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Accelerated Redox Cycles of Fe(III)/Fe(II) and Cu(III)/Cu(II) by Photo-Induced Electron from N-CQDs for Enhanced Photo-Fenton Capability of CuFe-LDH

Xingyuan Du ^{1,2}, Lu Liu ³, Zhe Dong ^{1,2}, Zheng Cui ⁴, Xiaochen Sun ⁴, Di Wu ⁵, Zhe Ma ^{1,2}, Zhang Fang ^{1,2,*}, Yang Liu ^{1,2} and Yonglei An ^{1,2,*}

¹ Key Laboratory of Groundwater Resources and Environment (Jilin University), Ministry of Education, Changchun 130021, China; dxy15094155986@163.com (X.D.); dongzhe2516@163.com (Z.D.); wsmz@jlu.edu.cn (Z.M.); liuyang2517@mails.jlu.edu.cn (Y.L.)

² Jilin Provincial Key Laboratory of Water Resources and Environment, Jilin University, Changchun 130021, China

³ Changchun Institute of Technology, Changchun 130012, China; liulujlu@163.com

⁴ State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China; cuizheng18@mails.jlu.edu.cn (Z.C.); sxc19941004@163.com (X.S.)

⁵ Jilin Tuoda Environmental Protection Equipment & Engineering Co., Ltd., Changchun 130062, China; wudi250303@163.com

* Correspondence: azhang9456@jlu.edu.cn (Z.F.); anyonglei85@jlu.edu.cn (Y.A.)

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Abstract: Layered double hydroxide (LDH) materials have shown charming photo-Fenton capability for the treatment of refractory organic wastewater. In this study, CuFe-LDH hybridized with N-doped carbon quantum dots (N-CQDs) was investigated to further enhance the photo-Fenton capability. The results showed that the assembly techniques of coprecipitation and the hydrothermal method could synthesize the target material, CuFe-LDH/N-CQDs, successfully. CuFe-LDH/N-CQDs could possess a 13.5% higher methylene blue (MB) removal rate than CuFe-LDH in 30 min due to the accelerated redox cycles of Fe(III)/Fe(II) and Cu(III)/Cu(II), resulting from the photo-induced electron transfer from N-CQDs to CuFe-LDH via a d- π conjugation electronic bridge. Moreover, CuFe-LDH/N-CQDs has excellent photo-Fenton capability in the pH range of 2–11, even after being reused five times. This study would provide an efficient and stable photo-Fenton catalyst for the treatment of refractory organic wastewater.

Keywords: CuFe-LDH; N-CQDs; redox cycle; photo-Fenton; wastewater

1. Introduction

Refractory organic wastewater derived from dyeing, printing, pharmaceutical manufacturing and spraying has caused serious pollution of natural water and soil environments and has resulted in tremendous health risks to humans [1–3]. Traditional chemical or biological techniques for wastewater treatment tend to be unavailable to treat refractory organic wastewater. As one of the most popular advanced oxidation processes (AOPs), the Fenton technique exhibits promising capability to degrade refractory organic pollutants in wastewater due to nonselective oxidative degradation of organics by hydroxyl radicals ($\cdot\text{OH}$) [2,4,5]. In a typical Fenton reaction, bivalent iron can be oxidized to trivalent iron rapidly with the catalytic decomposition of hydrogen peroxide (H_2O_2) (Equation (1)), but the regeneration of bivalent iron from trivalent iron is difficult (Equation (2)), finally resulting in

a bogged-down Fenton reaction [6]. Therefore, the regeneration of bivalent iron is a key step in the Fenton technique.

In recent years, a variety of organic ligand metal materials were synthesized as heterogeneous photo-Fenton catalysts according to the ligand-to-metal charge transfer theory (LMCT), resulting in the reduction of iron from trivalent to bivalent under UV-vis light irradiation [7,8]. The reported organic ligands include ethylenediamine-N, N-disuccinic acid, nitrilotriacetic acid, benzenetricarboxylic acid, ethylenediamine tetraacetic acid, citric acid, tartaric acid and phthalocyanine [9–12]. Although these organic ligand metal materials possessed charming photo-Fenton capabilities, the structural stability of the materials would be cause for concern because the organic ligands would likely be destroyed by $\cdot\text{OH}$ in the photo-Fenton system.

