



## Research Article

# Photocatalytic Degradation of Microcystins-LR over Mesoporous graphitic Carbon Nitride (mpg-CN)

Laiyan Wu<sup>1</sup>, Jirong Lan<sup>1</sup>, Anping Yang<sup>3</sup>, Yanxi Zhao<sup>1</sup>, Songbo Wang<sup>1</sup> and Junjiang Zhu<sup>1,2\*</sup>

<sup>1</sup>Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs & Commission Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China

<sup>2</sup>Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, China

<sup>3</sup>Department of Testing and Analysis, Hubei Provincial Environmental Monitoring Center Station, Wuhan 430072, China

**\*Address for Correspondence:** Dr. Junjiang Zhu, Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs & Commission Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China, Email: ciaczjj@163.com

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**Keywords:** Mpg-CN; Microcystin-LR; Photo degradation; Reusability; Mechanism



## ABSTRACT

Mesoporous graphitic carbon nitrides (mpg-CN) were synthesized by a templating method using Ludox (SiO<sub>2</sub>) as hard template and guanidine hydrochloride (GndCl) as precursor, and were used as metal-free photocatalysts for microcystin-LR (MC-LR) degradation in aqueous solution. By tuning the mass ratio of SiO<sub>2</sub> to GndCl, mpg-CN with varied surface areas and condensation degrees were obtained. Catalytic results showed that sample prepared at mass ratio equals 0.4, i.e., mpg-CN(0.4), exhibits the best activity, with above 98% MC-LR conversion obtained at 120 min. Mechanism studies suggested that the reaction obeys the pseudo first-order equation and the produced superoxide anion radicals ( $\cdot\text{O}_2^-$ ) is the major reactive intermediates contributing to the reaction. Stability tests showed that no appreciable loss of activity is observed even the catalyst is recycled for five times, indicating that the material is stable in the reaction.

## INTRODUCTION

Occurrence of cyanobacterial harmful algal blooms causes water deterioration, shortage as well as damage to the ecosystem [1], and is becoming a worldwide environmental problem. Microcystins (MCs) are monocyclic heptapeptides produced by the freshwater cyanobacteria, having adverse effects on aquatic animals and human beings via food chain [2]. Among the 90+ variants of the MCs, Microcystin-LR (MC-LR) is commonly detected and has the most toxic effect [1]. For this, the World Health Organization (WHO) has issued a guideline value of 1  $\mu\text{g L}^{-1}$  MC-LR in drinking water and a tolerable daily intake (TDI) of 0.04  $\mu\text{g kg}^{-1}$  body weight per day of MC-LR in aquatic product [3,4].

MCs are stable in natural water, and can last for months or even years at high temperatures (40°C) and extreme pH solution, in the presence of sunlight and/or enzymes [5,6], making them hard to be removed by the conventional physical and biological technologies. Advanced oxidation processes (AOPs) could be effective for their elimination in the presence of strong oxidants, such as chlorine, ozone, hydrogen peroxide [7-9], but the continuous input of expensive chemical reagents and recontaminations are prohibitive. Recently, the photocatalysis technology with UV/TiO<sub>2</sub> system has been suggested to be a good strategy for the removal of organic pollutants in wastewaters. This system can exhibit fast, effective and environment-friendly properties in mineralizing the pollutants, by producing strongly oxidative

electron/hole pairs, e.g.,  $h^+$ ,  $\bullet O_2^-$  and  $\bullet OH$  radicals [10-14]. However,  $TiO_2$ -based photocatalysts require UV irradiation ( $\lambda < 400\text{nm}$ ) to activate the electrons, and less than 5% of the total solar energy could be utilized due to the large band gap ( $\sim 3.2\text{ eV}$ ) of  $TiO_2$ , limiting its practical use. The use of other photocatalysts, instead of  $TiO_2$ , with high utilization of solar energy is therefore needed.

Metal-free graphitic carbon nitride (g-CN) is a class of polymer material with semiconductor properties. The band gap of g-CN is 2.7 eV, smaller than that of  $TiO_2$ , thus is more suitable to be used as photocatalyst with respect to increasing the utilization efficiency of solar energy. Indeed, this material has been found to be a promising catalyst in various catalytic applications including photocatalysis [15-17], due to its tailorable textural structure and rich surface chemistries. Also, the g-CN has been proved to be stable either in acidic, neutral or basic solution [18,19], thus could be an ideal catalyst for reactions conducted in aqueous solution under various environmental conditions, like that in wastewater. However, g-CN prepared by the polycondensation method normally exhibits low surface area ( $< 10\text{ m}^2/\text{g}$ ) because of its graphitic layered structure, limiting the catalytic performances. In order to improve the surface area and the catalytic performances of g-CN, the preparation of materials with porous structure is anticipated, which can be achieved using a templating method, with either hard or soft template [20,21]. Indeed, it is reported that mesoporous graphitic carbon nitride (mpg-CN) exhibits high surface area ( $\sim 200\text{ m}^2/\text{g}$ ) and shows improved photocatalytic performances in, for example, hydrogen production [22] and degradation of organic dyes [23].

