Photodegradation of microcystin-LR catalyzed by metal phthalocyanines immobilized on TiO$_2$-SiO$_2$ under visible-light irradiation

Guotao Peng, Zhengqiu Fan, Xiangrong Wang, Xin Sui and Chen Chen

ABSTRACT

Microcystins (MCs) are a group of monocyclic heptapeptide toxins produced by species of cyanobacteria. Since MCs exhibit acute and chronic effects on humans and wildlife by damaging the liver, they are of increasing concern worldwide. In this study, we investigated the ability of the phthalocyanine compound (ZnPc-TiO$_2$-SiO$_2$) to degrade microcystin-LR (MC-LR) in the presence of visible light. X-ray diffraction (XRD) and UV-Visible diffuse reflectance spectra (UV-Vis DRS) were utilized to characterize the crystalline phase and the absorption behavior of this catalyst. According to the results, XRD spectra of ZnPc-TiO$_2$-SiO$_2$ powders taken in the 2θ configuration exhibited the peaks characteristic of the anatase phase. UV-Vis DRS showed that the absorption band wavelength shifted to the visible range when ZnPc was supported on the surface of TiO$_2$-SiO$_2$. Subsequently, several parameters including catalyst dose, MC-LR concentrations and pH were investigated. The MC-LR was quantified in each sample through high-performance liquid chromatography (HPLC). The maximum MC-LR degradation rate of 80.2% can be obtained within 300 minutes under the following conditions: catalyst dose of 7.50 g/L, initial MC-LR concentration of 17.35 mg/L, pH 6.76 and the first cycling run of the photocatalytic reaction. Moreover, the degradation process fitted well with the pseudo-first-order kinetic model.

Key words | microcystin-LR, photocatalytic degradation, phthalocyanines, TiO$_2$-SiO$_2$

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INTRODUCTION

Harmful algal blooms (HABs) are a global threat to the living water environment, aquaculture industries and human health (Zhang et al. 2013; Shen et al. 2014). *Microcystis, Anabaena, Nostoc* and *Oscillatoria*, species of freshwater cyanobacteria, can produce a family of monocyclic heptapeptides, termed microcystins (MCs), which are the most studied metabolites of cyanobacteria (Ren et al. 2010).

Structurally, MCs are monocyclic heptapeptides composed of the following residues: D-Ala, X, D-β-Me-Asp, Y, Adda, D-Glu, and Mdha. X and Y are two variable L-amino acids; D-Ala is D-Alanine; β-D-Me-Asp is D-erythro-β-methyl-D-aspartic acid; Adda is Addais(2S,3S,8S,9S)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid; D-Glu is D-Glutamic acid; and Mdha is N-methyldehydroalanine (Christiansen et al. 2008; Figure 1). Due to their cyclic structures, MCs are stable in the natural aquatic system and maintain their toxicity even after boiling (Vilela et al. 2012).

Many processes have been tested for the degradation of MCs, such as electrochemical oxidation processes, chlorination processes, potassium permanganate processes, and photo catalysis, among others (Iliev et al. 2003; Rodriguez et al. 2008; Zhang et al. 2009). Of these, photocatalysis is a promising technology because the solar radiation that reaches the Earth's surface covers the absorption range of many photocatalysts. TiO$_2$-based heterogeneous photocatalytic oxidation leads to water splitting. Jančula et al. (2010) have recently reported that phthalocyanines (PCs) are promising photosensitizers for use from both academic and industry points-of-view. The PCs can react to produce singlet oxygen to damage different molecules and tissues in the presence of visible light and diatomic oxygen (Jori & Brown 2004; Zhang et al. 2010). However, the degradation capacity of PCs for microcystin-LR (MC-LR) under visible light irradiation has been rarely reported.
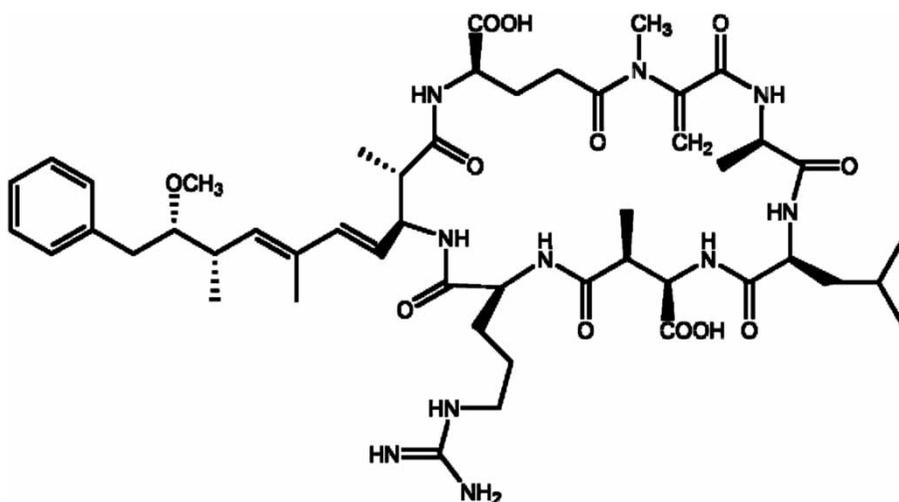
Figure 1 | The chemical structure of Microcystin-LR.