Layered double hydroxides (LDHs) have been synthesized widely as catalysts or catalyst carriers with different bivalent/trivalent metal host layers and exchangeable anion interlayers, due to their stable structures and excellent catalytic performance [3,5,13,14]. The current reported LDHs for photo-Fenton catalysis include MgAl-LDH, ZnAl-LDH, ZnFe-LDH and CuZnFe-LDH [12,15–17]. We also had synthesized CuFe-LDH as a photo-Fenton catalyst to degrade methylene blue (MB) dye in simulated wastewater [18]. However, single LDH usually possesses an unsatisfactory catalytic performance in degradation speed and final removal rate of organic pollutants, resulting from the low cycle efficiency of metal redox pairs, e.g., Fe(III)/Fe(II) and Cu(III)/Cu(II) [19].

As a kind of zero dimension carbon material, carbon quantum dots (CQDs) have been synthesized and widely used as catalytic assistants for photo-Fenton reactions due to their peculiar electronic structure and energy band structure. Until now, CQDs had been hybridized with other materials (e.g., ZVI@Fe₃O₄, CeO₂/g-C₃N₄/V₂O₅, α -FeOOH, BiFeO₃ and MgAl-LDH) as novel photo-Fenton catalysts to enhance the degradation efficiency of organic pollutants [16,20–24] due to their excellent capability of photo-induced charge separation, because CQDs can act as either an electron donor or an electron acceptor in composite materials. To enhance the electron donor capability, nitrogen has been doped into CQDs to synthesize N-doped carbon quantum dots (N-CQDs) [25–27]. However, there is no report relating to a LDH-based photo-Fenton reaction enhanced by N-CQDs.

In this study, we successfully synthesized CuFe-LDH/N-CQDs as a novel photo-Fenton catalyst. Our work emphasized the material characterization, pollutant removal capability and photo-Fenton mechanism. This study aimed to develop a high-efficiency photo-Fenton catalyst and provide a theoretical and practical basis for the applications of CuFe-LDH/N-CQDs on the treatment of refractory organic wastewater.

2. Results and Discussion

2.1. Characterization of CuFe-LDH/N-CQDs

Planar lamellar structure was clearly observed in the transmission electron microscopy (TEM) photo of as-prepared CuFe-LDH/N-CQDs (Figure 1a). Moreover, three typical crystal lattice diffraction fringes were found in the high-resolution transmission electron microscopy (HRTEM) photo (Figure 1b), and the lattice spacings were 0.199, 0.260 and 0.233 nm, corresponding to the crystal planes (1118), (0018) and (0210) of hydrotalcite, respectively. TEM results initially proved that the as-prepared CuFe-LDH/N-CQDs possessed a hydrotalcite-like structure. In addition to TEM, X-ray powder diffraction (XRD) was also performed to identify the phase structure of as-prepared CuFe-LDH/N-CQDs. As shown in Figure 2, N-CQDs had no diffraction peak due to their amorphous structure while CuFe-LDH and CuFe-LDH/N-CQDs displayed several sharp diffraction peaks located at 24.3, 35.8, 39.1, 44.7 and 65.0°, corresponding to the crystal planes (0012), (0018), (0210), (1118) and (1310) of hydrotalcite,

respectively, according to the PDF NO.22-700. XRD results further proved that CuFe-LDH/N-CQDs was synthesized successfully.

Figure 1. Transmission electron microscopy (TEM) (a) and high-resolution transmission electron microscopy (HRTEM) (b) photos of CuFe-LDH/N-CQDs.