The aim of this work is to study the photodegradation behaviors of MC-LR on mpg-CN and its reaction mechanism. There are lots of works discussing the catalytic performances of mpg-CN for photodegradation of organic in literature [24]. Relative to these reported organics, MC-LR is a biologicals with bigger molecular weight, and is rather stable in water, and only few works on the application of mpg-CN for MC-LR photodegradation are reported in literature. Herein, we systematically investigated the reaction and its mechanism, to provide fundamental knowledge on the application of mpg-CN for photodegradation of biological MC-LR in aqueous solution.

## MATERIALS AND METHODS

### Chemicals

MC-LR (>95% purity, Wako, Japan), methanol and acetonitrile with HPLC grade (TEDIA Company, Inc., Fairfield, OH, USA), formic acid (Merck, Germany), and ultra-pure water (Bedford, MA, USA) were purchased and used as received. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. with analytical reagent grade.

### Preparation of mpg-CN

4.0 g  $GndCl$  was added to 4 mL deionized water with stirring. After dissolution a certain amount of Ludox (namely, 5.7, 10.0 and 14.3 g. The  $SiO_2$  dispersion is 28%) was added dropwise, corresponding to a mass ratio ( $r$ ) of  $SiO_2$  to  $GndCl$  is 0.4, 0.7 and 1.0, respectively. The mixture was then heated at  $50^\circ\text{C}$  and after the water was evaporated, the resulting white solid was dried at  $100^\circ\text{C}$  overnight, heat-treated in  $N_2$  at  $550^\circ\text{C}$  for 3 h (ramping rate of  $3^\circ\text{C min}^{-1}$ ). The obtained samples were treated with 50 mL 4 M  $NH_4HF_2$  for 48 h with drastic stirring to remove the silica template, and finally dried in a vacuum oven at  $60^\circ\text{C}$  for 2 h. Depending on the mass ratio of  $SiO_2$  to  $GndCl$ , the products were named as mpg-CN( $r$ ), where  $r=0.4, 0.7$  and 1.0, respectively.

### Characterization of catalysts

The samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer), Fourier transform infrared spectroscopy (FT-IR, Nicolet 470 FT-IR spectrometer), thermal gravimetric analysis (TGA, NETZSCH TG 209F3), transmission

electron microscopy (TEM, Tecnai G2 20 S-Twin), X-ray photoelectron spectroscopy (XPS, VG Multi lab 2000),  $N_2$  physisorption (TriStar II 3020, Micromeritics, USA), temperature programmed desorption of  $CO_2$  ( $CO_2$ -TPD, TP-5080 TPD/TPR apparatus, Tianjing Xianquan technology company) and diffuse reflectance spectrum (DRS) with UV-vis spectrophotometer (Lambda, Bio 35, PE Co., USA), which were described in detail in previous works [25,26].

### Photocatalytic degradation of MC-LR

10 mL MC-LR suspensions and 5 mg mpg-CN were mixed and stirred at room temperature (which was controlled at 20°C by an air conditioner) for 60 min in the dark to achieve adsorption equilibrium. Thereafter a LED lamp (the wavelength centered mainly at  $420\pm 10$  nm) was switched on to initiate the photocatalytic reaction, keeping stirring. During the reaction 0.5 mL of reaction mixture was withdrawn by a syringe at given intervals, which was centrifuged at 10000 rpm for 10 min and filtered with a 0.22  $\mu m$  membrane filter before the HPLC analysis.

### HPLC/MS analysis

A stock of MC-LR solution ( $10\text{ mg L}^{-1}$ ) was prepared using methanol as solvent. A standard calibration curve was made with MC-LR concentrations ranging from 5 to 1000  $\mu g L^{-1}$ . The determination of MC-LR was carried out on a HPLC-MS/MS system that consists of an Agilent 1290 HPLC and an Agilent 6460 mass spectrometer. The compositions of solution were analyzed with a Zorbax Eclipse plus C18 column (3.5 $\mu m$ , 3.0 x100mm) and the sample injection volume was 10  $\mu L$ . The mobile phase consisted of 0.1% HCOOH aqueous solution (solvent A) and pure  $CH_3OH$  (solvent B). A gradient elution was used, starting with water: methanol volume ratio of 80:20 from 0 to 5 min, and then ramping to 20:80 from 5.1 min, until returning to the original conditions to re-equilibrate the system. The gas (nitrogen) temperature and flow rate were set at 325°C and 6 L  $min^{-1}$ . The sheath gas temperature and flow rate were set at 350°C and 11 L  $min^{-1}$ . The instrument was operated in a positive ion mode. MC-LR were monitored by MRM mode, using 210 V fragmentor and 78 eV collision energy.

