

## Iron based sustainable greener technologies to treat cyanobacteria and microcystin-LR in water

Virender K. Sharma, Long Chen, Blahoslav Marsalek, Radek Zboril, Kevin E. O'Shea and Dionysios D. Dionysiou

### ABSTRACT

The presence of the toxic cyanobacteria and cyanotoxin, microcystin-LR (MC-LR) and other cyanotoxins, in drinking water sources poses a serious risk to public health. Iron based technologies using magnetic zero-valent iron nanoparticles (nZVI) and ferrate ion ( $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ , Fe(VI)) represent greener approaches to remove cyanobacteria and degrade MC-LR in water. This paper reveals that nanoparticles of zero valent iron (nZVI) can destroy cyanobacteria in the source water and may play a preventive role in terms of the formation of cyanobacterial water blooms by removing nutrients like phosphate. Results on MC-LR showed that Fe(VI) was highly effective in removing MC-LR in water. Products studies on the oxidation of MC-LR by Fe(VI) demonstrated decomposition of the MC-LR structure. Significantly, degradation byproducts of MC-LR did not contain significant biological toxicity. Moreover, Fe(VI) was highly effective for the degradation of MC-LR in lake water samples. Mechanisms of removal and destruction of target contaminants by nZVI and Fe(VI) are discussed.

**Key words** | detoxification, ferrate, harmful algal bloom, microcystin, oxidation, zero valent iron nanoparticles

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### INTRODUCTION

Cyanobacteria have critical functions in terrestrial and aquatic ecosystems, which include oxygen evolution, fixation of nitrogen and carbon dioxide, and biomass production (Huo *et al.* 2015). However, cyanobacteria are associated with many serious environmental problems, which have implications for water quality and public health (Adamovsky *et al.* 2015). Cyanobacteria generate many toxins such as microcystins (MCs), cylindrospermopsin, anatoxins nodularins, and saxitoxins, which can cause a significant health hazard in drinking water (Sharma *et al.* 2012). Toxic effects include hepatotoxicity, cytotoxicity, neurotoxicity, embryotoxicity, dermatotoxicity or immunotoxicity. Additionally, cyanobacteria commonly

produce heptatoxic MCs, which are stable in water. MCs have been found in drinking waterbodies worldwide, causing potential risk to human health (Li *et al.* 2015). Moreover, MCs can easily accumulate in aquatic biota which has implications for human and environmental health. Among the various MCs, MC-LR is the most common of the microcystins. MC-LR is of great concern in water bodies due to its acute toxicity ( $\text{LD}_{50} = 50 \mu\text{g kg}^{-1}$  in mice) (Sharma *et al.* 2012). The World Health Organization has established a provisional guideline limit of  $1 \mu\text{g L}^{-1}$  for MC-LR (Ibelings *et al.* 2014).

In recent years, several technologies have been sought to remove extracellular cyanobacteria and MC-LR in water

(Sharma *et al.* 2012; Jiang *et al.* 2014). Treatment may be classified into two categories: physical removal and oxidative transformation. Activated carbon, coagulation–flocculation–sedimentation, and sand and membrane filtration are examples of physical–chemical methods. Applications of physical processes generally need replacement of materials (e.g. activated carbon and membranes) and/or cleaning because of fouling. Oxidation methods include UV-based advanced oxidation technologies, photocatalytic and chemical oxidation (Sharma *et al.* 2012, 2014). MC-LR is stable under natural sunlight and resistant to degradation by UV radiation (Westrick *et al.* 2010). Photocatalytic degradation of MC-LR using titanium dioxide (TiO<sub>2</sub>) is promising (Sharma *et al.* 2012); however, it requires separation of the catalyst after removal of MC-LR and needs additional energy for the photoactivation of photocatalyst. Chlorine, chlorine dioxide, chloramine, ozone, and permanganate have been applied to remove MC-LR in water (Sharma *et al.* 2012). The reaction of chlorine with MC-LR resulted in chlorine substitution, which generates potentially toxic chlorinated by-products (Acero *et al.* 2008; Huang *et al.* 2008). In addition, the possibility of the reaction between chlorine and bromide ion produces HOBr, which can produce toxic brominated by-products (Heeb *et al.* 2014). The degradation of MC-LR by chloramine was not significant. Chlorine dioxide is capable of degrading MC-LR, but high doses are required. This limits the practical application due to the generation of chlorite and chlorate as by-products after the use of chlorine dioxide (Kull *et al.* 2004). Applications of ozone and permanganate in oxidizing MC-LR are promising (Sharma *et al.* 2012).

