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Fe(VI)-assisted photocatalytic degradating of microcystin-LR using titanium dioxide

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Abstract

Microcystin cyanobacterial hepatotoxins represent an increasingly severe global health hazard. This study focused on enhancing photocatalytic degradation of microcystin-LR (MCLR) following the addition of ferrate as the indirect electron acceptors to the process. The degradation rate of MCLR by ferrate or the photocatalysis only was 54 and 63%, respectively. However, when relatively low ferrate dose (0.08 mmol/L) was added to the photocatalytic process, a significant enhancement in the photocatalytic rate was observed and the efficiency can be increased to 100%. Compared the effect of Fe(III) and Fe(VI) on the photocatalysis rate, the process of Fe(VI)-assisted photocatalytic degradation of MCLR apparently existed the synergistic effect and the photocatalysis rate constant k of Fe(VI)/UV/TiO_2 process was higher than Fe(III)/UV/TiO_2 by 2.5 times and than UV/TiO_2 by 4.4 times, but an overdose of ferrate will retard the rate due to the short circuiting reactions between Fe^{3+} and Fe^{2+} and the lower absorption of UV light. As expected, pH had a remarkable influence on the reaction rate of detoxification of microcystin-LR and pH 6 was beneficial to the photocatalytic process.

Keywords: Cyanobacteria; Microcystin-LR; Ferrate-assisted; Photocatalytic degradation; Synergetic effect; Removal efficiency

1. Introduction

The increasing eutrophication of fresh waters, many of which include drinking water reservoirs by human activity, has increased the occurrence and intensity of cyanobacterial blooms [1] and approximately 50% of them are known to be toxic [2]. The most commonly occurring toxins produced by cyanobacteria are microcystins. Microcystin, a cyclic hepatotoxin produced by some freshwater cyanobacteria such as *Microcystis*, *Planktothrix* and *Anabaena*, causes potent hepatotoxicity and tumor-promoting activity to animal and human through inhibition of protein phosphatases 1 and 2A [3]. Microcystins are a family of cyclic heptapeptides and generally contain five invariant amino acids (or derivatives of them) and two variable L-amino acids, whose one-letter nomenclature abbreviations are used to name the various analogues such as microcystin-LR (MCLR) contains leucine and arginine. They are strongly hepatotoxic due to their potent inhibition of protein phosphatases 1 and 2A [4]. They have been linked to the high incidence of liver cancer in areas of China where populations are largely dependent on surface drinking water, which can be contaminated with cyanobacteria and their microcystin metabolites [5,6]. The potential for these toxins to impact adversely on human health requires that these toxins be removed from water supplies prior to use.

In recent years, there has been extensive research into the use of photocatalysis for the degradation and removal of highly toxic organic compounds in water purification [7–10]. It involves oxidative decomposition achieved by UV irradiation of dispersions of suitable semiconductor (TiO_2). This process results in the complete mineralisation of organic pollutants to carbon dioxide, water and inorganic ions [11], but it exists the low quantum efficiency.

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Some researchers have shown that the addition of metal ions to the photocatalytic system that act as electron acceptor to prevent the immediate self-recombination of electron (e^-) and valence band hole (h^+), consequently to enhance the quantum efficiency and the rates of pollutant degradation [12,13]. Other researchers have shown that the addition of chemical oxidants such as H_2O_2 or O_3 to the photocatalytic system that may also act as electron acceptors results in enhanced rates of pollutant destruction [14,15]. However, little work has been carried out on the effectiveness of a reagent as both strong oxidant and metal ions to increasing the photocatalytic degradation of microcystins.