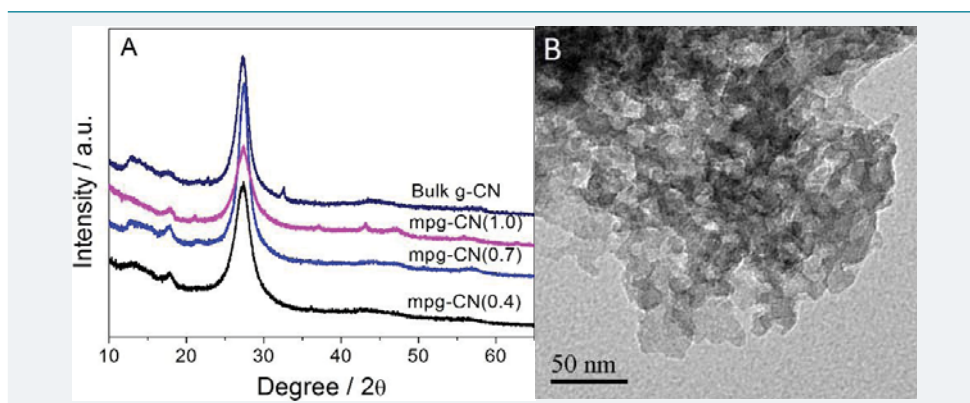
## RESULTS AND DISCUSSION

### Characterizations of the samples

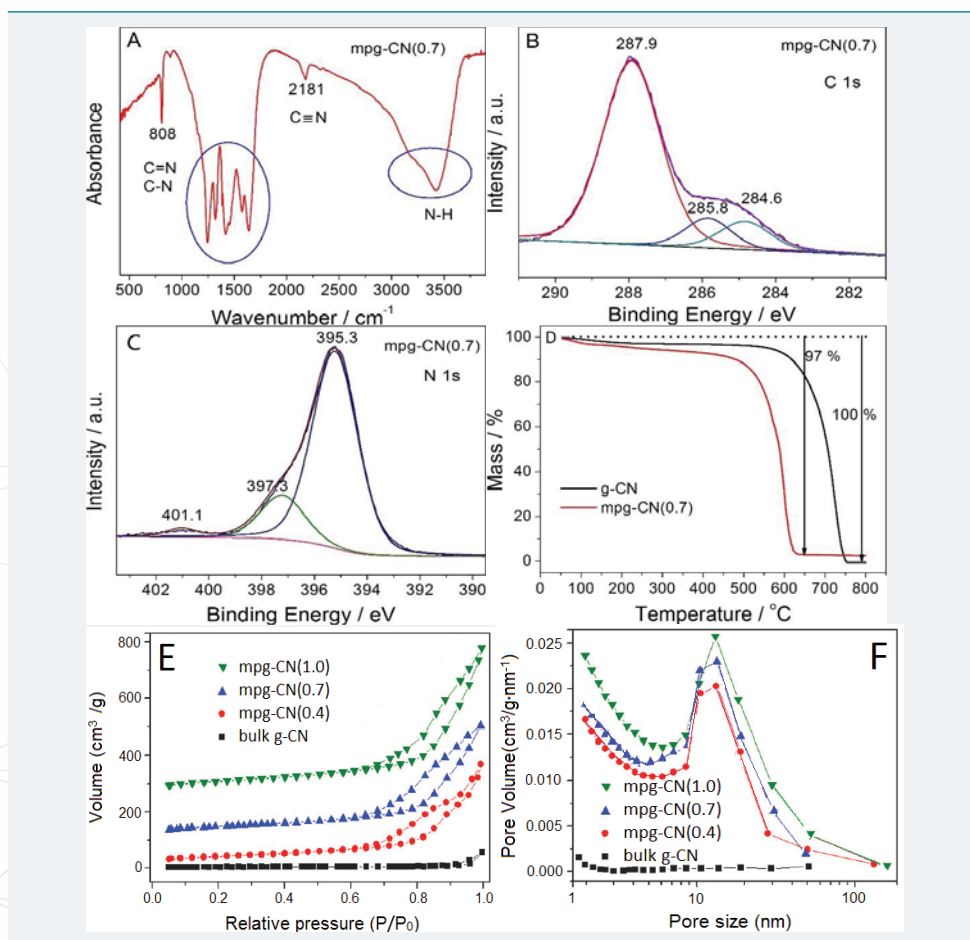
Figure 1A shows that a strong diffraction peak at  $2\theta=27.3^\circ$ , attributed to the characteristic diffraction peak of g-CN, appears in the XRD patterns of the three mpg-CN(*r*) samples, indicating that they all have the graphitic g-CN layered structure. This is further confirmed by the FT-IR and XPS spectra, where the stretching and/or bending vibrations assignable to the C-N-C and N-H groups, and the specific binding energy assignable to the C-(N)<sub>3</sub>, N-C=N, C-N-C groups, are observed, respectively, see figure S1A-C.