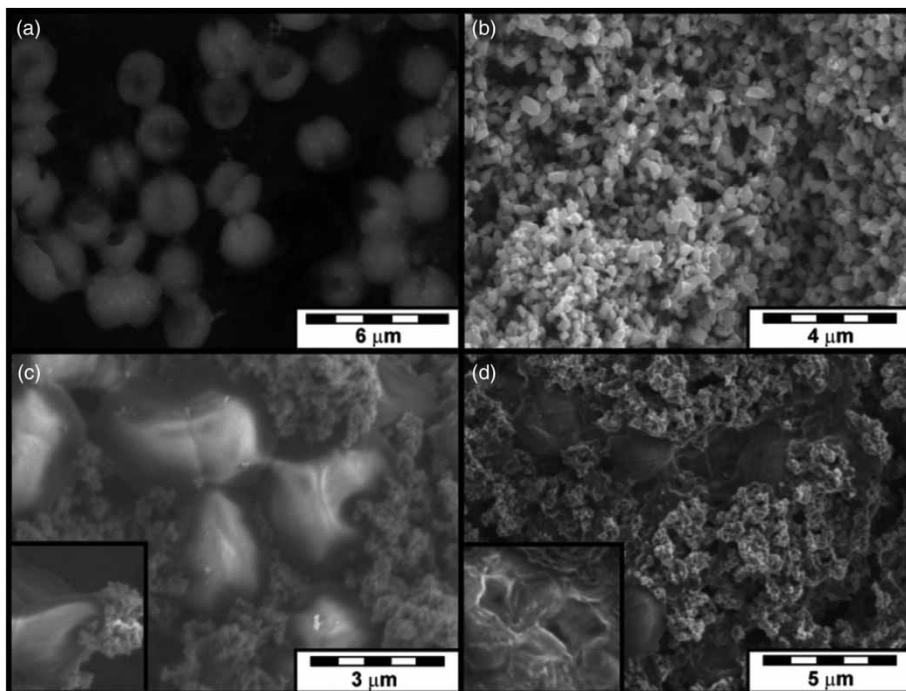
This paper deals with zero valent iron nanoparticles (nZVI) and high valent tetraoxy compound of iron (ferrate, Fe<sup>VI</sup>O<sub>4</sub><sup>2-</sup>, Fe(VI)) based technologies to treat cyanobacteria and MC-LR in water (Marsalek *et al.* 2012; Jiang *et al.* 2014). Both of these technologies are environmentally friendly and can address some of the drawbacks of other treatment methods. The effect of nZVI and Fe(VI) ions in treating cyanobacteria and MC-LR under various environmental conditions are reviewed.

## ZVI NANOPARTICLES

ZVI has received tremendous interest in removing various contaminants (Bae & Hanna 2015). ZVI has a high

capability to remove various contaminants from groundwater and wastewater. In the past few years, emphasis has been placed on the nano ZVI nanoparticles (nZVI), which have shown remarkable reduction properties to remediate numerous inorganic and organic contaminants (Crane & Scott 2012; Yan *et al.* 2013; Jarošová *et al.* 2015). Small size, large surface area, good transport properties and specific mechanism of reaction with water under anaerobic conditions are key properties for its effectiveness to remove contaminants (Klimkova *et al.* 2011; Mueller *et al.* 2012; Raychoudhury & Scheytt 2013; Yan *et al.* 2013; Filip *et al.* 2014; Baikousi *et al.* 2015; Jarošová *et al.* 2015; Soukupova *et al.* 2015). In recent years, developing composite materials containing nZVI has been emphasized to enhance removing contaminants due to the combination of reduction/sorption or reduction/antimicrobial properties of hybrids (Marková *et al.* 2013; Petala *et al.* 2013; Baikousi *et al.* 2015). ZVI has also shown inactivation of bacteria like *Escherichia coli* (Lee *et al.* 2008). In recent years, the role of nZVI in the destruction of cyanobacterial cells was explored (Marsalek *et al.* 2012).

Application of nZVI to remove cyanobacteria was carried out using water inoculated with a *Microcystis aeruginosa* laboratory strain that remained in the colonial form (CCT12/2–8) (Marsalek *et al.* 2012). The average particle size and surface area of applied nZVI were ~70 nm and ~25 m<sup>2</sup>/g, respectively. Detailed chemical, microscopic, and microbiological analyses were performed (Marsalek *et al.* 2012). The results on nZVI treatment of cyanobacteria showed multiple modes of action: (i) the removal of bioavailable phosphorus, (ii) the destruction of cyanobacterial cells, and (iii) the immobilization of MCs (Marsalek *et al.* 2012). Release of cyanobacteria may thus be influenced by nZVI. Significantly, the ecotoxicological study demonstrated that nZVI was a highly selective agent (EC<sub>50</sub> = 50 mg/L against cyanobacteria). This level of EC<sub>50</sub> was 20–100 times lower than that the EC<sub>50</sub> for fish, water plants, algae, and daphnids. Figure 1 shows the deformation of cells caused by the aggregated Fe(OH)<sub>3</sub>, which was generated as the major product from the nZVI treatment of cyanobacteria (Marsalek *et al.* 2012). Furthermore Fe(OH)<sub>3</sub>, a nontoxic product, was capable of promoting flocculation, resulting in gradual settling of the decomposed cyanobacterial biomass (Figure 1).



**Figure 1** | (a) Scanning electron microscope (SEM) images of cyanobacteria before treatment, (b) unused nZVI particles, (c) highly deformed cells after brief exposure to nZVI, and (d) completely destroyed cells surrounded by ferric oxide aggregates. (Adapted from Marsalek *et al.* (2012) with the permission of the American Chemical Society.)