In this study, zinc phthalocyanine (ZnPc), immobilized on a TiO_2-SiO_2 support, was investigated for the destruction of MC-LR. The influencing parameters, including catalyst dose, initial MC-LR concentration, initial pH values were controlled and analyzed and the dynamic analysis of different conditions were done. This work seeks to improve the degradation efficiency of MCs by optimizing the absorption characteristics of PCs and reaction conditions, which would be a new environmentally friendly method for the degradation of MCs.

MATERIALS AND METHODS

Materials

Microcystis aeruginosa (FACHB-905) was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China). Deionized-distilled water was obtained from a Milli-Q-Water system (Millipore, Bedford, MA, USA). MC-LR standard was purchased from Express Technology Co., Ltd (China) and prepared for a series of concentration gradients in deionized-water. HPLC grade methanol was purchased from Tedia Co., USA. C18 cartridges were purchased from Supelco Co., USA. ZnPc and n-octylamine (OA) were obtained from Sigma Co., USA. Tetrabutyl orthotitanate (TBOT) and tetraethyl orthosilicate (TEOS) were obtained from Dahe Co. Ltd, China.

Preparation of MC-LR

The algal cells of *Microcystis aeruginosa 905* were cultured in BG-11 medium under the conditions of temperature of 25 °C,

light intensity of 2,000 lux, and a light and dark rotation of 12 hours. A freezing and thawing extraction method was used to extract MC-LR when the algae had grown to near the maximum biomass. After centrifugation of cells (5,000 rpm, 10 minutes), MC-LR was extracted by the following steps: The algae cells were crushed by freezing and thawing in methanol with liquid nitrogen three times, and the supernatant was collected after centrifugation (5,000 rpm, 10 minutes each time). The residual methanol in the supernatant was removed by rotary evaporation at 50 °C in a water bath. The liquid extract was then filtered through a Whatman GF/C filter and purified through a conventional SPE procedure using Supelco-C18 cartridges (500 mg, 3 mL). The extracted and purified MC-LR was stored at 4 °C for further use.

Synthesis and characterization of the catalyst

Preparation of TiO_2-SiO_2 nanoparticles

TBOT (10 mL) was added to HCl (60 mL, 1.0 mol/L) to produce solution A. Solution B was obtained by mixing TEOS (21.4 mL) and n-octylamine (20.4 mL). Solution A was added dropwise to B with stirring at 50 °C to form a white precipitate. After centrifugation, the precipitate was washed several times with distilled water and ethanol, dried and calcined at 550 °C to yield TiO_2-SiO_2.

Preparation of ZnPc-TiO_2-SiO_2 complex

Using absolute ethanol as the loading solvent, 5 µmol of ZnPc was mixed with each gram of TiO_2-SiO_2 support in

a container for 24 hours at 25 °C. When the reaction was completed, the catalyst was separated by filtration, and then washed with water several times and dried at 100 °C. The catalyst was then characterized.