With respect to the pore creation or the removal of silica template, TGA curves (figure S1D) show that less than 5% residues is left after the sample was heat-treated in air at 800°C, suggesting that the  $SiO_2$  template is mostly removed and pores are created. The creation of pores and the increase of surface area, from g-CN to mpg-CN(*r*), are supported by the  $N_2$  physisorption isotherms, which show that the surface area increase from 11  $m^2/g$  for g-CN to 144, 166 and 151  $m^2/g$  for *r*=0.4, 0.7 and 1.0, respectively, with average pore size of ca. 14 nm (figure S1E, 1F). It is noted that the surface area of the samples increase not linearly with the *r* increase, but reaches the maximum at *r*=0.7. This is explained by the thin wall of mpg-CN, thus it will be collapsed during the template removing process if higher *r*=1.0 is used, leading to decreased surface area. TEM image confirms further that pores with diameter of 16 nm are created in the samples, as seen in figure 1B. Detailed discussion on these characterizations can be found in a previous work [25] and are not going to describe here, to avoid repetition.

Besides the phase and textural structure, the surface chemistries of the samples were also evaluated, by a  $\text{CO}_2$ -TPD measurement, and the results are presented in figure S2, which shows that mpg-CN (0.4) has the most, and mpg-CN (1.0) has the least amount of surface basic sites. It is known that g-CN is a base material, and the amount of surface basic sites depends intimately on the condensation degree of the sample. Sample with less condensation degree has more surface basic sites, and can absorb more  $\text{CO}_2$ . Thus the large  $\text{CO}_2$  desorption peak of mpg-CN (0.4) suggests that it has a less condensed structure. On the other hand, it has been reported that the condensation degree of g-CN relates intimately to the energy of electron excitation, and sample with more condensed structure needs higher energy for excitation [24]. Thus,



**Figure 1:** (A) XRD patterns of the mpg-CN(r) and that of the bulk g-CN; (B) TEM image of mpg-CN (0.4).



**Figure S1:** (A) FT-IR, (B) C 1s XPS spectrum, (C) N 1s XPS spectrum, (D) TGA curves of the specific mpg-CN(0.7) sample; (E)  $\text{N}_2$  physisorption isotherms and (F) pore size distributions of the bulk g-CN and mpg-CN(r) samples. Note: for simplicity we show here only the characterization result of sample at r=0.7 in the A-D picture.

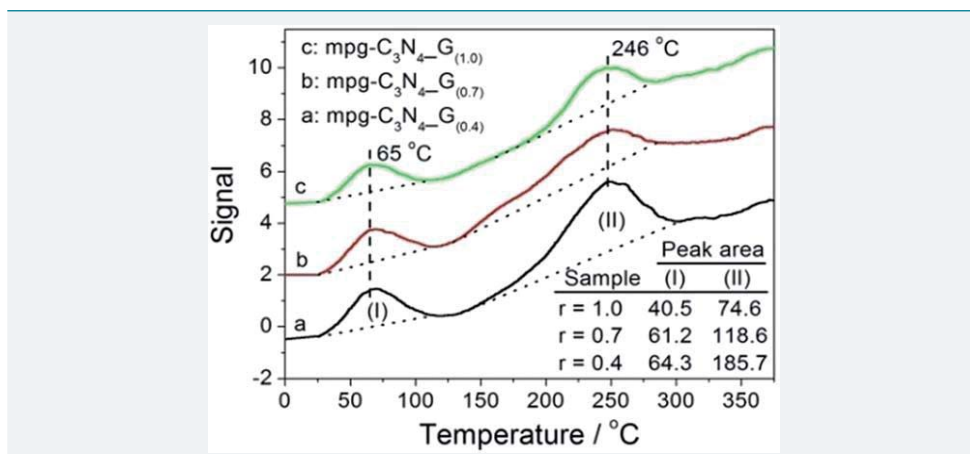


Figure S2: CO<sub>2</sub>-TPD profiles of mpg-CN(*r*) (*r*=0.4, 0.7 and 1.0).

the absorption band edge in the UV-Vis spectra was red-shifted with the decrease of condensation degrees, from mpg-CN (1.0) to mpg-CN (0.7) and to mpg-CN (0.4), as depicted in figure 2.

### Effect of SiO<sub>2</sub> to GndCl mass ratio (*r*)

Figure 3A shows the photocatalytic activity of mpg-CN(*r*) for MC-LR degradation with 420 nm irradiation. For comparison, the photocatalytic activity of two blank experiments, without light irradiation or without catalyst, were also tested under identical experimental conditions. The blank tests show that MC-LR conversion is negligible in both cases, suggesting that the catalyst cannot catalyze the reaction without light irradiation and the reaction hardly occurs by direct photolysis. Therefore, the activity observed thereafter should be attributed to a photocatalysis process, which depends both on the catalyst and the light irradiation.