## FERRATE ION

Fe(VI) ion in the aquatic environment has strong oxidation capability (Sharma 2002). For example, the redox potential of Fe(VI) in aqueous solution is the highest among other conventional disinfectant and oxidants used in water and wastewater treatment (Jiang & Lloyd 2002). Numerous examples have displayed simultaneously disinfection, oxidation, and coagulation properties of Fe(VI) (Eng *et al.* 2006; Sharma 2007a; Filip *et al.* 2011; Jiang 2015; Prucek *et al.* 2015; Sharma *et al.* 2016). In a single Fe(VI) dose treatment, inactivation of microorganisms, oxidative transformation of inorganic and organic contaminants, and toxins, as well as removal of toxic metals and phosphate can be achieved (Sharma 2010; Jiang 2014, 2015; Yates *et al.* 2014; Sharma *et al.* 2015). Fe(VI) as a disinfectant can inactivate a wide range of microorganisms (Sharma 2007b; Jiang 2014). The kinetics of the reactions with various pollutants with a variety of molecular and structural configurations (e.g. sulfide, bisulfite, iodide, cyanides, ammonia, selenium, arsenic, azide, thiols, amines, amino acids) showed the feasibility of their removal by Fe(VI) (Lee *et al.* 2009, 2014; Lee & von Gunten 2010; Sharma 2011, 2013; Zimmermann *et al.* 2012). The ferric

oxide, generated from Fe(VI), acts as an efficient coagulant to remove humic acids, radionuclides, metals, arsenic and non-metals (Horst *et al.* 2013; Prucek *et al.* 2013, 2015). Fe(VI) as a pre-oxidant is able to decrease the concentration of disinfection byproducts, formed during chlorination of water (Gan *et al.* 2015; Yang *et al.* 2015). Recently, research in our laboratories has focused on the role of Fe(VI) in removing and oxidatively transforming toxins such as MC-LR. Below is the summary of results observed in studying the kinetics and oxidized products (OPs) and their toxicity in the oxidation of MC-LR by Fe(VI) (Jiang *et al.* 2014).

## Kinetics

The oxidation of the MC-LR by Fe(VI) followed a second-order kinetics ( $-d[\text{Fe(VI)}]/dt = k_{\text{app}}[\text{Fe(VI)}][\text{MC-LR}]$ ). The values of  $k_{\text{app}}$  showed a pH dependence with values ranged from  $1.3 \pm 0.1 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$  at pH 7.5 to  $8.1 \pm 0.08 \text{ mol}^{-1} \text{ L s}^{-1}$  at pH 10.0. This indicates a rapid degradation of MC-LR (Jiang *et al.* 2014). The comparison of the rate constants for the oxidation of MC-LR with different oxidants at neutral pH is presented in Table 1 (Kull *et al.* 2004;

**Table 1** | Second-order rate constants and half-lives for oxidation of MC-LR by different oxidants at 22–25 °C

Oxidant	Species	$k$ , $M^{-1}s^{-1}$	$k_{app} M^{-1}s^{-1}$ pH 7.0	$t_{1/2}$
Ferrate(VI) <sup>a</sup> ( $pK_3 = 7.23$ ) <sup>f</sup>	$HFeO_4^-$	$(3.9 \pm 0.2) \times 10^2$	$2.5 \times 10^2$	155 s
	$FeO_4^{2-}$	$8.0 \pm 2.0$		
Permanganate <sup>b</sup>	$MnO_4^-$	$3.6 \times 10^2$	$3.6 \times 10^2$	107 s
Chlorine <sup>c</sup> ( $pK_a = 7.54$ ) <sup>g</sup>	$HOCl$	$1.2 \times 10^2$	$7.2 \times 10^1$	504 s
	$OCl^-$	6.8		
Chlorine dioxide <sup>d</sup>	$ClO_2$	1.0	1.0	13.1 h
Ozone <sup>e</sup>	$O_3$	$4.1 \times 10^5$	$4.1 \times 10^5$	0.08 s

<sup>a</sup>This study and half-life at dose  $[Fe] = 1 \text{ mg L}^{-1}$  or  $[FeO_4^{2-}] = 2.2 \text{ mg L}^{-1}$ .

<sup>b</sup>From Rodríguez *et al.* (2007) and half-life at dose  $[Mn] = 1 \text{ mg L}^{-1}$  or  $[MnO_4^-] = 2.2 \text{ mg L}^{-1}$ .

<sup>c</sup>Values at pH 7.2 taken from Acero *et al.* (2005) and half-life at  $[HOCl] = 1 \text{ mg L}^{-1}$ .

<sup>d</sup>From Kull *et al.* (2004) and half-life at  $[ClO_2] = 1 \text{ mg L}^{-1}$ .

<sup>e</sup>From Onstad *et al.* (2007) and half-life at  $[O_3] = 1.0 \text{ mg L}^{-1}$ .

<sup>f</sup>At 25 °C.

<sup>g</sup>At 25 °C from Carrell Morris (1966).

Acero *et al.* 2005; Onstad *et al.* 2007; Rodríguez *et al.* 2007). Ozone showed the highest value of  $k_{app}$  (Table 1). The efficient attack on the double bond of MC-LR by ozone may be responsible for orders of magnitude faster reactivity in comparison with other oxidants. The increasing order of the reactivity with MC-LR may be presented as chlorine dioxide < chlorine < Fe(VI) < Mn(VII) <  $O_3$  (Table 1). The half-life ( $t_{1/2}$ ) for oxidizing MC-LR by  $O_3$  is less than a second whereas Fe(VI), Mn(VII), and chlorine oxidize MC-LR in seconds. Ozone, chlorine, Mn(VII), and Fe(VI) are thus suitable oxidants to eliminate MC-LR in water treatment.