Ferrate, the iron(VI) oxyanion FeO_4^{2-}, is a powerful oxidant throughout the pH scale, and decomposes in aqueous solution yielding oxygen radicals, peroxide radicals, Fe(V), Fe(IV), and Fe(III). Gilbert et al. [16] have shown that ferrate is an effective disinfectant and oxidant of organic contaminants such as phenol and allylbenzene. Our previous research [17] had proved that ferrate could degrade microcystin effectively due to its strong oxidation, but the required dose of ferrate is very high and the oxidation process was not complete. The purpose of this study was to investigate the potential of ferrate enhancing photocatalytic process as a mean of degradation of microcystin-LR. The objective of the addition of ferrate is to degrade the microcystins partially and provides sequential reduction product Fe(V), Fe(IV), and Fe(III) as alternative electron acceptors to prevent the immediate self-recombination of electron and valence band hole and then enhances the photocatalytic efficiency [18,19]. The study examined conditions for optimal treatment with variation of parameters such as ferrate doses, residual iron, pH, and contact time.

2. Experimental

2.1. Chemicals

Culture of *Microcystis aeruginosa* (FACHB-ds) was purchased from the Culture Collection of Algae, Wuhan Institute of Hydrobiology, China. Microcystin-LR was isolated and purified from cell blooms that were purely cultured in laboratory using the method described by Meriluoto and Eriksson [20]. Standard microcystin-LR was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Potassium ferrate (K_2FeO_4) was synthesized according to the method [21] through hypochlorite oxidation of ferric nitrate in a strong alkaline solution. Titanium dioxide (TiO_2) with BET surface areas of 10 m^2/g obtained from Beijing Chemistry Factory (Reagent Grade, China) was used in this study. UV lamp (100 W, Spectral output 340–420 nm) with the lamp irradiance of 40 W/m^2 determined with a radiometer (Photoelectric Factory of Beijing Normal University, Model UV-A).

2.2. Photocatalysis

The initial concentration of microcystin-LR (1–2 mg/L) in aqueous solution was illuminated in the presence of air, ferrate (variable concentrations) and TiO_2 catalyst (2 g/L slurry) using a UV lamp (40 W/m^2, spectral output 340–420 nm) at reaction pH 6. All reactions were carried out in a series of thick-walled glass universal bottles with constant stirring. Samples were taken at different time intervals, quenched with sodium sulphite and centrifuged to remove catalyst. Microcystin-LR was determined by HPLC analysis after isolation by reversed-phase (C_{18}) solid phase extraction [17].

2.3. Analytical method

The destruction of microcystin-LR was monitored by HPLC with a high-resolution diode array detector (Shimadzu SPD-M10A detector) at 238 nm. Separations were performed on a C_{18} column (5 μm, 250 mm × 4.6 mm i.d., Agilent). The mobile phase used for the analysis was acetonitrile and milli-Q water containing 0.01 mol/L ammonium acetate (pH 6.8) (32:68) at a flow rate of 1 mL/min. The amount of iron remaining in the solution after photo-oxidation was measured with a polarized Zeeman atomic absorption spectrometer (Hitachi, Z-6100).

3. Results and discussion

3.1. Effect of ferrate concentration in enhancing and retarding the efficiency of photocatalytic degradation of microcystin-LR

The rate-determining step for photocatalytic oxidation is the reduction of oxygen at the conductance band [22]. Fe(VI) can act as an alternative electron acceptor to oxygen which is a thermodynamically more favorable reaction of oxygen reduction [23] ($E^0 = -0.13$ V for O_2 reduction, $E^0 = 0.72$ V for Fe(VI) reduction). The reduction of Fe(VI) by Ve^-_{cb} (−0.7 V) will take place through three one-electron steps that would result in the sequential formation of Fe(V), Fe(IV), and Fe(III) as metal ions (electron acceptors) to enhance the photocatalytic efficiency and Fe(V) is 10^3–10^5 times more reactive with compounds than is Fe(VI) [24]. In this study, the effect of adding ferrate to the photocatalysis of MCLR was investigated with five different dosages of ferrate (0.04, 0.08, 0.13, 0.17, and 0.33 mmol/L) and the results are shown in Fig. 1. Metal ion of Fe^{3+} was generated by ferrate decomposing in water and the concentrations of residual Fe depended on the dosages of ferrate. With the addition of ferrate, the photocatalytic efficiency of removing microcystin-LR increased. Above 81% degradation can be achieved at the ferrate concentration of 0.08–0.17 mmol/L within 10 min of contact time. Furthermore, the efficiency can be improved greatly to 100% with lengthening the contact time to 30 min. However, the efficiency decreased to 83% after 30 min contact time when