The conversion increases abruptly when light irradiation and catalyst are simultaneously presented, in sequence of g-CN < mpg-CN (1.0) < mpg-CN (0.7) < mpg-CN (0.4). The increase of activity from g-CN to mpg-CN(*r*) can be attributed to the increased surface area and/or the creation of pores, which provide more surface to contact, and subsequently catalyze the degradation of substrate (MC-LR). For mpg-CN(*r*), the best activity is observed on mpg-CN (0.4). This can be attributed to its less condensed structure, enabling the electron excitation occurs at a relatively low light energy, as compared to that at *r*=0.7 and 1.0, see figure 2.

Kinetic calculation shows that the constant  $k_{app}$  increases abruptly from  $0.98 \times 10^{-2} \text{ min}^{-1}$  for g-CN to  $4.03 \times 10^{-2} \text{ min}^{-1}$  for mpg-CN(0.4), figure 3B, due to the improvement

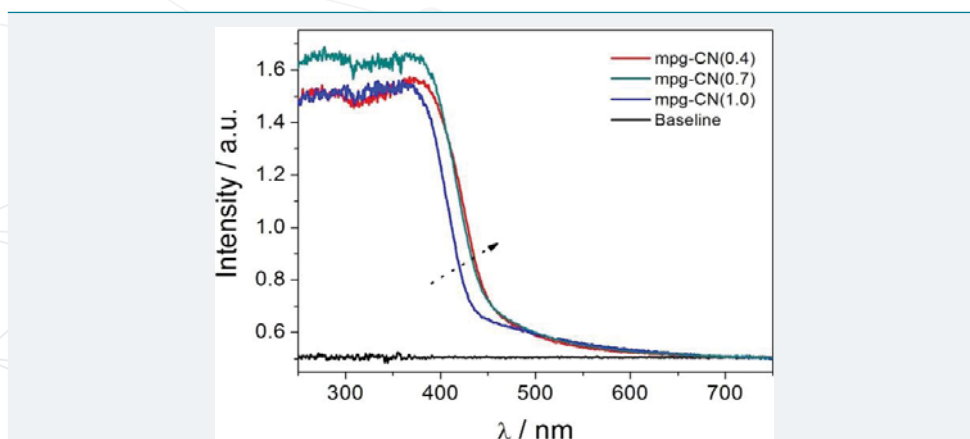


Figure 2: Diffuse reflectance spectra (DRS) of mpg-CN(*r*) samples (*r*=0.4, 0.7, 1.0).

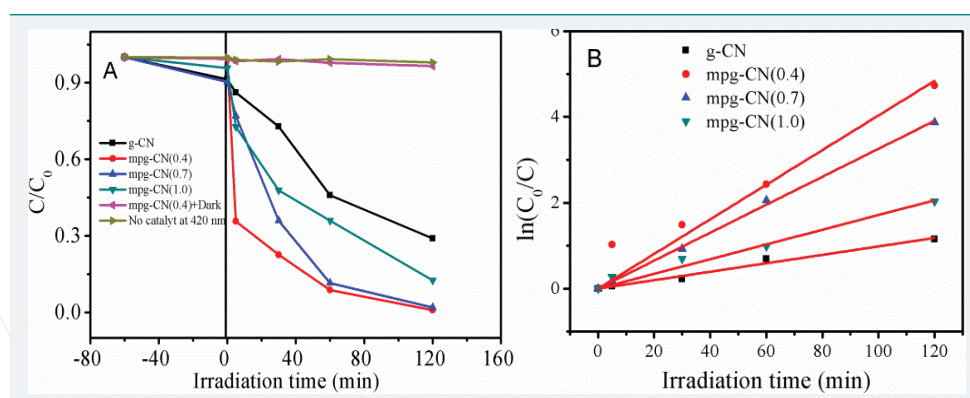
of surface area and the less condensed structure of mpg-CN(0.4). The well linear relationship between the  $\ln(C_0/C)$  and irradiation time ( $t$ ) suggests that the reaction obeys the pseudo first-order equation. Because of the best activity, mpg-CN (0.4) is selected for the following experiments.