## OPS

Analysis of OPs of degradation of MC-LR was carried out by high resolution liquid chromatography–mass spectrometry/mass spectrometry technique (Jiang *et al.* 2014). The proposed structures for the OPs were based on the molecular formula and are summarized in Table 2. Basically, four primary reactions occurred from the attacks of Fe(VI) on the aromatic ring, diene, enone, and amide functionalities of MC-LR by Fe(VI) (Figure 2). In hydroxylation of the aromatic ring, mono, di and trihydroxylation of the aromatic ring were obtained with corresponding  $m/z = 1011.5510$ , 1027.5459, and 1043.5408 (Table 2). Monohydroxylation involved the loss of a hydrogen atom to yield a highly stabilized aromatic product ( $M + 16$ ). Further hydroxylation thus formed di-

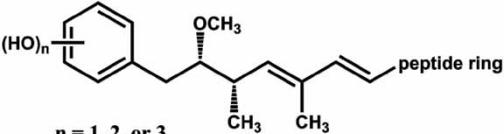
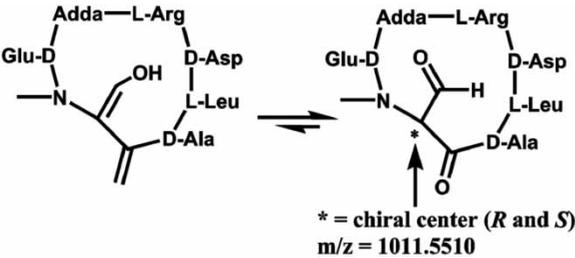
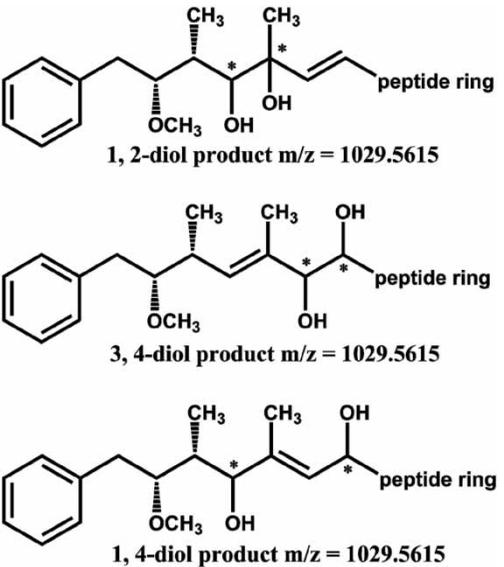
and tri- hydroxylation products. Hydroxylation of the carbon–carbon double bond in the MHDA moiety also occurred, which resulted in the formation of an enol functional group through the elimination of an H atom. Tautomerization of the enol group gave a chiral center at the alpha position. A pair of diastereotopic isomers consistent with  $m/z$  1011.5510 ( $M + 16$ ) were thus obtained (Table 2). Fe(VI) also oxidized the diene group of the Adda moiety of MC-LR via dihydroxylation to yield products with  $M + 34$  (Table 2). This corresponded to addition of two HO groups without loss of H atoms. Hydroxylation yielded 1,2-, 3,4-, and 1,4-diol products (Table 2). Significantly, the products seen from the attack on diene moiety were also reported in oxidation performed by photocatalytic and electrochemical process (Antoniou *et al.* 2008; Zhang *et al.* 2013; Zong *et al.* 2013; Liao *et al.* 2014). The cleavage of peptide bonds in MC-LR by Fe(VI) was also seen, which caused the hydrolysis of amide bonds of D-glu-MDHA and the L-Arg-Methyl D-Asp of the MC-LR by Fe(VI) (Jiang *et al.* 2014). This step of the attack of Fe(VI) on the peptide bond was similar to the transformation of  $-NH = C-$  amino acid functionality by Fe(V) (Bielski *et al.* 1994; Rush & Bielski 1995).

## Removal and biological toxicity assessment tests

Removal of MC-LR by Fe(VI) was confirmed by conducting tests in water and lake water samples (Brno, Czech Republic) (Jiang *et al.* 2014). The lake water had total organic carbon of  $7.9 \text{ mg L}^{-1}$ . In performing tests, the water samples were spiked with MC-LR ( $25.0 \mu\text{g L}^{-1}$ ) and an addition of  $FeO_4^{2-}$  into the samples was  $5.0 \text{ mg L}^{-1}$ . The removal of MC-LR in deionized water was almost complete over the entire pH range of 6.0–8.0 at 20 °C (Figure 3). At pH 7.0 and 8.0, the removal percentages were >99.0% (or  $<1 \mu\text{g L}^{-1}$ ), while a slight decrease at pH 6.0 (96.2%) was noticed. As shown in Figure 3, an Fe(VI) dose of  $5.0 \text{ mg L}^{-1}$  as  $FeO_4^{2-}$  could remove ~75% in lake water at pH 7.0. This indicates that the other components present in the lake water (e.g. dissolved organic matter) may also be reacting with Fe(VI) (Horst *et al.* 2013). Fe(VI) dose  $>5.0 \text{ mg L}^{-1}$  would be required to completely remove MC-LR in the lake water (Jiang *et al.* 2014).