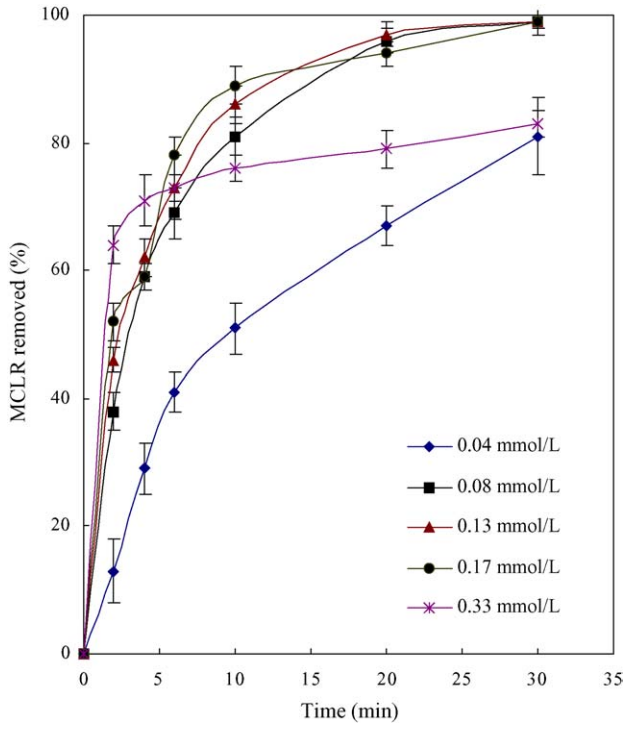

Fig. 1. Effect of ferrate concentration on enhancing the efficiency of photocatalytic degradation of microcystin-LR.

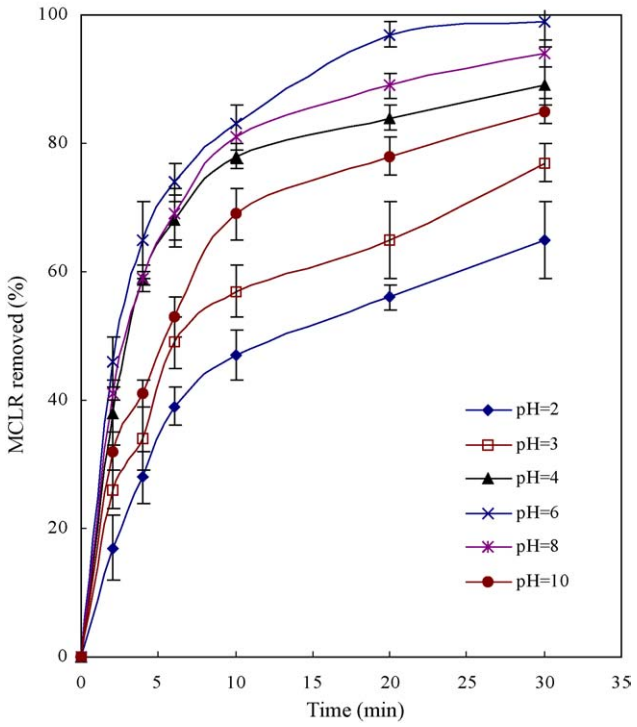

Fig. 2. Effect of pH on efficiency of ferrate enhanced photocatalysis of microcystin-LR.

adding the ferrate dosage to 0.33 mmol/L, although the corresponding theoretical addition dosage of Fe increased greatly. So the optimal ferrate dose is 0.08 mmol/L considering cost. The detrimental effects of high residual Fe on the photocatalytic rate possibly can be explained by two factors. The reason for the deleterious effect of high concentrations of iron is the filter effect due to UV light absorption of species [25]. The decrease in the rate can also be caused by the short-circuiting reaction, Eqs. (1) and (2) that create a cyclic process without reducing the recombination rate and generating active $HO^{\bullet}$ radical through the photo-Fenton reaction, Eq. (3), and retard the photocatalytic efficiency [26].