### Effect of catalyst concentration

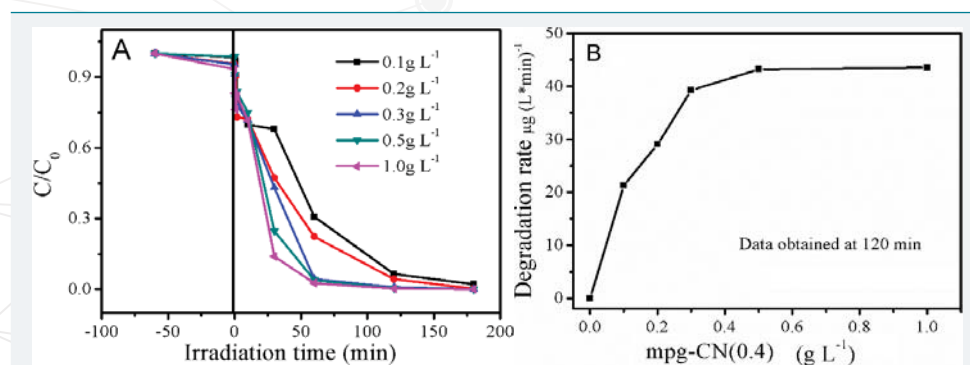
It was reported that photocatalysis is a catalyst mass dependent reaction [27]. Larger catalyst mass can produce more hydroxyl radicals and/or electrons by absorbing more photons, but excessive catalyst mass will reduce the opacity of suspension, blocking the energy from light radiation, thereby decreasing the degradation efficiency. To optimize the catalyst mass, we used five different catalyst concentrations (0.1, 0.2, 0.3, 0.5 and 1.0 g L<sup>-1</sup>) for investigation. Figure 4A shows the influence of catalyst concentration on the photocatalytic degradation activity of MC-LR. With the increase of catalyst concentration, from 0.1 to 0.5 g L<sup>-1</sup>, the degradation rate increases rapidly from 21.3 to 43.2  $\mu\text{g (L min)}^{-1}$ . But the further increase, from 0.5 to 1.0 g L<sup>-1</sup>, affects less on the degradation rate, which varied only from 43.2 to 43.5  $\mu\text{g (L min)}^{-1}$ , as shown in figure 4B, indicating that the optimum catalyst's concentration of the present study is 0.5 g L<sup>-1</sup>.

### Effect of initial MC-LR concentration

Figure 5A presents the photocatalytic activity of mpg-CN (0.4) for MC-LR degradation at different MC-LR initial concentrations. More than 75% MC-LR is degraded within 30 min and the reaction can be completed at 120 min, indicating that the catalyst is active and effective for MC-LR degradation within the investigated concentrations, from 0.1 to 5 mg L<sup>-1</sup>.



**Figure 3:** (A) Photodegradation activity of MC-LR over mpg-CN( $r$ ) and that obtained from blank experiments. (B) Pseudo-first-order kinetics of MC-LR degradation over the mpg-CN( $r$ ). Reaction conditions: 10 mL MC-LR (1.0 mg L<sup>-1</sup>), 5 mg catalysts, 420 nm irradiation.



**Figure 4:** (A) Photocatalytic activity of mpg-CN (0.4) for MC-LR degradation as a function of irradiation time. (B) Effect of catalyst concentration on the degradation rate of MC-LR over mpg-CN (0.4). Reaction conditions: 10 mL 1.0 mg L<sup>-1</sup> MC-LR, 420 nm irradiation.

The Langmuir-Hinshelwood (L-H) expression is a widely used method for the determination of relationship between the degradation rate and the substrate concentration in heterogeneous photocatalytic process, but it reflects only the “apparent” rate constant and reaction order [28,29]. To reveal the intrinsic relationship between them, pseudo-first order kinetics modified from the L-H expression is often used [30], as below.

$$r = -\frac{dC}{dt} = \frac{k_r K_s C}{1 + K_s C} \quad (1)$$

$$\frac{dC}{dt} = k_{app} C \quad (2)$$

Where  $k_r$  is the reaction rate constant,  $K_s$  is the adsorption rate constant and  $k_{app}$  is the apparent constant, with the restriction of  $C=C_0$  at  $t=0$ ,  $C_0$  being the initial concentration in the bulk solution after dark adsorption and  $t$  is the reaction time.

According to equation (2), the relationship between the degradation rate and the initial MC-LR concentration is plotted, as shown in the insert of figure 5A. The initial degradation rate increases from 6.28 to 145.95  $\mu\text{g (L min)}^{-1}$  with increasing the MC-LR initial concentration from 0.1 to 5  $\text{mg L}^{-1}$ , and unlike the typical L-H model depicted [28,31], no platform appears in the profile, suggesting that the catalyst can be applied to higher MC-LR concentration. However, we did not try to study that further, as the MC-LR concentration in the real environment is far lower than the values studied herein [32,33].