Catalyst characterization

The crystalline phases of the samples were characterized by X-ray diffractometry (XRD) (Bruker, Germany) with Cu Kα radiation. UV-Visible diffuse reflectance spectra (UV-Vis DRS) of the catalyst was carried out on a Lambda 35 UV/Vis Spectrometer (Perkin Elmer Co., USA) using spectral grade $BaSO_4$ as the reference material.

Photocatalytic experiments and analysis

Experimental design

Experiments were carried out to investigate the effect of different parameters including catalyst dose, initial MC-LR concentrations and initial pH values on the degradation capacity of MC-LR.

Four levels of catalyst dose were investigated: 3.25 g/L, 5.25 g/L, 7.50 g/L and 10.00 g/L. Initial MC-LR concentrations were 8.08 mg/L, 14.92 mg/L, 17.37 mg/L and 22.74 mg/L, and MC-LR degradation was measured at five different initial pH values (3.00, 5.34, 6.76, 8.65 and 10.50). Each group composed of triplicate samples and the data are reported as the average ± standard deviation. The stability by three successive cycling runs of experiments with pH 6.76, and the catalyst dose and the initial MC-LR concentration used in each run were 7.50 g/L and 17.35 mg/L, respectively.

Photochemical procedures

The reaction was performed in a photochemical reaction instrument (DZ47–60, Bilang Co., Shanghai). All the MC-LR photocatalytic degradation experiments were carried out in test tubes (30 mL) with 20 mL of MC-LR solution and $ZnPc$-TiO_2-SiO_2 powders. The suspension was magnetically stirred in the dark for three hours to ensure establishment of MC-LR adsorption-desorption equilibrium on the surface of the catalyst. The reactor was then irradiated with visible light emitted by a 500 W xenon lamp with a 420 nm cutoff filter. At given irradiation time intervals, samples were collected and filtered through a millipore filter (0.22 μm). The filtrates were analyzed using high performance liquid chromatography (HPLC, Agilent

1200) to examine the degradation of MC-LR. The HPLC was equipped with an autosampler (model), an Agilent pump (model), a PDA detector (model) and a ZORBAX SB-C18 column (5 μm, 4.6 × 250 mm, Agilent, USA). For the HPLC analysis, the mobile phase with a flow rate of 0.8 mL/min was a mixture of 40% acetonitrile and 60% water, both containing 0.05% trifluoroacetic acid (TFA). The wavelength of the UV absorbance detector was set at 238 nm and the sample injection volumes were 20 μL. The standard solution of MC-LR was used to determine the retention time (RT) of the characteristic peak. A linear regression equation between the standard MC-LR gradient concentration and the peak area was fitted. Therefore, the MC-LR concentration of each sample was quantified by the peak area appeared at the specific RT (6.8 minutes in this study).

Degradation kinetic analysis

The influence of each factor on the MC-LR degradation was calculated using the pseudo-first-order kinetic model (Chen *et al.* 2012; Ma *et al.* 2012):

$$In(c_0/c_t) = kt$$

where c_0 and c_t were the concentrations of reactant at time 0 and t, respectively, and k was the pseudo-first-order rate constant, which was obtained from the gradient of the figure of $In(c_0/c_t)$ versus t.