Figure 2. X-ray powder diffraction (XRD) spectra of N-CQDs, CuFe-LDH and CuFe-LDH/N-CQDs.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface elemental chemical state in CuFe-LDH/N-CQDs. C 1s, N 1s, O 1s, Fe 2p and Cu 2p were all monitored simultaneously (Figure 3a). For Cu 2p, two peaks located at 954.84 and 935.05 eV corresponded to Cu 2p_{1/2} and Cu 2p_{3/2}, and the other two peaks located at 963.35 and 943.39 eV were the satellite peaks of Cu 2p (Figure 3b), indicating bivalent copper with an outermost electron configuration of 3d⁹ [5,18,28,29]. For Fe 2p, one flat peak located at 724.88 eV and one sharp peak located at 712.33 eV were detected (Figure 3c), suggestive of trivalent iron with an outermost electron configuration of 3d⁵ [18,24,28]. For C 1s, a large peak was divided into two independent peaks located at 284.48 and 285.23 eV, which suggested plenty of C-C and C=C structures in N-CQDs due to their nonpolar σ and π bonds (Figure 3d), which could make the outer layer valence electron density of the carbon atom keep a high level, resulting in low binding energy for C 1s. However, the other flat peak composed by two divisive peaks located at 288.71 eV and 288.12 eV possessed higher binding energy (Figure 3d), indicating a lower outer layer valence electron density of the carbon atom, ascribed to the polar σ and π bonds of C=O and C=N in N-CQDs [18,30]. For N 1s, only one single peak located at 400.26 eV was detected and possessed a low binding energy (Figure 3e), suggesting a high outer layer valence electron density of the nitrogen atom, ascribed to the polar σ and π bonds of C-N and C=N in N-CQDs, which was consistent with the XPS result of C 1s. In addition, the XPS results of C 1s and N 1s could not only prove the successful hybridization of CuFe-LDH and N-CQDs, but also imply the triazine-like structure in N-CQDs due to the C-N and C=N structures. For O 1s, one broad convex peak was detected and divided into three independent peaks located at 530.03, 531.05 and 532.13 eV (Figure 3f), corresponding to the hydroxyl structure (e.g., Fe(III)-OH, Cu(II)-OH) and metal-oxygen-metal structure (e.g., Fe(III)-O-Fe(III), Cu(II)-O-Cu(II) and Fe(III)-O-Cu(II)) in

CuFe-LDH, and the C-O and C=O structures in N-CQDs, respectively, according to the analysis on the outer layer valence electron density of the oxygen atom.

Figure 3. (a) Full-range XPS spectra of CuFe-LDH/N-CQDs. (b) XPS peaks for Cu 2p. (c) XPS peaks for Fe 2p. (d) XPS peaks for C 1s. (e) XPS peaks for N 1s. (f) XPS peaks for O 1s.

2.2. Photo-Fenton Activity of CuFe-LDH/N-CQDs

Fenton reactions with CuFe-LDH and CuFe-LDH/N-CQDs were conducted in darkness and under simulated solar irradiation. In darkness, the removal rate of MB after 30 min reached 35.8% and the degradation rate constant ($k_{\text{CuFe-LDH}}$) was 0.0157 min^{-1} with CuFe-LDH, while the MB removal rate was 37.0% and $k_{\text{CuFe-LDH/N-CQDs}}$ was 0.0165 min^{-1} with CuFe-LDH/N-CQDs (Figure 4a,b). This was attributed to their intrinsic catalytic activities without outer energy input. However, under simulated solar irradiation, the removal rate of MB reached 74.9% with CuFe-LDH and 88.3% with CuFe-LDH/N-CQDs after 30 min, and the corresponding degradation rate constants were 0.0467 min^{-1} ($k_{\text{CuFe-LDH}}$) and 0.0728 min^{-1} ($k_{\text{CuFe-LDH/N-CQDs}}$) (Figure 4c,d), which are higher than those of previously reported LDH materials, e.g., $\text{Fe}_3\text{O}_4/\text{CoCr-LDH}$ [13], CuFe-LDH/ND [18], MgAl-LDH and FePcS-LDH [31]. These results indicate that N-CQDs actually improve the photo-Fenton capability of CuFe-LDH efficiently under simulated solar irradiation.

Figure 4. (a) Degradation of methylene blue (MB) in darkness. (b) Pseudo-first-order kinetic fit for MB degradation in darkness. (c) Photo-Fenton degradation of MB under simulated solar irradiation and (d) Pseudo-first-order kinetic fit for MB photodegradation under simulated solar irradiation. Error bars represent standard deviation of triplicate runs.

Total organic carbon (TOC) variation of MB solution was also monitored, and the results showed that 68.1% of TOC was removed after 30 min with CuFe-LDH, while 81.2% was removed with CuFe-LDH/N-CQDs (Figure 5a). Moreover, the TOC removal rate constant of CuFe-LDH ($k_{\text{TOC, CuFe-LDH}}$) was 0.0394 min^{-1} , obviously lower than the 0.0574 min^{-1} rate of CuFe-LDH/N-CQDs ($k_{\text{TOC, CuFe-LDH/N-CQDs}}$) (Figure 5b). The TOC results indicated that the photo-Fenton reaction based on CuFe-LDH/N-CQDs mineralized MB efficiently, as opposed to simple decoloration, and N-CQDs actually played an important role in enhancing the removal efficiency of TOC.

Figure 5. (a) Total organic carbon (TOC) variation of MB solution and (b) pseudo-first-order kinetic fit for TOC removal during the photo-Fenton process. Error bars represent standard deviation of triplicate runs.