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (1)$$

$$Fe^{2+} + h^{+} \rightarrow Fe^{3+} \quad (2)$$

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + HO^{\bullet} + H_2O \quad (3)$$

3.2. Effect of pH on efficiency of ferrate enhanced photocatalysis of microcystin-LR

In this study, pH is an important factor for enhancing the photocatalytic rate because it affects not only the oxidative stability of ferrate and the formation of reduction products (Fe^{3+} or $Fe(OH)_3$), but also the ability of electrons and holes to enact redox chemistry in photocatalytic process $h^{+} + OH^{-} \rightarrow HO^{\bullet}$. In Fig. 2, effect of pH on ferrate enhancing photocatalytic process for microcystin-LR decomposition was investigated by using a range of buffer solutions from pH 2 to 10 at ferrate concentration of 0.13 mmol/L. The efficiency of removing MCLR increased with the increasing of pH at low pH level. When the pH value was 2, only 65% microcystin-LR was removed. One hundred percent removal efficiency was achieved at the optimal pH 6. An increasing pH value could enhance free radical generation through photooxidation by holes as indicated by $h^{+} + OH^{-} \rightarrow HO^{\bullet}$ at the same time strengthening the stability of ferrate as a strong oxidant in water. But with the increase of pH to 10, the efficiency decreased gradually to 85% after 30 min contact time. An increase in pH has two combined deleterious effects on the Fe(VI) enhancement of photocatalysis at TiO_2 surfaces. Literature results suggest the existence of four Fe(VI) species: $H_3FeO_4^{+}$, H_2FeO_4, $HFeO_4^{-}$, and FeO_4^{2-}, over the entire pH range [27]. The dissociation constants for protonated Fe(VI) species are $pK_1 = 1.6 \pm 0.2$, $pK_2 = 3.5$, and $pK_3 = 7.3 \pm 0.1$ [27]. The reduction rates of Fe(VI) by substrates decreased with an increase in pH 6–10 and were largely related to the concentration of $HFeO_4^{-}$ [28,29]. An increase in electrostatic repulsion between the negatively charged TiO_2 surface and the two Fe(VI) species may result from an increase in the more negative FeO_4^{2-} species relative to $HFeO_4^{-}$ at higher pH values. A combined effect of these processes will result in slower photo-reduction of Fe(VI) at TiO_2 surfaces with an increase in pH. There is also a possibility of a decrease, both in the available active sites of TiO_2, due to possible adsorption of $Fe(OH)_3$, a product of Fe(VI) reduction and the filter effect is due to UV light absorption of the species as $Fe(OH)^{2+}$ and $Fe(OH)^{+}$ [13]. These results demonstrate that pH should be

controlled carefully to avoid inhibiting the reaction. In this study, the optimal range of pH is 6.

3.3. Efficiency of removing microcystin-LR by ferrate or Fe(VI)/UV/TiO_2 photocatalysis

Both ferrate and photocatalysis using TiO_2 degraded microcystin-LR are shown in Fig. 3. The removal efficiency of microcystin by ferrate depended on the dosage of ferrate and the pH of the reaction solution. When pH was 6 and the ferrate dose was 0.08 mmol/L, about 54% microcystin was removed after 30 min reaction time. At the same condition, the photocatalytic efficiency of degradating microcystin-LR by TiO_2 was 63%. When microcystin-LR was pre-oxidized by ferrate (0.08 mmol/L) for 10 min, and then photocatalyzed for 20 min, the removal of microcystin-LR reached to 79% [30]. However, when ferrate was added to the photocatalytic process, a significant enhancement in the rate of the photocatalytic degradation was observed. The photocatalytic rate could be achieved 100% with 0.08 mmol/L ferrate after 30 min contact time. This indicates the possible synergistic effects exist between ferrate and photocatalytic system. One reason is the photocatalytic reduction of Fe(VI) in TiO_2 suspensions produces Fe(V), Fe(IV), and Fe(III) as metal ion (electron acceptor) to enhance the photocatalytic efficiency and Fe(V) is 10^3–10^5 times more reactive with microcystin-LR than is Fe(VI). The other reason is the by-products of the photocatalytic process may not adsorb to the surface of TiO_2 in the absence of ferrate and so will not be oxidized by the surface adsorbed hydroxyl radicals. The addition of ferrate could generate the oxygen radicals and peroxide radicals [31] or hydroxyl radicals [10]. These radicals could react with the by-products which do not interact with radicals on the TiO_2 surface.