RESULTS AND DISCUSSION

Catalyst characterization

XRD analysis of catalyst

The powders were subjected to XRD to determine the crystal phase composition of TiO_2-SiO_2 and $ZnPc$-TiO_2-SiO_2. With the testing conditions of calcination temperature of 450 ± 20 °C, scanning angle 10–90 °C, and scanning speed 8 °/min, the prepared $ZnPc$-TiO_2-SiO_2 was mainly anatase with characteristic diffraction peaks at $2\theta = 25.70$ °, the same as TiO_2-SiO_2 (Figure 2), which was consistent with other reports (Yu *et al.* 2002; Zhu & Zhang 2011). The result indicated that the ZnPc supported on the surface of TiO_2-SiO_2 did not change the crystal structure of TiO_2-SiO_2.
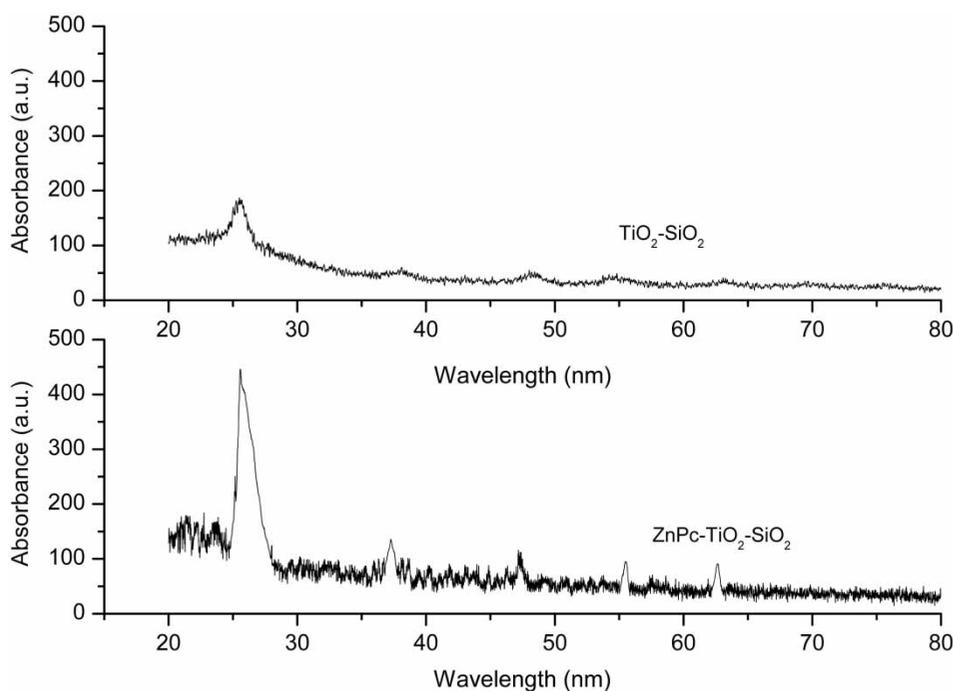
Figure 2 | XRD patterns of TiO_2-SiO_2 and ZnPc-TiO_2-SiO_2.

UV-Vis DRS of catalyst

Figure 3 displays the UV-Vis diffuse reflectance spectra of ZnPc-TiO_2-SiO_2 composite powder and TiO_2-SiO_2 powder, which showed the optical properties of the photocatalyst. As shown in Figure 3, the absorption band edge of the prepared TiO_2-SiO_2 was at about 390 nm. Rawal *et al.* (2012) reported that the optical absorption near the band edge of a crystal obeys the following equation:
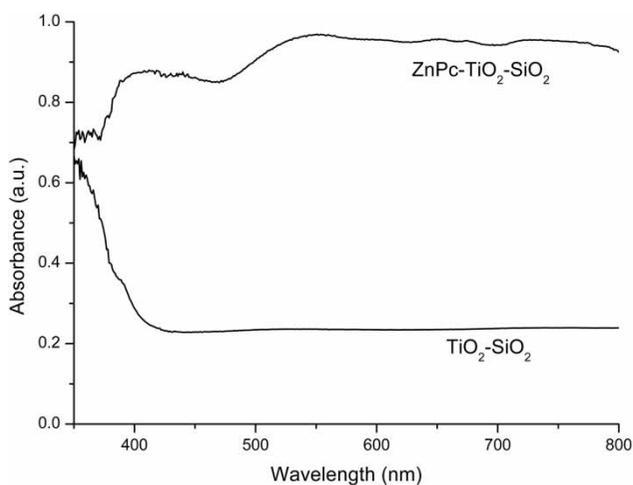
$$E_g = 1240/\lambda_0$$

where λ_0 is the wavelength. By calculating, the band gap of prepared TiO_2-SiO_2 was approximated as 3.18 eV, which was almost the same as the reports of other researchers (Antoniou *et al.* 2008; Zhou *et al.* 2013). Furthermore, the absorption band wavelength shifted to the visible range when ZnPc was supported on the surface of TiO_2-SiO_2. Additionally, the absorbance above 400 nm largely increased for ZnPc-TiO_2-SiO_2 compared to TiO_2-SiO_2.