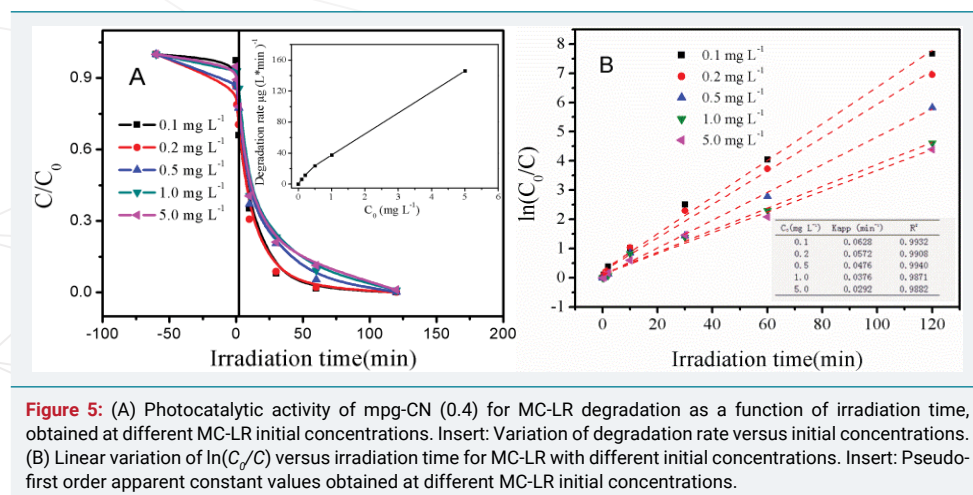
Equation (2) can be further transformed into equation (3) after integration:

$$\ln\left(\frac{C_0}{C}\right) = k_{app} t \quad (3)$$

According to equation (3) and based on the data of figure 4A, the function between  $\ln(C_0/C)$  and irradiation time can be plotted, figure 5B, showing a well linear relationship between them, thus supports the assumption that the reaction obeys the pseudo first-order kinetics. The  $k_{app}$  value, obtained from the regression analysis of the linear curve, decreases with increasing the MC-LR initial concentration. This can be explained by the limitation of active centers on the photocatalyst. Namely, with the addition of excessive MC-LR, the active center of the catalyst was mostly occupied (by the MC-LR and/or the produced intermediates), thereby reducing the solar light adsorption capability and leading to decreased reaction rate.

### Reusability tests

Figure 6 shows the reusability of mpg-CN (0.4) for photodegradation of MC-LR within five cycles. Before the light irradiation, the reaction mixture was stirred in dark for 60 min to ensure adsorption equilibrium. Less than 7% MC-LR was removed



**Figure 5:** (A) Photocatalytic activity of mpg-CN (0.4) for MC-LR degradation as a function of irradiation time, obtained at different MC-LR initial concentrations. Insert: Variation of degradation rate versus initial concentrations. (B) Linear variation of  $\ln(C_0/C)$  versus irradiation time for MC-LR with different initial concentrations. Insert: Pseudo-first order apparent constant values obtained at different MC-LR initial concentrations.

during this process, demonstrating that the activity observed thereafter is not due to the adsorption of MC-LR on the catalyst, but to the photocatalytic action. In the reusability tests, the catalyst was filtered and reused directly without any treatment. No appreciable decrease in the activity is observed and the activity profile is almost the same within the tests, indicating that the material is highly stable in the reaction and can be potential catalyst for MC-LR degradation in practical application.

### Degradation mechanism

To study the reaction mechanism and inspect the reactive species influencing the reaction, quenching experiments were conducted. From literature we know that there are normally three reactive species responsible for the solar light induced photocatalytic reactions, namely, photogenerated holes ( $h^+$ ) [34,35], hydroxyl radicals ( $\bullet OH$ ) [36] and superoxide anion radicals ( $\bullet O_2^-$ ) [37]. To clarify their contributions to the reaction, three types of scavengers were added, including ammonium oxalate (AO, 1 mmol/L), *tert*-butanol (TBA, V (tBuOH:H<sub>2</sub>O)=1:20) and benzoquinone (BQ, 1 mmol/L), which are used to quench the  $h^+$ , the  $\bullet OH$  and the  $\bullet O_2^-$  species, respectively.

Figure 7A shows that the addition of scavengers can influence the MC-LR photodegradation process, suggesting that the above three reactive intermediates contributes to the reaction. By comparison, it is found that the influence of the scavengers is in order of AO < TBA < BQ, suggesting that the  $\bullet O_2^-$  species has the most, and the  $h^+$  species has the least contribution to the reaction, in sequence of  $\bullet O_2^- > \bullet OH > h^+$ . That is, the  $\bullet O_2^-$  species is the major factors accounting for the reaction. This is in accordance to previous results observed for the photodegradation of RhB and SMT conducted on g-CN [24,38]. Whereas, remember that the  $\bullet OH$  radicals is a stronger oxidant than the  $\bullet O_2^-$  species, the low contribution of  $\bullet OH$  radicals must be