3.4. Efficiency of removing microcystin-LR by UV/TiO_2, Fe(III)/UV/TiO_2 or Fe(VI)/UV/TiO_2 photocatalytic process

The degradation of MCLR by photocatalysis with and without the presence of different metal ion as electron acceptor was studied in Fig. 4. This indicates that the removal efficiency by photocatalytic treatment after the addition of Fe^{3+} or FeO_4^{2-} was faster than that by photocatalysis only. By comparing Fe(VI)/UV/TiO_2 photocatalysis at ferrate dose (0.08 mmol/L) with Fe(III)/UV/TiO_2 photocatalysis at Fe^{3+} dose (0.36 mmol/L), it was found that the Fe(VI)/UV/TiO_2 photocatalytic system was more effective for destroying the toxin. In the presence of ferrate, microcystin was decomposed entirely after 30 min, at the same time the efficiency of photocatalysis in the presence of $FeCl_3$ was only 85%. The decay reaction of MCLR by three photocatalytic processes mentioned above can be described by pseudo-first-order reaction kinetics with good correlations of $r^2 \geq 0.99$ throughout the reaction. The photocatalytic rate constants (k) for UV/TiO_2, Fe(III)/UV/TiO_2, and Fe(VI)/UV/TiO_2 photocatalysis were 0.035, 0.061, and 0.154 min^{-1}, respectively, as shown in Fig. 5. The photocatalysis rate constant of Fe(VI)/UV/TiO_2 process was higher than Fe(III)/UV/TiO_2 by 2.5 times and UV/TiO_2 by 4.4 times.

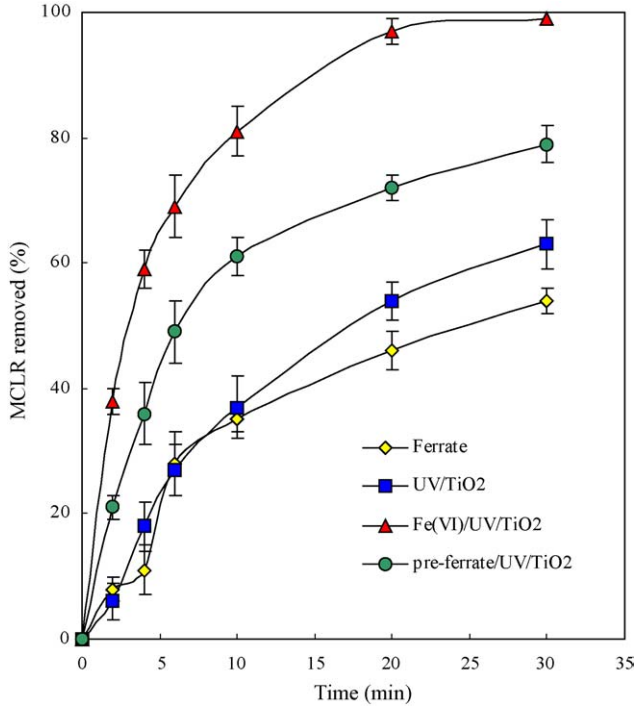

Fig. 3. Efficiency of removing microcystin-LR by ferrate or Fe(VI)/UV/TiO_2 photocatalysis.