As an important factor in Fenton reaction, the effect of pH on the photo-Fenton capability of CuFe-LDH/N-CQDs was investigated by varying the initial pH of the MB solution. The degradation efficiency and speed of MB were the greatest when the initial pH was 4; this was followed by pH 2, pH 7, pH 9 and pH 11, in decreasing order of degradation efficiency and speed (Figure 6). CuFe-LDH/N-CQDs could possess charming photo-Fenton capability under acidic, neutral and

alkaline conditions, which means that CuFe-LDH/N-CQDs can be widely applied for the photo-Fenton treatment of various organic wastewaters without pH adjustment.

Figure 6. (a) Effect of pH on the photo-Fenton capability of CuFe-LDH/N-CQDs; and (b) pseudo-first-order kinetic fit for MB removal. Error bars represent standard deviation of triplicate runs.

As a kind of heterogeneous photo-catalyst, CuFe-LDH/N-CQDs was recycled five times to investigate the catalyst stability without washing. The results showed that CuFe-LDH/N-CQDs still possessed an 86.0% MB removal rate after 30 min for the fifth recycle, only 2.3% lower than the first use (Figure 7), suggesting the excellent stability and photo-Fenton capability of CuFe-LDH/N-CQDs.

Figure 7. Photo-Fenton degradation cycle of MB on CuFe-LDH/N-CQDs.

2.3. Photo-Fenton Mechanism of CuFe-LDH/N-CQDs

It is widely known that $\cdot\text{OH}$ is the main active species in the Fenton reaction. To verify the main active species in the photo-Fenton reaction based on CuFe-LDH/N-CQDs, $\cdot\text{OH}$ scavengers, namely TBA and EtOH, were added into the photo-Fenton system, each with a dosage of 5 mL/L [2,5]. The results showed that the removal rate and degradation speed of MB with TBA or EtOH were lower than those without $\cdot\text{OH}$ scavengers (Figure 8), demonstrating that $\cdot\text{OH}$ was still the main active species to oxidatively degrade MB in the photo-Fenton reaction catalyzed by CuFe-LDH/N-CQDs.

Figure 8. (a) Effect of free radical scavengers (TBA and EtOH) on MB removal under simulated solar irradiation and (b) pseudo-first-order kinetic fit for MB removal. Error bars represent standard deviation of triplicate runs.

Generally, Fe(II), Cu(II) and Cu(I) can all catalytically decompose H_2O_2 into $\cdot\text{OH}$, and effective cycles of metal redox pairs (e.g., Fe(III)/Fe(II), Cu(III)/Cu(II), Cu(II)/Cu(I)) are essential prerequisites for a successful photo-Fenton reaction [2,4,5,32]. Moreover, Cu(III)/Cu(II) is more suitable than Cu(II)/Cu(I) for photo-Fenton reaction according to the thermomechanical analysis [5]. In this study, CuFe-LDH/N-CQDs were more efficient than CuFe-LDH for photo-Fenton reaction, suggesting that the cycle efficiencies of Fe(III)/Fe(II) and Cu(III)/Cu(II) in the former were higher than those in the latter. To verify this conjecture, UV-vis diffuse reflectance (DRS) of CuFe-LDH and CuFe-LDH/N-CQDs were collected, and the results showed that CuFe-LDH/N-CQDs, compared to CuFe-LDH, had a drastic absorption peak at 370 nm (Figure 9a), corresponding to the electronic $\pi\text{-}\pi^*$ transition in C-N and C=N of the triazine-like structure in N-CQDs. In addition to $\pi\text{-}\pi^*$ transition, $n\text{-}\pi^*$ transition could also contribute to the UV-vis absorption of CuFe-LDH/N-CQDs in the region of 380–500 nm (Figure 9a), resulting from the lone pair electrons of the nitrogen atom located at a nonbonding orbital in a triazine-like structure. Then, the band gap energy (E_g) was calculated from the following expression [18,33–35]:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (3)$$

Figure 9. UV-vis diffuse reflectance (DRS) (a) and calculated band gap (E_g) (b) for CuFe-LDH and CuFe-LDH/N-CQDs.

