narrowing [43–45], (2) enhancing the conductivity of TiO_2 so that the transfer of electrons from most of the TiO_2 structure to the surface region is less complex [46,47], (3) enhancing the adsorption of contaminants [48–50] and (4) TiO_2 oxygen sites substituted by non-metal atoms forming isolated impurity energy levels above the VB, and visible light illumination exciting electrons at the impurity energy level [51–53].