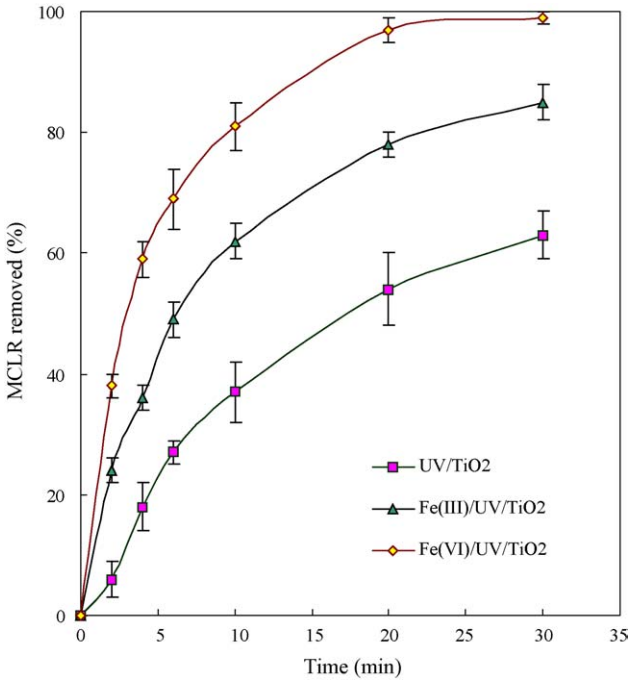

Fig. 4. Efficiency of removing microcystin-LR by UV/TiO_2, Fe(III)/UV/TiO_2 or Fe(VI)/UV/TiO_2 photocatalysis (ferrate = 0.08 mmol/L and Fe^{3+} = 0.36 mmol/L).

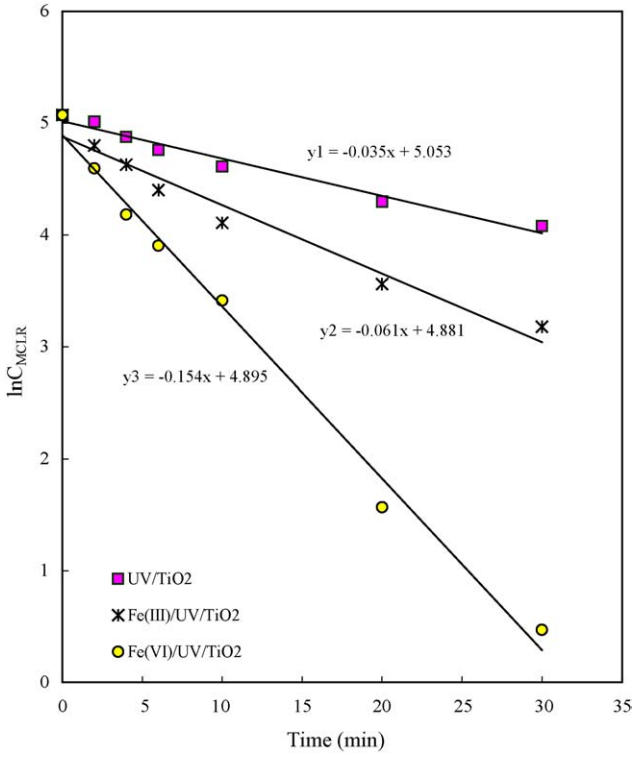

Fig. 5. Pseudo-first-order decay constant k (min^{-1}) of UV/TiO_2, $Fe^{3+}/UV/TiO_2$ or $Fe(VI)/UV/TiO_2$ photocatalysis (ferrate = 0.08 mmol/L and Fe^{3+} = 0.36 mmol/L).

To further investigate the different effects of Fe(VI) and Fe(III) on photocatalytic destruction of microcystin, the control experiments were performed to study the photocatalysis at different concentrations of calculated Fe. From Fig. 6, the complete removal could be obtained by the addition of 0.08 mmol/L ferrate and the theoretical concentration of Fe was 4.48 mg/L accordingly. In the presence of Fe^{3+}, the highest removal 85% occurred at the concentration of Fe^{3+} 0.36 mmol/L and the calculated Fe was 20.16 mg/L which was about five-fold of calculated Fe in 0.08 mmol/L ferrate. However, with more addition of ferrate or $FeCl_3$ to the photocatalytic process, the same rule observed in both processes was that the microcystin removal dropped with increasing residual Fe concentration. These results support the proposal that metal cations at low concentrations can increase the oxidation rate by participating not only in the heterogeneous pathways but also in alternative homogeneous Fenton-type reactions [13]. The inhibition of the photocatalytic rate at high concentrations is attributed to the competition of Fe^{2+} with the organic substrate for the oxidant species. The resulting Fe^{3+} can react with surface trapped electrons, regenerating Fe^{2+} and decreasing the efficiency even further [13]. Ferrate could enhance the photocatalytic efficiency only with relative low residual Fe compared with $FeCl_3$ addition. It was possibly attributed to ferrate decomposition in natural solution to provide an extra source of oxidizing species because its reduction in water can generate the oxygen radicals and peroxide radicals that strengthen the photocatalytic oxidation [31].