Photocatalytic degradation of MC-LR by immobilized ZnPc-TiO_2-SiO_2

Effect of catalyst dose

Figure 4 shows the degradation of MC-LR ($c_0 = 17.30$ mg/L) for various initial concentration of ZnPc-TiO_2-SiO_2 at pH 6.70. The control experiment displays that the removal of MC-LR without the catalyst under visible light irradiation was almost negligible. The degradation rate of MC-LR increased from 60.9% to 80.0% when the dose of ZnPc-TiO_2-SiO_2 increased from 3.25 g/L to 7.50 g/L within 300 minutes.

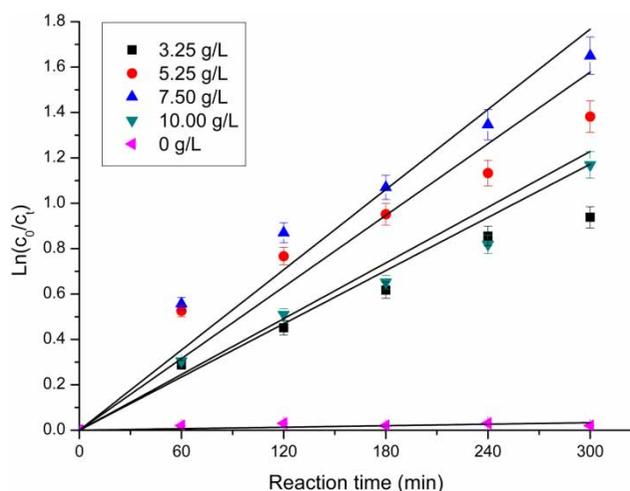**Figure 3** | UV-Vis DRS of ZnPc-TiO_2-SiO_2 and TiO_2-SiO_2.

Figure 4 | Pseudo-first-order kinetics of MC-LR degradation under different initial catalyst dosages.

Figure 5 | Pseudo-first-order kinetics of MC-LR degradation under different initial MC-LR concentrations.

The pseudo-first-order kinetic constant k reached $0.0058 \ \text{min}^{-1}$ when the catalyst concentration was 7.50 g/L. However, when the catalyst dose was increased to 10.00 g/L, the degradation rate of MC-LR did not increase any further, and in fact it was reduced to 68.9% while the pseudo-first-order kinetic constant k reduced to $0.0034 \ \text{min}^{-1}$. Consequently, under the experimental conditions, the optimal amount of catalyst was concluded to be 7.50 g/L. In heterogeneous photocatalytic oxidation reactions, the degradation rate of toxic organic pollutants accelerates as the catalyst dose increases. Nevertheless, lots of reports have revealed that the excess catalyst would, on the contrary, decrease the reaction rate. This may be generally explained that the absorption of the photon energy reached saturation at a certain value of catalyst dose, and the excessive dose of catalyst led to the scattering effect of light, which influenced the light transmittance of the solution, resulting in the decrease of removal rate (Zanjanchi *et al.* 2010; Teng *et al.* 2012).

Effect of initial MC-LR concentrations

Figure 5 shows the effect of initial MC-LR concentration on the photocatalytic activity of ZnPc-TiO$_2$-SiO$_2$ when the initial catalyst concentration was 7.50 g/L at pH 6.74. The MC-LR degradation presented a pseudo-first-order behavior with the pseudo-first-order rate constant of 0.0072, 0.0059, 0.0049 and $0.0040 \ \text{min}^{-1}$ at the initial MC-LR concentrations of 8.08 mg/L, 14.92 mg/L, 17.37 mg/L and 22.74 mg/L, respectively. Moreover, the removal efficiency after 300 minutes reaction was found to decrease from 87.6% to 65.9% when the initial MC-LR concentration
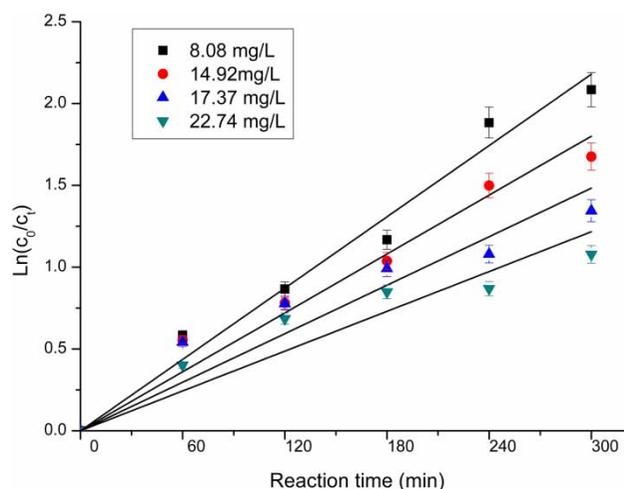
ranged from 8.08 mg/L to 22.74 mg/L. These results indicated that the degradation efficiency was decreasing with the MC-LR concentration, which might be because the yield rate of singlet oxygen remains constant under the same catalyst dose and pH value, the increasing concentration of MC-LR results in a decreased ratio of oxidized MC-LR to the total MC-LR.