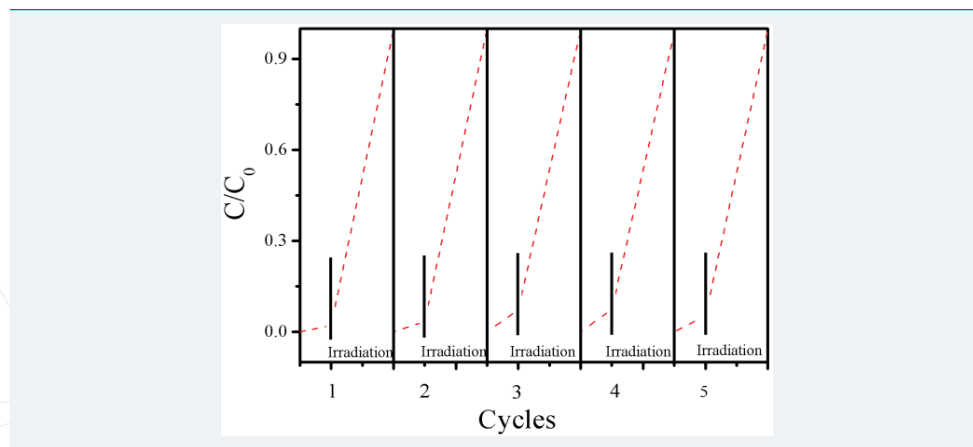


Figure 6: Reusability of mpg-CN (0.4) for MC-LR photodegradation within five cycles.

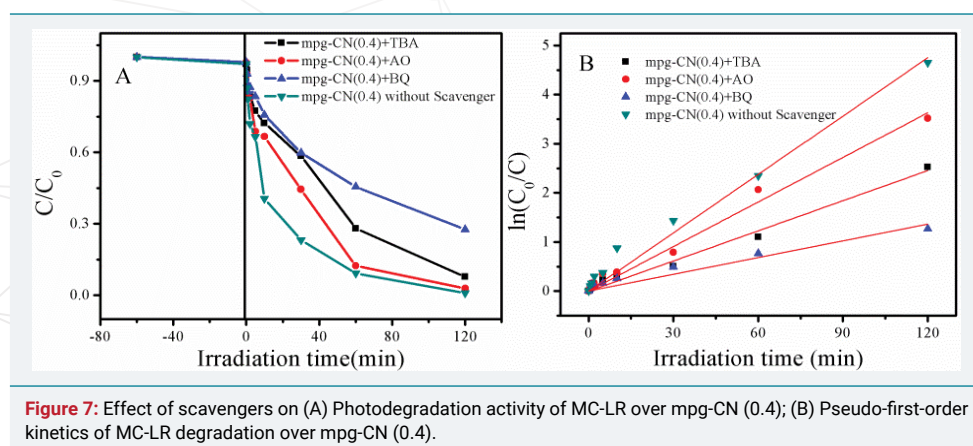


Figure 7: Effect of scavengers on (A) Photodegradation activity of MC-LR over mpg-CN (0.4); (B) Pseudo-first-order kinetics of MC-LR degradation over mpg-CN (0.4).



that it is hard to produce or that the produced  $\bullet\text{OH}$  radicals is quickly consumed before participating in the reaction. On the one hand, the direct generation of  $\bullet\text{OH}$  radicals by hole oxidation ( $E^0_{(-\text{OH}/\bullet\text{OH})}=2.4\text{ V}$ ) is unfavorable due to the low valence band position of g-CN (1.4 V), and on the other hand, the produced  $\bullet\text{OH}$  radicals will be consumed by the hydrogen of the surface basic  $-\text{NH}_2$  or  $=\text{NH}$  groups of g-CN [39,40]. This explains why the  $\bullet\text{OH}$  species has less contribution to the reaction than that of the  $\bullet\text{O}_2^-$  species.

The kinetics of MC-LR photodegradation on mpg-CN (0.4) in the absence and presence of scavengers are also calculated and shown in figure 7B. The  $k_{app}$  values obtained without the scavenger, and in the presence of TBA, AO and BQ are 0.03958, 0.02045, 0.03025, 0.01135  $\text{min}^{-1}$ , respectively. The well linear relationship between the  $\ln(C_0/C)$  and irradiation time supports that the reaction obeys the pseudo first order reaction, as discussed above.

## CONCLUSIONS

Mesoporous graphitic carbon nitride (mpg-CN) was synthesized and applied as catalyst for photodegradation of MC-LR in aqueous solution. Results indicated that mpg-CN (0.4), synthesized at mass ratio of  $\text{SiO}_2$  to  $\text{GndCl}$  equals 0.4, shows the best photocatalytic activity for the reaction, with more than 75% MC-LR being degraded within 30 min and full degradation at 120 min, at reaction conditions of  $0.5\text{ g L}^{-1}$  mpg-CN (0.4) and 420 nm irradiation. In addition to the good photocatalytic activity, mpg-CN (0.4) is also highly stable for the reaction, thus no appreciable loss of activity was observed even after five runs. Mechanism studies suggested that reaction obeys the pseudo first-order equation, and the oxidation of MC-LR was conducted mainly via the superoxide anion radicals ( $\bullet\text{O}_2^-$ ). These results showed that mpg-CN(r) could have the potential application of treating MC-LR in water by photocatalysis.

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