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A comparative study on the removal of cylindrospermopsin and microcystins from water with NF-TiO_2-P25 composite films with visible and UV–vis light photocatalytic activity

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ABSTRACT

In this investigation, in order to develop photocatalyst materials with improved photo-efficiency and visible light response compared to the state of the art materials, the role of Evonik Aeroxide® P25-TiO_2 (P25) nanoparticles incorporated in a modified sol–gel process to yield composite nitrogen and fluorine doped TiO_2-P25 (NF-TiO_2-P25) films was investigated. The addition of P25 nanoparticles in the sol leads to higher BET surface area, pore volume, porosity and total TiO_2 mass, as well as larger thickness and roughness of the films after heat treatment. Microscopy techniques confirmed partial sintering of NF-TiO_2 sol–gel formed and P25 nanoparticles having different average size. The existence of well defined regions of only anatase from NF-TiO_2 and anatase–rutile mix from P25 was verified in the micro-Raman spectra. The photocatalytic degradation of four microcystins (microcystin-LR, -RR, -LA and -YR) and cylindrospermopsin was evaluated with NF-TiO_2 and NF-TiO_2-P25 films under visible and UV–vis light. The general reactivity for the microcystins under acidic conditions (pH 3.0) was: MC-LA > MC-LR ≥ MC-YR > MC-RR where the highest initial degradation rate was achieved with the NF-TiO_2-P25 films ($5\,g\,L^{-1}$ of P25 in sol when irradiated with visible light and $15\,g\,L^{-1}$ of P25 in sol when irradiated with UV–vis light). Cylindrospermopsin showed negligible adsorption at pH 3.0 for all films. Nevertheless, significant photocatalytic removal was found under UV–vis light with maximum P25 loaded films indicating that the degradation was mediated by the involvement of photogenerated reactive oxygen species and not by the trapping reaction of the positive hole.

1. Introduction

The presence of cyanotoxins in surface waters has been reported and documented throughout the literature [1–8]. Cyanotoxins are highly toxic secondary metabolites that can be produced by cyanobacteria during harmful bloom events. They can also be released into the water after cell lyses, which may be caused by mechanical forces in drinking water treatment plants. Cyanotoxins in water are a potential health risk to humans and aquatic life. The most commonly occurring cyanotoxins reported are microcystins (MCs) and more recently cylindrospermopsin (CYN). The general structure of microcystins and the chemical structure of CYN are depicted in Fig. 1S. Microcystins are monocyclic heptapeptide hepatotoxins with five invariant amino acids and two variant L-amino acids in the structure, which are related to the name of the molecule. For instance, microcystin-LR (MC-LR) derives from the presence of the amino acid leucine (L) and arginine (R) in these variant positions and is the most toxic and most frequently found cyanotoxin. Other commonly detected variants include MC-RR, MC-YR and MC-LA, however, more than 90 derivatives are known so far. Several species of cyanobacteria produce MCs including *Anabaena* spp., *Oscillatoria* spp., and *Microcystis aeruginosa* [4]. Microcystins' mode of action consists of the inhibition activity of the protein phosphatases types 1 and 2A (PP1 and PP2A) which categorized them as potent tumor promoters.

Advances in analytical chemistry have helped identify the cyanotoxin, CYN, a tricyclic alkaloid consisting of a tricyclic guanidine moiety bridged to a hydroxymethyluracil group that is highly soluble in water [4,6,9–12]. Several species of cyanobacteria have been identified producing CYN, such as *Cylindrospermopsis raciborskii*,

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Aphanizomenon ovalisporum, and *Raphidiopsis* spp. [4,6]. They are predominantly found in tropical and subtropical regions but their spatial distribution has extended to temperate zones, including the United States and other northern hemisphere countries [10]. CYN has neurotoxic effects (inhibition of protein synthesis by binding to liver DNA and forms single DNA adducts which results in liver damage), hepatotoxic effects (inhibition of glutathione synthesis in hepatocytes), and cytotoxic effects (inhibitor of cytochrome p450) [11]. Moreover, CYN has been found to be relatively stable when exposed to different environmental factors (e.g., pH, temperature) [12].

Conventional treatment processes in drinking water plants (e.g., coagulation, flocculation, sedimentation and filtration) are inadequate for the removal of cyanotoxins [13], nevertheless these cyanotoxins are susceptible to chemical oxidation. Common oxidants, such as chlorine, chlorine dioxide and permanganate, have been able to oxidize several microcystin analogues and CYN. In the case of chlorine, a dose of 1.5 mg L^{-1} with a reaction time of 30 min was sufficient for at least 90% oxidation of MC-LR, MC-RR, MC-LA and MC-YR in two natural water samples [13]. The general reactivity towards chlorine was MC-YR > MC-RR > MC-LR > MC-LA and it was related to the structural differences of the functional groups present in the cyanotoxins with respect to chlorine. CYN chlorination at pH 7.0 had the maximum oxidation rate according to Rodriguez et al. [14]. The predominant species at circumneutral pH is HOCl, the most reactive form of chlorine, and can react with the dissociated form of CYN. Chlorine dioxide and permanganate are weaker oxidants and were inefficient to remove MCs and CYN due to their low reaction kinetic constants ($<1\ M^{-1}\ s^{-1}$) [15]. The removal of MC-LR, MC-RR and MC-LA, as well as CYN, via ozonation (O_3) was successfully achieved as well as with CYN [15–18]. The reactivity of MC-LR was slightly faster than that of MC-RR during ozonation of algae-laden source water [16]. The degradation efficiency was influenced by the effect of the dissolved organic matter present in solution which inhibits O_3 treatment. Spiked samples with MC-LR and MC-LA from two Australian reservoir waters (Edenhope and Myponga) were also subjected to batch ozonation [17]. It was found that a dose of 0.5 and 1.0 mg L^{-1} was necessary to achieve complete removal of the toxins for Myponga and Edenhope samples, respectively. Differences between the degradation efficiencies were due to the substantially different water quality parameters. In a separate study, a static dose of 0.38 mg L^{-1} of O_3 was used by Rodriguez et al. [15] to achieve a degradation of approximately 95% of CYN spiked in a eutrophic Swiss lake (Lake Greifensee) sample.

