



Effect of humic acid, oxalate and phosphate on Fenton-like oxidation of microcystin-LR by nanoscale zero-valent iron



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ABSTRACT

This study investigates the effect of humic acid, oxalate and phosphate on the heterogeneous Fenton-like oxidation efficiency of microcystin-LR (MC-LR) using zero-valent iron nanoparticles (nZVI) as a catalyst at neutral pH. The degradation efficiency of MC-LR in the Fenton-like system increases significantly from 59.1% to 78%, and 59.1% to 72.1% in the presence of humic acid and oxalate, respectively. These mean that humic acid and oxalate are able to form complexes with iron and iron oxide, thus promote the Fenton-like oxidation of MC-LR. However, the degradation efficiency reduces from 59.1% to 47.8% in the existence of phosphate, because phosphate adsorbs competitively with MC-LR to the nZVI surface, consequently inhibits the heterogeneous Fenton-like oxidation of MC-LR. The oxidation kinetics of MC-LR fits well with the pseudo first-order kinetic model. The results illustrate that humic acid was more effective than oxalate and phosphate to generate hydroxyl radicals. The surface changes of nZVI before and after reaction were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Magnetite, maghemite, lepidocrocite and other iron complexes were detected at nZVI surfaces after reaction with MC-LR.

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1. Introduction

Toxic cyanobacterial blooms are a growing environmental health concern. Cyanobacteria can produce a range of potent toxins, including hepatotoxins and tumour-promoters, neurotoxins, and skin irritants [1,2]. Microcystin-LR (MC-LR) is the most abundant microcystins, which the World Health Organization has set a provisional guideline value of 1.0 µg/L as the highest acceptable concentration for MC-LR in drinking water [2–6]. Cyanobacteria present water-borne hazards to health via drinking water and recreational water, so the water from the water supply need to purification. Due to the cyclic structure and presence of novel amino acids, the microcystins are stable and resistant to chemical hydrolysis or oxidation. A variety of traditional methods have been examined to assess the removal of cyanotoxins, including coagulation/sedimentation, activated carbon adsorption and membrane separation. However, to date these methods have only achieved limited success [7–9].

Research in the past two decades mainly focused on finding appropriate treatment technologies for the purification treatment of microcystins contaminated water [10–12]. Among them, advanced oxidation processes (AOPs) have received significant attention because they generate hydroxyl radicals and demonstrate potential for the degradation of biorefractory organic compounds. However, the obtained electrophiles react rapidly and non-selectively with organic molecules. The rate constants are in the order of 10^6 – 10^9 L mol⁻¹ s⁻¹ [13]. Fenton reagent, an advanced oxidation technology (AOT), has been applied to detoxify the microcystins, and the toxin's decomposition is complete in 30 min [14]. However, the homogeneous Fenton process has limitations, including: firstly, the need for additional processing to deal with the dissolved iron ions and sludge during the sewage treatment process; secondly, the acidification of effluents before decontamination to avoid the formation and subsequent precipitation of iron oxyhydroxides; and thirdly, further treatments for neutralization [15–18].

Recently, zero-valent iron (Fe⁰) nanoparticles (nZVI) have been investigated as potential catalysts in the heterogeneous Fenton-like oxidation of organic contaminants [19–24], as nZVI are corroded in acidic solution and generate ferrous ions, leading to Fenton oxidation of organic contaminants in the presence of hydrogen

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peroxide. However, waste water and ground water contain many dissolved electron acceptors (e.g., nitrate or sulfate) that can react with nZVI surface and lead to surface passivation [25]. The effect of both contaminant and solute concentrations on the performance of nZVI are still unclear. Recently, anions such as phosphate, silicate, sulfate, and nitrite have been observed to adsorb to the surface of ion-based nanoparticles and hence affect the fate of contaminants [26]. In addition, natural organic matters (NOM), such as humic acids, are ubiquitous in the environment and can perform as electron shuttles. They tend to adsorb onto iron oxides and enhance electron transfer between nZVI and contaminants [26]. However, it is still not clear how different NOM, complexing agents and inorganic anions affect the heterogeneous Fenton-like oxidation [19,20]. Therefore, in this study we addressed this issue by investigating the impact of NOM (humic acid), complexing agent (oxalate) and anion (phosphate) on heterogeneous Fenton oxidation of MC-LR using nZVI as the catalyst. The objectives here were to: (1) understand the effect of humic acid, oxalate and phosphate as a function of concentration on the Fenton-like oxidation of MC-LR; (2) analyze the degradation kinetics of MC-LR to understand both oxidation and adsorption in Fenton-like systems; and (3) characterize nZVI before and after reaction with MC-LR to determine surface changes using various techniques.

2. Experimental

2.1. Materials and chemicals

All chemical reagents used in this study were of analytical reagent grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaBH_4 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, anhydrous ethanol were obtained from Xilong Chemical Co., Ltd. (China) without further purification. Oxalic acid and humic acid were purchased from Qyzhou Chemical Co., Ltd. (China) and Jvfeng Chemical Co., Ltd. (China), respectively. MC-LR was obtained from the Institute of Aquatic Organisms (purity > 95%, Wuhan, China), Chinese Academy of Sciences and stored at -25°C .