The results showed that $E_g(\text{CuFe-LDH/N-CQDs})$ was 1.59 eV while $E_g(\text{CuFe-LDH})$ was 1.92 eV (Figure 9b), suggesting a broadened visible-light absorption region, attributed to the introduction of N-CQDs. For LDH, the calculated E_g is the splitting energy of metal 3d orbitals (Δ_0) in crystalline field from t_{2g} to e_g^* [18]. Therefore, the reason for shrunken E_g of CuFe-LDH/N-CQDs was probably due to the orbital conjugation between the π^* molecular orbital of N-CQDs and the t_{2g} orbitals of Fe/Cu in CuFe-LDH causing an increase in electron cloud density of e_g^* , resulting in e_g^* energy bands bending downwards and decreasing the Δ_0 (Figure 9b). Thus, the energy of valence band (VB) maximum (E_{VB}) was determined by XPS valence spectra, and both $E_{\text{VB}}(\text{CuFe-LDH})$ and $E_{\text{VB}}(\text{CuFe-LDH/N-CQDs})$ were

1.00 eV (Figure 10). Then, the energy of conduction band minimum (E_{CB}) was calculated from the following expression [18,30,33]:

$$E_{CB} = E_{VB} - E_g \quad (4)$$

Figure 10. VB XPS spectra of CuFe-LDH and CuFe-LDH/N-CQDs.

Then, the $E_{CB}(\text{CuFe-LDH})$ and $E_{CB}(\text{CuFe-LDH/N-CQDs})$ were calculated as -0.92 eV and -0.59 eV, respectively.

According to the above discussion, the mechanism by which N-CQDs enhance the CuFe-LDH photo-Fenton reaction was inferred as follows [2,5]:

When single CuFe-LDH was the photo-Fenton catalyst, the ligand oxygen atom or hydroxyl ion would provide photo-induced electrons for Fe(III) and Cu(III) to promote the redox cycles of Fe(III)/Fe(II) and Cu(III)/Cu(II). However, the photoelectron donating capability of the oxygen atom or the hydroxyl ion was so finite that Fe(III) and Cu(III) could not be reduced efficiently in CuFe-LDH, resulting in low photodegradation efficiency of MB (Figure 4c). When CuFe-LDH was hybridized with N-CQDs, electronic π - π^* transition and n - π^* transition would occur in the triazine-like structure of N-CQDs. The photoinduced hole located at π bonding orbital or nonbonding orbital would oxidatively degrade MB directly rather than produce $\cdot\text{OH}$ due to its low oxidability ($E(\text{h}^+) < E(\text{OH}^-/\cdot\text{OH}) = 1.99$ eV) [17,36]. More importantly, the photoinduced electron could transfer from the π^* antibonding orbital of N-CQDs

to the t_{2g} orbital (d_{xy} , d_{yz} , d_{xz}) of CuFe-LDH through the d- π conjugation electron bridge between the N atom and the Fe/Cu atom, then be excited by solar light from t_{2g} orbital to e_g^* orbital and accelerate the redox cycles of Fe(III)/Fe(II) and Cu(III)/Cu(II) [1] (Figure 11), corresponding to the high photodegradation efficiency of MB (Figure 4c).

Figure 11. Proposed mechanism of the charge transfer in CuFe-LDH/N-CQDs for the photo-Fenton degradation of MB dye under solar irradiation.

3. Materials and Methods

3.1. Chemicals

The chemicals used in this study included CuSO₄ (99.0%), FeCl₃·6H₂O (99.0%), NaOH (99.8%), citric acid monohydrate (99.8%), urea (99.0%), MB (99.0%), H₂O₂ (30.0%), absolute ethanol (EtOH) (99.7%) and *t*-butanol (TBA) (98.0%). All the chemicals were purchased from Sinopharm (Shanghai, China) and used as received, without further purification.

3.2. Synthesis of Powdered CuFe-LDH/N-CQDs

First, N-CQDs were synthesized by a facile microwave method. In a general procedure, 50 mL of N-CQDs precursor solution containing 3.000 g citric acid monohydrate and 0.600 g urea was prepared and then treated in a microwave oven at 900 W until the precursor solution dried up to a golden-brown solid matter. Subsequently, a dialysis experiment was carried out with a 200 D dialysis membrane to remove the residual small molecules such as citric acid and urea, until the outer dialysis solvents did not turn yellow. Ultrapure water and absolute ethanol were chosen as the outer dialysis solvents. Then, the ~20 mL concentrated dialysate was evaporated at 60 °C overnight and ground into fine powder with an agate mortar, named N-CQDs.