Recently, advanced oxidation processes (AOPs) have been established as an alternative to conventional chemical oxidation. These so-called AOPs are based on the formation of highly oxidizing and non-selective hydroxyl radical that exhibit higher second-order rate constants (10^8–$10^9\ M^{-1}\ s^{-1}$) than those of other oxidants [19]. Among AOPs, titanium dioxide (TiO_2) photocatalysis has gained significant attention for drinking water treatment due to its capacity to destroy recalcitrant organic contaminants [20–22]. The photocatalytic removal of several isoforms of MCs with TiO_2 under UV light has been investigated by many groups [23–28]. Lawton et al. [25] evaluated the influence of the solution pH on the surface interaction of MC-LR, -RR, -LW, and–LF with TiO_2 and the photocatalytic removal with UV light. Higher degradation rates were related to the higher extent of adsorption of the MCs at acidic pH values compared to alkaline values. Shephard et al. [26,27] used TiO_2 in suspension and immobilized as films illuminated with UV-C light for the removal of MC-LR, -YR and -YA. The effects of photolysis, TiO_2 loading, oxygen flow and the lake water matrices were investigated. Relatively high microcystin degradation rate constants ($0.25 \pm 0.01\ min^{-1}$ for MC-LR and $0.19 \pm 0.01\ min^{-1}$ for MC-RR) were achieved in synthetic water but slower degradation rate constants were obtained in natural water samples ($0.11 \pm 0.01\ min^{-1}$ for MC-LR and $0.09 \pm 0.008\ min^{-1}$ for MC-RR). Limited literature is found on the photocatalytic degradation of CYN with TiO_2 photocatalysis. Senogles et al. [28] used two commercially available TiO_2 nanoparticles under UV light to examine their efficiency on the degradation of this cyanotoxin. Several water parameters such as pH, dissolved organic carbon, temperature and initial CYN concentration were evaluated and high degradation efficiencies (75–80% at pH 4.0) were obtained indicating the feasibility of this photocatalyst for CYN degradation under UV light.

Second generation TiO_2 photocatalysis, where visible light photoactivation is possible via non-metal doping, has already being recognized as a potential and sustainable alternative for environmental remediation [29–32], including the treatment of drinking water supply sources contaminated with cyanotoxins [33–39]. Nitrogen and fluorine doped TiO_2 (NF-TiO_2) photocatalytic films have been successfully synthesized by a fluorosurfactant-assisted sol–gel method and the effectiveness of this catalyst was demonstrated for the photocatalytic degradation of MC-LR under visible light irradiation [35]. The incorporation of Evonik P25 nanoparticles into the sol can improve the NF-TiO_2 film physicochemical and optical properties. Chen and Dionysiou [40] developed a porous TiO_2-P25 composite film by modifying a previous method [41] by using low P25 loading (10 g L^{-1}) in the surfactant-assisted sol formulation employed. Following heat treatment, the film showed bimodal mesopore structure and good structural integrity [40]. The composite films demonstrated higher photocatalytic activity towards the degradation of creatinine as compared to pristine TiO_2 films. In addition, the composite mix of P25 nanoparticles and NF-TiO_2 should contribute to a more efficient utilization of the solar spectrum towards the photocatalytic degradation of cyanotoxins in water. In this study, we investigated the role of Evonik P25 in the physicochemical properties of NF-TiO_2-P25 composite films. The application of such composite TiO_2 films for the remediation of water contaminated with cylindrospermopsin and four microcystins (i.e., MC-LR, MC-RR, MC-YR and MC-LA) was further explored, under visible and UV–vis light.

2. Materials and methods

2.1. Reagents and sample preparation

MC-LR and MC-RR standards were obtained from Calbiochem. Other microcystin isoforms, such as MC-YR and MC-LA were obtained from Sigma and CYN was purchased from GreenWater Laboratories (Palatka, FL, USA). NF-TiO_2 was prepared using a modified sol–gel method previously developed [35]. In brief, a flurosurfacant (Zonyl FS 300, Fluka) was used as a pore template and fluorine dopant and ethylenediamine (Fisher) as nitrogen precursor. The fluorosurfactant was dissolved in isopropyl alcohol (99.8%, Pharmco), followed by the addition of acetic acid (glacial, Fisher) and ethylenediamine. Titanium tetraisopropoxide (Aldrich, 97%) was added dropwise to the sol and more acetic acid was added for peptidization. A stable sol was obtained after stirring overnight at room temperature. For the preparation of the mixed NF-TiO_2-P25, Aeroxide® P25-TiO_2 powder (Evonik; BET surface area of 53.9 $m^2\ g^{-1}$, pore volume of 0.172 $m^3\ g^{-1}$, 70% anatase/30% rutile) was added in each modified sol at a concentration of 5 and 15 g L^{-1} and sonicated for 15 min to improve dispersion. The pristine and composite films were immobilized on borosilicate glass substrates by dip-coating with a withdrawal velocity of 12.5 ± 0.3 cm min^{-1} and a total covered surface area of 10 cm^2. High temperature treatment was performed in a multi-segment programmable furnace (Paragon HT-22-D, Thermcraft) in air atmosphere where the