2.2. Synthesis of iron nanoparticles

nZVI were prepared using ferric salts with sodium borohydride [27]. Briefly, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (4.84 g) was dissolved in 50 mL of distilled water and stirred with an electric rod for 5 min. Then 100 ml of NaBH_4 (0.054 M) was added drop-wisely into the ferric chloride solution. The whole process was taken under a N_2 atmosphere. When the reaction ended, the black nano-scale aggregates (nZVI) produced were collected by vacuum filtration and all the prepared samples were dried at 60°C under vacuum overnight.

2.3. Batch experiments

To compare the removal efficiency of MC-LR by Fenton-like oxidation in the presence of humic acid, oxalate and phosphate, batch experiments were carried out by adding humic acid (0.04 mM, 0.4 mM, 4 mM), oxalate (0.04 mM, 0.4 mM, 4 mM) and phosphate (0.4 mM, 4 mM, 13 mM) to a solution containing 5.0 mg L^{-1} MC-LR (10 mL) respectively, using nZVI (0.05 g) and H_2O_2 (6.6 mM) added to a solution in the neutral condition. These were placed on a rotary shaker at 298 K and 250 r min^{-1} .

Following the reaction the mixtures were filtered through $0.22 \mu\text{m}$ membranes at different times, and the residual MC-LR in solution was measured using a UV-Spectrophotometer (752, Shanghai, China) at 238 nm. A Ultra Performance Liquid Chromatography instrument (Waters Acquity UPLC System Separations) was used to further identify the degradation of MC-LR, equipping with a $10 \text{ cm} \times 2.1 \text{ mm}$ Waters Acquity BEH C18

$1.7\text{-}\mu\text{m}$ UPLC column. The sample injection volume was $2\text{-}\mu\text{L}$ [28]. The COD of MC-LR dilute solution was measured using a COD tester (5B-6c, Lanzhou, China).

2.4. Kinetic analysis

According to previous studies [19,21,22], pseudo-first-order kinetics can be used to describe the organic compound degradation by Fenton system. In this study, pseudo-first-order kinetics was used to analyze the effects of reagents on heterogeneous Fenton-like oxidation of MC-LR.

2.5. Characterizations and measurements

Morphology and distribution of nZVI before and after 90 min Fenton-like reaction with MC-LR containing 4 mM humic acid, oxalate and phosphate, respectively were characterized using a Scanning electron microscopy (SEM, JSM 7500F, Japan). These powder samples were fixed onto the adhesive tapes supported on metallic disks and then coated with a gold film. Sample images were recorded at different magnifications at an operating voltage of 5.0 kV.

X-ray diffraction (XRD) patterns of the powder samples before and after oxidation reactions were detected utilizing a Philips-X'Pert Pro MPD (Netherlands) with a high-powered Cu $\text{K}\alpha$ radioactive source ($k = 0.154 \text{ nm}$) at 40 kV/40 mA.

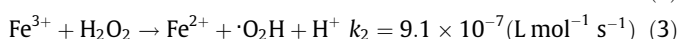
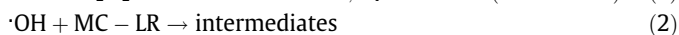
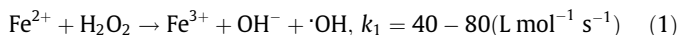
Fourier transform infrared spectra (FTIR) of nZVI before and after oxidation reactions with humic acid, oxalate or phosphate were recorded using FTIR Nicolet 5700 (Thermo Corp., USA). Samples were prepared by mixing 1% (w/w) specimen with 100 mg of KBr powder and pressing the mixture into a sheer slice.

3. Results and discussion

3.1. Effect of humic acid on the Fenton-like oxidation of MC-LR

Humic acid contains various types of carboxylate, phenolic, and carbonyl functional groups, which can complex with iron and iron oxide. It can increase the degradation efficiency of nitro aromatic or halogenated compounds as an electron-transfer media [29]. In addition, humic acid adsorbs more strongly to the active sites of the iron surface than the contaminants, leading to reduced Fenton-like oxidation efficiency [29]. In this study, three concentrations of humic acid (0.04 mM, 0.4 mM and 4 mM) were added to the reaction system to understand the Fenton-like oxidation efficiency of MC-LR.

As shown in Fig. 1(a), the oxidation (removal) efficiency of MC-LR increased from 55.1% to 78.0%, while the removal efficiency of chemical oxygen demand (COD) increased from 20.1% to 26.6% as the concentrations of humic acid rose from 0.04 mM to 4 mM. This indicates that humic acid promoted the breakdown of H_2O_2 and generated reactive oxygen species (ROS) through nZVI [13,30]. As described in Eqs. (1) and (2), the oxidation of ferrous ions into ferric ions decompose H_2O_2 and generate hydroxyl radicals, thus degrade MC-LR. Meanwhile, the generated ferric ions can be reduced to ferrous ion through the Fenton-like reaction as shown in Eq. (3) [30]:



However, the reaction rate of Eq. (1) is significantly faster than that of Eq. (3) which means that the Fe^{2+} is rapidly consumed and the low Fe^{2+} concentration restricts the Fenton oxidation [31].

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