The MC-LR is an inhibitor of protein phosphatase (PP1 and PP2A) enzymes, therefore, the PP1 inhibition was utilized to evaluate the biological activity of the Fe(VI)

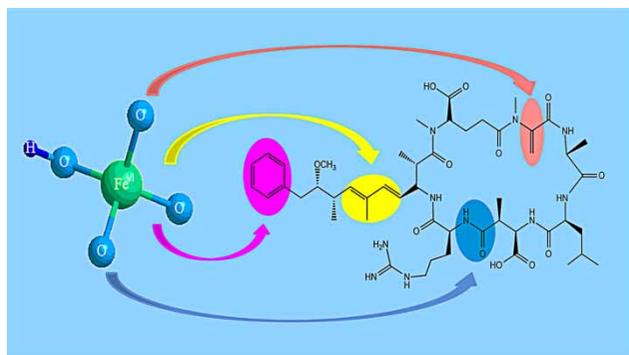
**Table 2** | OPs observed during hydroxylation of moieties of MC-LR by Fe(VI)

Moiety	OPs
Benzene ring	 <p> <math>n = 1, 2, \text{ or } 3</math>            Monohydroxylation <math>\Rightarrow m/z = 1011.5510</math>  <i>ortho, meta, and para</i> isomers            Dihydroxylation <math>\Rightarrow m/z = 1027.5459</math>            Trihydroxylation <math>\Rightarrow m/z = 1043.5408</math> </p>
MDHA	 <p>           * = chiral center (<i>R</i> and <i>S</i>)  <math>m/z = 1011.5510</math> </p>
Diene	 <p> <b>1, 2-diol product <math>m/z = 1029.5615</math></b>  <b>3, 4-diol product <math>m/z = 1029.5615</math></b>  <b>1, 4-diol product <math>m/z = 1029.5615</math></b> </p>

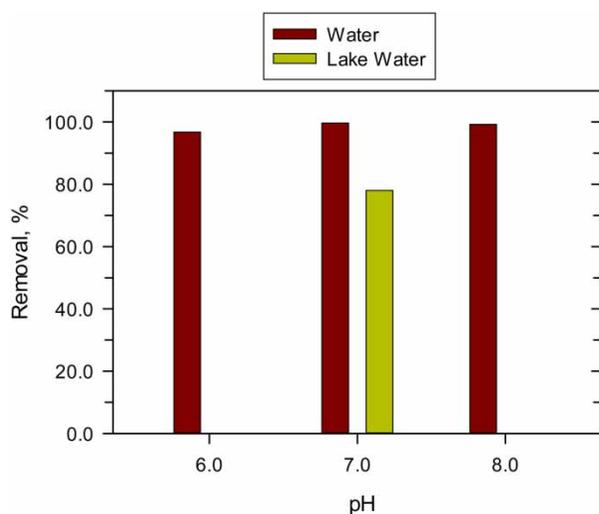
treated solutions (Jiang *et al.* 2014). When MC-LR was totally removed by Fe(VI) ion, the biological activity of OP was almost completely eliminated. This demonstrated that the OPs of MC-LR were not biologically toxic (Jiang *et al.* 2014).

The removal of MC-LR by photocatalytic oxidation system was also sought (Yuan *et al.* 2006; Sharma *et al.* 2010). Figure 4 shows the results in the TiO<sub>2</sub>-UV-MC-LR, Fe(III)-TiO<sub>2</sub>-UV-MC-LR, and Fe(VI)-TiO<sub>2</sub>-UV-MC-LR systems. Both Fe(III)

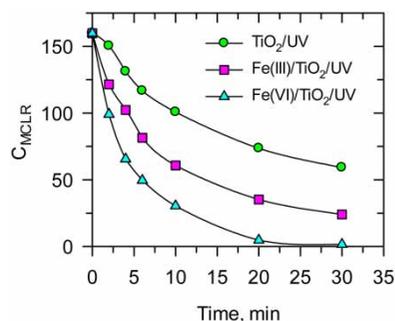
and Fe(VI) ions in the system enhanced the photocatalytic oxidation of MC-LR (Figure 4). The effectiveness of Fe(VI) ion was more than that of Fe(III) ion. Significantly, complete removal of MC-LR was achieved by Fe(VI) in 30 min (Figure 4). Formation of highly reactive intermediate Fe(V) species and also increasing amount of holes (i.e. oxidant) in iron species containing TiO<sub>2</sub> photocatalytic systems may have resulted in enhanced removal of MC-LR (Sharma *et al.* 2010).



**Figure 2** | Fe(VI) attacks on different moieties of MC-LR. (Adapted from Jiang *et al.* (2014) with the permission of the American Chemical Society.)



**Figure 3** | Removal of MC-LR in deionized water and lake water by Fe(VI) ([MC-LR] = 25.0  $\mu\text{g L}^{-1}$ ,  $[\text{FeO}_4^{2-}] = 5.0 \text{ mg L}^{-1}$ , and temperature 20 °C). (Adapted from Jiang *et al.* (2014) with the permission of the American Chemical Society.)



**Figure 4** | The photocatalytic degradation of MCLR. Conditions: [ferrate(VI)] = 0.08  $\text{mmol L}^{-1}$  and Fe(III) = 0.36  $\text{mmol L}^{-1}$ . (Adapted from Sharma *et al.* (2010) with the permission of Springer Inc.)