CuFe-LDH/N-CQDs was synthesized by a facile coprecipitation method. First, 0.500 g of CuSO₄ and 0.423 g of FeCl₃·6H₂O (Cu/Fe molar ratio was 2:1) were dissolved together into 400 mL of ultrapure water, marked as solution A. Second, 0.500 g of N-CQDs was dispersed in a 200 mL NaOH solution with a pH of 9, marked as solution B. Third, solution A was added into solution B dropwise with continuous stirring at 60 °C, and the pH of solution B was controlled at 9 at all times via adding 1.0 M of NaOH solution. After blending solutions A and B, ~600 mL of dark-brown suspension liquid was generated, which was then evaporated to ~60 mL with continuous stirring at 60 °C. Subsequently, the ~60 mL dark-brown suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at a constant temperature of 120 °C for 12 h. Then, the as-prepared CuFe-LDH/N-CQDs was obtained by centrifugation at 10,000 rpm for 10 min and dried at 80 °C overnight. Finally, the as-prepared

CuFe-LDH/N-CQDs was ground into fine powder with an agate mortar before use. The whole preparation process of CuFe-LDH/N-CQDs can be illustrated detailedly in Figure 12.

Figure 12. The preparation process of CuFe-LDH/N-CQDs.

3.3. Characterization of CuFe-LDH/N-CQDs

The morphological structure was shown by TEM (JEOL JEM2100, Tokyo, Japan). The crystal lattice structure was shown by HRTEM (JEOL JEM2100, Tokyo, Japan) and XRD (XRD-6000 Shimadzu, Kyoto, Japan). The surface elemental chemical state was characterized by XPS (ESCALAB250, Thermo Fisher Scientific, Waltham, MA, USA) using monochromatic Al K α X-ray (1486.6 eV) as the excitation source radiation. UV-vis diffuse reflectance spectra (DRS) were collected on a Shimadzu spectrophotometer (UV-2550) with BaSO₄ as the reference.

3.4. Photo-Fenton Degradation Experiments

MB dye was chosen as the target organic pollutant to evaluate the photo-Fenton capability of CuFe-LDH/N-CQDs. A 500 W Xe lamp (GXZ500) was used as the simulated sun without any filter. The distance between the Xe lamp and reaction suspension was 15 cm. For a typical photo-Fenton degradation experiment, 80 mL of MB solution (10 mg/L) with 10.0 mg of CuFe-LDH/N-CQDs and 100 μ L of H₂O₂ was illuminated under a Xe lamp. At a 5 min interval, a 3 mL sample was withdrawn from the photo-Fenton reaction, then centrifuged at 10,000 rpm for 5 min. The MB concentration in supernatant was monitored using a UV-vis spectrophotometer (UV-1240 Shimadzu) at the wavelength of 664 nm. In addition, the initial catalyst's loading and initial pH of MB solution were optimized, and catalyst stability was investigated based on catalyst reuse. To verify the degradation degree of MB, total organic carbon (TOC, mg/L) of MB solution was determined by a TOC analyzer (SSM-5000A Shimadzu) during the photo-Fenton degradation process. Furthermore, EtOH and TBA were added into photo-Fenton reactions as the hydroxyl radical scavengers to verify the active species.

The degradation efficiency of MB can be calculated by following equation [18,37]:

$$\text{Degradation (\%)} = (1 - C/C_0) \times 100\% \quad (17)$$

where C and C₀ represent the MB concentration at time *t* and the initial concentration of MB dye, respectively. The error analysis was also calculated using the following standard deviation formula with triplicate runs of the degradation experiment [18,38]:

$$\sigma^2 = \lim_{n \rightarrow \infty} \left[\frac{1}{N} \sum (x_i - \mu)^2 \right] \quad (18)$$

where σ is the standard deviation, x_i is the observed values and μ is the mean value from triplicate experiments. The degradation kinetics of MB was also investigated by fitting the pseudo-first-order kinetic Equation (19) with experimental data [18,39].

$$\ln(C/C_0) = -kt \quad (19)$$

where k is the apparent reaction rate constant (min^{-1}) for pseudo-first-order kinetic.

4. Conclusions

CuFe-LDH and N-CQDs were hybridized together successfully as a novel heterogeneous photo-Fenton catalyst, named CuFe-LDH/N-CQDs. The triazine-like structure in N-CQDs can provide sufficient photo-induced electrons for CuFe-LDH through the d- π conjugation electronic bridge, accelerating the redox cycles of Fe(III)/Fe(II) and Cu(III)/Cu(II). Hence, CuFe-LDH/N-CQDs showed better photo-Fenton capability than CuFe-LDH in the pH range of 2~11 and possessed excellent stability. Therefore, CuFe-LDH/N-CQDs is a promising photo-Fenton catalyst for efficiently treating actual refractory organic wastewater.

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