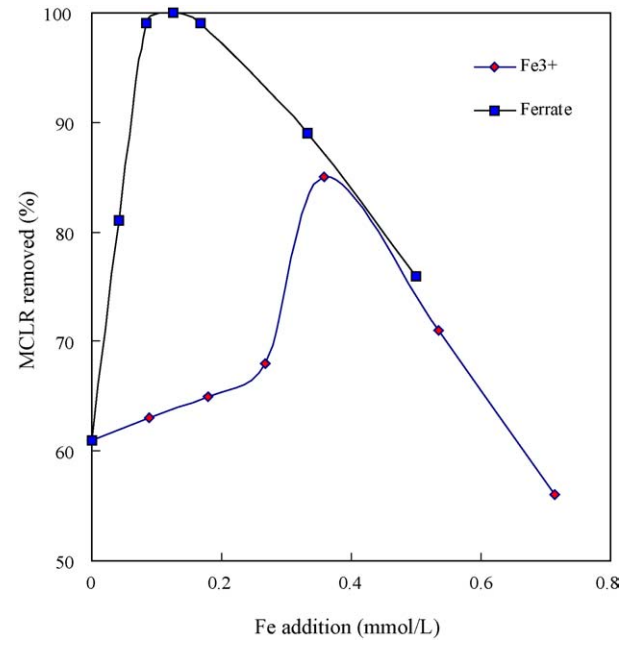

Fig. 6. Efficiency of removing microcystin-LR by photocatalysis with different concentrations of ferric or ferrate.

3.5. The mechanism of microcystin-LR removal by ferrate-assisted photocatalysis

In order to observe the ferrate-assisted effect on microcystin-LR in detail, a preliminary assessment of the structural changes was performed after ferrate-assisted photocatalysis at a dose of 0.08 mmol/L at the wavelength 238 and 210 nm. After 30 min contact time, microcystin-LR was structurally destroyed and no peaks of MCLR can be detected. The wavelength of 238 nm detects the aromatic portion of the Adda side chain which is a unique C_{20} β-amino acid, (2*S*,3*S*,8*S*,9*S*)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4(*E*),6(*E*)-dienoic acid, and the wavelength of 210 nm detects the peptide bonds in the ring of MCLR. These results indicated that the chromatographic properties of MCLR had changed. The results also suggested that (a) the 'Adda' group was modified, resulting in a loss of absorbance at 238 nm, and (b) the heptapeptide ring of MCLR has been opened or destroyed, resulting in a loss of absorbance at 210 nm. Thus, MCLR appears to have been extensively removed after Fe(VI)-assisted photocatalysis oxidation.

4. Conclusions

With the addition of ferrate to the photocatalytic process, it appears to significantly enhance the photocatalytic degradation microcystin-LR using TiO_2. Ferrate was very strong oxidant and can degrade partly organic substrates including microcystin-LR in solution at the same time it

decomposed in solution generating the oxygen radicals, peroxide radicals and sequential products Fe(V), Fe(IV), and Fe(III). The reduction products enhanced the following photocatalytic oxidation. The optimal value in concentration of ferrate (about 0.08 mmol/L) was very important to enhance the rate of the photocatalytic transformation. Solution pH was also important to degradation rates, with greatest degradation occurring at pH 6. No HPLC detectable MCLR at 238 and 210 nm was observed with the Fe(VI)/UV/TiO_2 process indicating that the toxin was removed more quickly and completely compared with Fe(III)/UV/TiO_2 and UV/TiO_2 processes.

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