## CONCLUSIONS

- Both nZVI and Fe(VI) showed their potential as sustainable green materials to remove cyanobacteria and cyanotoxins in water.
- nZVI was highly effective in destroying cyanobacteria via multiple modes of action.
- The products of MC-LR oxidation by Fe(VI) were observed from the hydroxylation of benzene ring, diene, enone, and peptide bond of MC-LR, which did not have any significant toxicity.
- Fe(VI) could degrade MC-LR in water and lake water samples on a time scale of seconds.
- Magnetic separation of generated iron oxides from nZVI and Fe(VI) treatment can be achieved using a cost effective low-gradient magnetic field.

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## REFERENCES

- Acero, J. L., Rodríguez, E. & Meriluoto, J. 2005 Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins. *Water Res.* **39** (8), 1628–1638.
- Acero, J. L., Rodríguez, E., Majado, M. E., Sordo, A. & Meriluoto, J. 2008 Oxidation of microcystin-LR with chlorine and permanganate during drinking water treatment. *J. Water Supply: Res. Technol. -AQUA* **57** (6), 371–380.
- Adamovsky, O., Moosova, Z., Pekarova, M., Basu, A., Babica, P., Svihalkova Sindlerova, L., Kubala, L. & Blaha, L. 2015 Immunomodulatory potency of microcystin, an important water-polluting cyanobacterial toxin. *Environ. Sci. Technol.* **49** (20), 12457–12464.

- Antoniou, M. G., Shoemaker, J. A., de la Cruz, A. A. & Dionysiou, D. D. 2008 LC/MS/MS structure elucidation of reaction intermediates formed during the TiO<sub>2</sub> photocatalysis of microcystin-LR. *Toxicon* **51** (6), 1103–1118.
- Bae, S. & Hanna, K. 2015 Reactivity of nanoscale zero-valent iron in unbuffered systems: effect of pH and Fe(II) dissolution. *Environ. Sci. Technol.* **49**, 1036–1045.
- Baikousi, M., Georgiou, Y., Daikopoulos, C., Bourlinos, A. B., Filip, J., Zboril, R., Deligiannakis, Y. & Karakassides, M. A. 2015 Synthesis and characterization of robust zero valent iron/mesoporous carbon composites and their applications in arsenic removal. *Carbon* **93**, 636–647.
- Bielski, B. H. J., Sharma, V. K. & Czapski, G. 1994 Reactivity of ferrate(V) with carboxylic acids: a pre-mix pulse radiolysis study. *Radiat. Phys. Chem.* **44** (5), 479–484.
- Carrell Morris, J. 1966 The acid ionization constant of HOCl from 5 to 35 °C. *J. Phys. Chem.* **70**, 3798–3805.
- Crane, R. A. & Scott, T. B. 2012 Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *J. Hazard. Mater.* **211–212**, 112–125.
- Eng, Y. Y., Sharma, V. K. & Ray, A. K. 2006 Ferrate(VI): green chemistry oxidant for degradation of cationic surfactant. *Chemosphere* **63** (10), 1785–1790.
- Filip, J., Yngard, R. A., Siskova, K., Marusak, Z., Ettler, V., Sajdl, P., Sharma, V. K. & Zboril, R. 2011 Mechanisms and efficiency of the simultaneous removal of metals and cyanides by using ferrate(VI): crucial roles of nanocrystalline iron(III) oxyhydroxides and metal carbonates. *Chem. Eur. J.* **17** (36), 10097–10105.
- Filip, J., Karlický, F., Marušák, Z., Lazar, P., Cerník, M., Otyepka, M. & Zboril, R. 2014 Anaerobic reaction of nanoscale zerovalent iron with water: mechanism and kinetics. *J. Phys. Chem. C* **118** (25), 13817–13825.
- Gan, W., Sharma, V. K., Zhang, X., Yang, L. & Yang, X. 2015 Investigation of disinfection byproducts formation in ferrate (VI) pre-oxidation of NOM and its model compounds followed by chlorination. *J. Hazard. Mater.* **292**, 197–204.
- Heeb, M. B., Criquet, J., Zimmermann-Steffens, S. G. & Von Gunten, U. 2014 Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds – a critical review. *Water Res.* **48** (1), 15–42.