Effect of initial pH value

Figure 6 shows the influence of different pH values on the degradation profile of MC-LR with the initial catalyst dose of 7.50 g/L and initial MC-LR concentration of 17.35 mg/L.
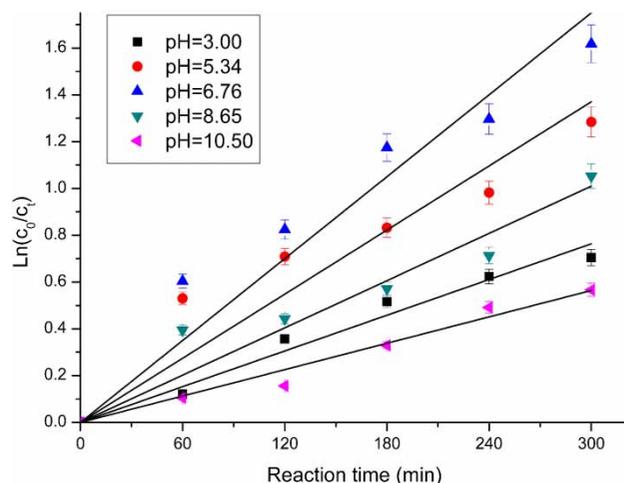

Figure 6 | Pseudo-first-order kinetics of MC-LR degradation under different initial pH values.
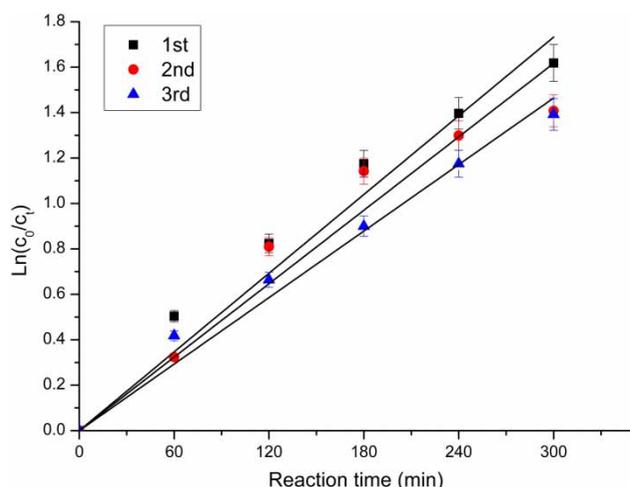
Figure 7 | Pseudo-first-order kinetics of MC-LR degradation for three cycling runs.

Five values of pH were employed (3.00, 5.34, 6.76, 8.65, 10.50), and after being irradiated by visible light, the MC-LR degradation rates were 50.5%, 72.3%, 80.2%, 65.1% and 43.2%, respectively. The maximum degradation rate occurred at pH 6.76, with a pseudo-first-order constant k of 0.0058 min^{-1}.

The optimal pH value for the removal of organic pollutants varies because of the complex reactions occurring in aqueous systems. The hydrophobic effect of MC-LR makes itself prefer moving to the objects with larger surface area (Lawton et al. 2003). The hydrophobicity of MC-LR also

decreases as the pH increases, which give a good explanation of the lower absorbance of MC-LR with the catalyst under the alkaline condition in this study (pH 8.65 and 10.50). Besides, the catalyst remained stable in the weak acidic conditions since the surface of TiO_2 is acidulous (Muthukumaran et al. 2014). However, the strong acid would promote the breakaway of the center ion (Zn) from the phthalocyanine cycle (Huang et al. 2002), which resulted in the decrease of the removal rate.