- Horst, C., Sharma, V. K., Clayton Baum, J. & Sohn, M. 2013 Organic matter source discrimination by humic acid characterization: synchronous scan fluorescence spectroscopy and ferrate(VI). *Chemosphere* **90** (6), 2013–2019.
- Huang, T., Zhao, J. & Chai, B. 2008 Mechanism studies on chlorine and potassium permanganate degradation of microcystin-LR in water using high-performance liquid chromatography tandem mass spectrometry. *Water Sci. Technol.* **58** (5), 1079–1084.
- Huo, X., Chang, D. W., Tseng, J. H., Burch, M. D. & Lin, T. F. 2015 Exposure of microcystis aeruginosa to hydrogen peroxide under light: kinetic modeling of cell rupture and simultaneous microcystin degradation. *Environ. Sci. Technol.* **49** (9), 5502–5510.
- Ibelings, B. W., Backer, L. C., Kardinaal, W. E. A. & Chorus, I. 2014 Current approaches to cyanotoxin risk assessment and risk management around the globe. *Harmful Algae* **40**, 63–74.
- Jarošová, B., Filip, J., Hilscherová, K., Tucek, J., Šimek, Z., Giesy, J. P., Zboril, R. & Bláha, L. 2015 Can zero-valent iron nanoparticles remove waterborne estrogens? *J. Environ. Manage.* **150**, 387–392.
- Jiang, J. Q. 2014 Advances in the development and application of ferrate(VI) for water and wastewater treatment. *J. Chem. Technol. Biotechnol.* **89**, 165–177.
- Jiang, J. Q. 2015 The role of ferrate(VI) in the remediation of emerging micropollutants: a review. *Desalin. Water Treat.* **55** (3), 828–835.
- Jiang, J. Q. & Lloyd, B. 2002 Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Res.* **36**, 1397–1408.
- Jiang, W., Chen, L., Batchu, S. R., Gardinali, P. R., Jasa, L., Marsalek, B., Zboril, R., Dionysiou, D. D., O'Shea, K. E. & Sharma, V. K. 2014 Oxidation of microcystin-LR by ferrate (VI): kinetics, degradation pathways, and toxicity assessment. *Environ. Sci. Technol.* **48**, 12164–12172.
- Klimkova, S., Cernik, M., Lacinova, L., Filip, J., Jancik, D. & Zboril, R. 2011 Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. *Chemosphere* **82** (8), 1178–1184.
- Kull, T. P. J., Backlund, P. H., Karlsson, K. M. & Meriluoto, J. A. O. 2004 Oxidation of the cyanobacterial heptotoxin microcystin-LR by chlorine dioxide: reaction kinetics, characterization, and toxicity of reaction products. *Environ. Sci. Technol.* **38**, 6025–6031.
- Lee, Y. & von Gunten, U. 2010 Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate<sup>VI</sup>, and ozone) and non-selective oxidants (hydroxyl radical). *Water Res.* **44**, 555–566.
- Lee, C., Jee, Y. K., Won, I. L., Nelson, K. L., Yoon, J. & Sedlak, D. L. 2008 Bactericidal effect of zero-valent iron nanoparticles on *Escherichia coli*. *Environ. Sci. Technol.* **42** (13), 4927–4933.
- Lee, Y., Zimmermann, S. G., Kieu, A. T. & von Gunten, U. 2009 Ferrate (Fe(VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal. *Environ. Sci. Technol.* **43**, 3831–3838.
- Lee, Y., Kissner, Y. & von Gunten, U. 2014 Reaction of ferrate(VI) with ABTS and self-decay of ferrate(VI): kinetics and mechanisms. *Environ. Sci. Technol.* **48**, 5154–5162.
- Li, X., Zhao, Q., Zhou, W., Xu, L. & Wang, Y. 2015 Effects of chronic exposure to microcystin-LR on hepatocyte mitochondrial DNA replication in mice. *Environ. Sci. Technol.* **49** (7), 4665–4672.
- Liao, W., Muruganathan, M. & Zhang, Y. 2014 Electrochemical degradation and mechanistic analysis of microcystin-LR at boron-doped diamond electrode. *Chem. Eng. J.* **243**, 117–126.
- Marková, Z., Šišková, K. M., Filip, J., Cuda, J., Kolár, M., Šafářová, K., Medrík, I. & Zboril, R. 2013 Air stable magnetic bimetallic Fe-Ag nanoparticles for advanced antimicrobial treatment and phosphorus removal. *Environ. Sci. Technol.* **47** (10), 5285–5295.

- Marsalek, B., Jancula, D., Marsalkova, E., Mashlan, M., Safarova, K., Tucek, J. & Zboril, R. 2012 Multimodal action and selective toxicity of zerovalent iron nanoparticles against cyanobacteria. *Environ. Sci. Technol.* **46** (4), 2316–2323.
- Mueller, N. C., Braun, J., Bruns, J., Cerník, M., Rissing, P., Rickerby, D. & Nowack, B. 2012 Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. *Environ. Sci. Pollut. Res.* **19** (2), 550–558.
- Onstad, G. D., Strauch, S., Meriluoto, J., Codd, G. A. & Von Gunten, U. 2007 Selective oxidation of key functional groups in cyanotoxins during drinking water ozonation. *Environ. Sci. Technol.* **41** (12), 4397–4404.
- Petala, E., Dimos, K., Douvalis, A., Bakas, T., Tucek, J., Zboril, R. & Karakassides, M. A. 2013 Nanoscale zero-valent iron supported on mesoporous silica: characterization and reactivity for Cr(VI) removal from aqueous solution. *J. Hazard. Mater.* **261**, 295–306.
- Prucek, R., Tuček, J., Kolářik, J., Filip, J., Marušák, Z., Sharma, V. K. & Zbořil, R. 2015 Ferrate(VI)-induced arsenite and arsenate removal by in situ structural incorporation into magnetic iron(III) oxide nanoparticles. *Environ. Sci. Technol.* **47** (7), 3283–3292.
- Prucek, R., Tucek, J., Kolarik, J., Huskova, I., Filip, J., Varma, R. S., Sharma, V. K. & Zboril, R. 2015 Ferrate(VI)-prompted removal of metals in aqueous media: mechanistic delineation of enhanced efficiency via metal entrenchment in magnetic oxides. *Environ. Sci. Technol.* **49**, 2319–2327.
- Raychoudhury, T. & Scheytt, T. 2013 Potential of zerovalent iron nanoparticles for remediation of environmental organic contaminants in water: a review. *Water Sci. Technol.* **68** (7), 1425–1439.
- Rodríguez, E., Onstad, G. D., Kull, T. P. J., Metcalf, J. S., Acero, J. L. & von Gunten, U. 2007 Oxidative elimination of cyanotoxins: comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Res.* **41** (15), 3381–3393.
- Rush, J. D. & Bielski, B. H. J. 1995 The oxidation of amino acid by ferrate(V). A pre-mix pulse radiolysis study. *Free Rad. Res.* **22**, 571–579.
- Sharma, V. K. 2002 Potassium ferrate(VI): environmental friendly oxidant. *Adv. Environ. Res.* **6**, 143–156.
- Sharma, V. K. 2007a Disinfection performance of Fe(VI) in water and wastewater: a review. *Water Sci. Technol.* **55** (1–2, Wastewater Reclamation and Reuse for Sustainability), 225–232.
- Sharma, V. K. 2007b Ferrate studies for disinfection and treatment of drinking water. In: *Advances in Control of Disinfection By-Products in Drinking Water Systems* (A. Nikolaou, L. Rizzo & H. Selcuk, eds). Nova Science Publishers, Hauppauge, New York, pp. 373–380.
- Sharma, V. K. 2010 Oxidation of nitrogen containing pollutants by novel ferrate(VI) technology: a review. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **45**, 645–667.
- Sharma, V. K. 2011 Oxidation of inorganic contaminants by ferrates (Fe(VI), Fe(V), and Fe(IV))- kinetics and mechanisms – a review. *J. Environ. Manage.* **92**, 1051–1073.
- Sharma, V. K. 2013 Ferrate(VI) and ferrate(V) oxidation of organic compounds: kinetics and mechanism. *Coord. Chem Rev.* **257**, 495–510.
- Sharma, V. K., Graham, N. J. D., Li, X. Z. & Yuan, B. L. 2010 Ferrate (VI) enhanced photocatalytic oxidation of pollutants in aqueous TiO<sub>2</sub> suspensions. *Environ. Sci. Pollut. Res.* **17** (2), 453–461.
- Sharma, V. K., Triantis, T. M., Antoniou, M. G., He, X., Pelaez, M., Han, C., Song, W., O’Shea, K. E., De La Cruz, A. A., Kaloudis, T., Hiskia, A. & Dionysiou, D. D. 2012 Destruction of microcystins by conventional and advanced oxidation processes: a review. *Sep. Purif. Technol.* **91**, 3–17.
- Sharma, V. K., Zhao, J. & Hidaka, H. 2014 Mechanism of photocatalytic oxidation of amino acids: Hammett correlations. *Catalysis Today* **224**, 263–268.
- Sharma, V. K., Zboril, R. & Varma, R. S. 2015 Ferrates: greener oxidants with multimodal action in water treatment technologies. *Acc. Chem. Res.* **48**, 182–191.
- Sharma, V. K., Chen, L. & Zboril, R. 2016 A review on high valent Fe<sup>VI</sup> (ferrate): a sustainable green oxidant in organic chemistry and transformation of pharmaceuticals. *ACS Sustainable Chem. Eng.* **4** (1), 18–34.
- Soukupova, J., Zboril, R., Medrik, I., Filip, J., Safarova, K., Ledl, R., Mashlan, M., Nosek, J. & Cernik, M. 2015 Highly concentrated, reactive and stable dispersion of zero-valent iron nanoparticles: direct surface and site application. *Chem. Eng. J.* **262**, 813–822.
- Westrick, J. A., Szlag, D. C., Southwell, B. J. & Sinclair, J. 2010 A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment. *Anal. Bioanal. Chem.* **397** (5), 1705–1714.
- Yan, W., Lien, H.-L., Koel, B. E. & Zhang, W.-X. 2013 Iron nanoparticles for environmental clean-up: recent developments and future outlook. *Environ. Sci. Process Impacts* **15** (1), 63–77.
- Yang, X., Gan, W., Zhang, X., Huang, H. & Sharma, V. K. 2015 Effect of pH on the formation of disinfection byproducts in ferrate(VI) pre-oxidation and subsequent chlorination. *Sep. Purif. Technol.* **156**, 980–986.
- Yates, B. J., Zboril, R. & Sharma, V. K. 2014 Engineering aspects of ferrate in water and wastewater treatment – a review. *J. Environ. Sci. Health A* **49**, 1603–1604.
- Yuan, B., Li, Y., Huang, X., Liu, H. & Qu, J. 2006 Fe(VI)-assisted photocatalytic degradation of microcystin-LR using titanium dioxide. *J. Photochem. Photobiol. A* **178** (1), 106–111.
- Zhang, Y., Zhang, Y., Yang, N., Liao, W. & Yoshihara, S. 2013 Electrochemical degradation and mechanistic analysis of microcystin-LR. *J. Chem. Technol. Biotechnol.* **88** (8), 1529–1537.
- Zimmermann, S. G., Schmukat, A., Schulz, M., Benner, J., von Gunten, U. & Ternes, T. A. 2012 Kinetic and mechanistic investigations of the oxidation of tramadol by ferrate and ozone. *Environ. Sci. Technol.* **46** (2), 876–884.
- Zong, W., Sun, F. & Sun, X. 2013 Oxidation by-products formation of microcystin-LR exposed to UV/H<sub>2</sub>O<sub>2</sub>: toward the generative mechanism and biological toxicity. *Water Res.* **47** (9), 3211–3219.