Catalyst recycling

The stability of the immobilized catalyst plays an important role for its application in environmental technology (Guan 2005). For this reason, the recycling of $ZnPc\text{-}TiO_2\text{-}SiO_2$ was examined for the degradation of MC-LR over three cycling runs. After each experiment, the solution residue from the photocatalytic degradation was filtered, washed and dried. The dried catalyst samples were used again for the degradation of MC-LR with identical experimental conditions (Figure 7). The removal efficiency of MC-LR were 80.2%, 75.5% and 75.1% for the three cycling runs, with the degradation kinetic constants of 0.0059 min^{-1}, 0.0053 min^{-1}, and 0.0049 min^{-1} respectively, which confirmed that the activity of $ZnPc\text{-}TiO_2\text{-}SiO_2$ was able to keep constant. The result suggested that the immobilized

Table 1 | The degradation rate of MC-LR and parameters of pseudo-first-order kinetics under different conditions

| Factors | Conditions | The concentration of MC-LR | | The degradation rate of MC-LR (%) | $Ln(C_0/C_t) = kt$ | |
		C_0	C_t		k (min^{-1})	R^2
Catalyst (g/L)	0.00	17.30	17.30	0	0.0001	0.72300
	3.25	17.30	6.77	60.9	0.0034	0.97274
	5.25	17.30	4.34	74.9	0.0050	0.91628
	7.50	17.30	3.46	80.0	0.0058	0.95061
	10.00	17.30	5.37	68.9	0.0034	0.97274
MC-LR (mg/L)	8.08	8.08	1.01	87.6	0.0072	0.97789
	14.92	14.92	2.79	81.3	0.0059	0.96785
	17.37	17.37	4.60	73.9	0.0049	0.88023
	22.74	22.74	7.74	65.9	0.0040	0.85725
Initial pH value	3.00	17.35	8.58	50.5	0.0025	0.97287
	5.34	17.35	4.80	72.3	0.0045	0.88397
	6.76	17.35	3.44	80.2	0.0058	0.92560
	8.65	17.35	6.05	65.1	0.0034	0.91786
	10.50	17.35	9.85	43.2	0.0019	0.97395
Cycling runs	1st run	17.35	3.44	80.2	0.0059	0.96029
	2nd run	17.35	4.25	75.5	0.0053	0.93798
	3rd run	17.35	4.31	75.1	0.0049	0.97877

ZnPc-TiO$_2$-SiO$_2$ is an effective and stable photocatalyst for the degradation of MC-LR.

The parameters including initial catalyst dose, initial MC-LR concentration, initial pH values and recycling experiment were in line with the pseudo-first-order kinetic model. All the factors are listed in Table 1. The maximum MC-LR degradation rate of 80.2% can be obtained within 300 minutes under the following conditions: initial catalyst dose of 7.50 g/L, initial MC-LR concentration of 17.35 mg/L, pH 6.76 and the first cycling run of the photocatalytic reaction.

CONCLUSIONS

The photocatalytic oxidation system of immobilized ZnPc-TiO$_2$-SiO$_2$ efficiently degraded the MC-LR in an aqueous solution. XRD and UV-Vis DRS showed that the TiO$_2$ and SiO$_2$ composite enhanced the binding of ZnPc to the support, broadened the absorption range of visible light, and also increased the stability of ZnPc-TiO$_2$-SiO$_2$. The MC-LR degradation behavior under various conditions were evaluated and the removal efficiency reached 80.2% within 300 minutes under the following optimal reaction conditions: initial catalyst dose of 7.50 g/L, initial MC-LR concentration of 17.35 mg/L, pH 6.76 and the first cycling run. Additionally, the degradation process fitted well with the pseudo-first-order kinetic model, and the maximum value of the degradation kinetic constant k was 0.0059 min^{-1}.

The photocatalyst was easily collected from the reaction solution by simple filtration, and could be recycled for photocatalytic experiments with minor loss of activity. The reaction intermediates and degradation pathways are currently being studied and further research is needed to clarify the reaction mechanisms.

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