

Efficient decolorization of Methylene Blue catalyzed by MgFe-layered double hydroxides in the presence of hydrogen peroxide

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ABSTRACT

MgFe-layered double hydroxides (LDHs) were prepared by co-precipitation method with the ratios of $[Mg^{2+}]/[Fe^{3+}]$ varied in the range of 2:1–6:1, and occupied as heterogeneous catalysts for the degradation of Methylene Blue (MB) in the Fenton process. MgFe-LDH prepared with the ratio of $[Mg^{2+}]/[Fe^{3+}]$ at 3:1 was verified to be of high purity. The Fenton-like process catalyzed by MgFe-LDH performed excellently, and more than 97% degradation of MB was obtained with 0.5 mmol/L H_2O_2 and 0.50 g/L MgFe-LDH at initial pH 2 at room temperature. The occurrence of hydroxyl radicals ($\cdot OH$) was detected and the mechanism was proposed. MgFe-LDH is of excellent catalytic activity and good reusability.

Key words | degradation, Fenton, hydroxyl radicals, mechanism, MgFe-layered double hydroxides

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INTRODUCTION

Organic dyes are widely used in modern industries (Martínez-Huitle & Brillas 2009), leading to the discharge of dyeing wastewaters on a large scale. Dyeing wastewaters are characterized by high chemical oxygen demand (COD), deep color, non-biodegradability and toxicity (Natarajan *et al.* 2011). Traditional methods including adsorption, coagulation, precipitation and so on (Rfn & Fajardo 2017) were occupied for the treatment of dyeing wastewaters, but limited by disadvantages such as low efficiency, secondary pollution, high cost and so on (Gong *et al.* 2017). Advanced oxidation processes (AOPs) characterized by generation of hydroxyl radicals ($\cdot OH$) are promising in degradation of refractory contaminants in aqueous solutions or air. Fenton, which consists of the ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2), is efficient and environmentally friendly, but only available in narrow pH window. Fe^{2+} involved is hard to separate, and it transforms to iron sludge as a secondary pollutant. So, there is an urgent need to fabricate novel solid catalysts for Fenton

processes. Fida *et al.* 2017 synthesized a La-Fe montmorillonite (La-Fe MMT) composite and applied it for the degradation of organic dyes. The as-prepared La-Fe MMT is of high stability and can be recycled. Li *et al.* (Zhu *et al.* 2016; Li *et al.* 2017) fabricated $Fe_3O_4/C/Cu$ as a catalyst for the degradation of Methylene Blue (MB). $Fe_3O_4/C/Cu$ was reported to be of good stability and can be separated easily for recycling. These catalysts are of high cost and hard to prepare. Layered double hydroxides (LDHs) as typical lamellar materials have drawn a lot of attention in recent years. LDHs are usually formulated as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-}]^{x-} \cdot mH_2O$, in which M(II) and M(III) are divalent and trivalent cations (Shao *et al.* 2013), and A^{n-} is the interlayered anion. LDHs with large surface area and porous structure have already been used as adsorbent and catalyst in photo-assisted Fenton systems (Tang & Liu 2016; Gong *et al.* 2017). Iron-based LDHs with easy preparation methods and low costs have drawn increasing attention, and are actively considered for the catalysis of

the Fenton process. In our previous study (Wang *et al.* 2014), FeFe-LDH was prepared and used as a catalyst for the degradation of MB, but FeFe-LDH was hard to prepare under an air atmosphere. The samples obtained were of low purity for the oxidation of ferrous in the preparation process under an air atmosphere. In this study, Mg^{2+} was occupied to complex with Fe^{3+} to fabricate MgFe-LDH for its stability in air. MgFe-LDHs synthesized by co-precipitation method were used as the catalyst to establish a heterogeneous Fenton system. The morphology and chemical properties of MgFe-LDHs are investigated. Influences of parameters including initial solution pH, concentration of H_2O_2 , dosage of catalyst and temperature on the degradation of MB were investigated. Active species were identified to propose the reaction mechanism. The stability and reusability of MgFe-LDHs were also investigated.

MATERIAL AND METHODS

Materials

All chemicals bought from Jingchun Chemical Regent Co. were analytical grade. All solutions were freshly prepared with ultrapure water from Milli-Q device (18.2 M Ω -cm at 25 °C).

Synthesis of MgFe-LDH

The MgFe-LDH materials were synthesized by co-precipitation method. At first, mixed solutions A (NaOH and Na_2CO_3) and B ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were slowly dropped into a glass reactor containing 100 mL de-ionized water with stirring at 260 r/min at room temperature. The LDH was denoted as LDHx as the ratio of $[\text{Mg}^{2+}]/[\text{Fe}^{3+}]$ varied in the range of 2:1–6:1, with concentrations of NaOH ($[\text{OH}^-] = 1.6([\text{Mg}^{2+}] + [\text{Fe}^{3+}])$) and Na_2CO_3 ($[\text{CO}_3^{2-}] = 2[\text{Fe}^{3+}]$) pre-determined (Table S1). The obtained suspensions were aged at 80 °C for 3 h, and then centrifuged and washed several times with deionized water until neutral. Finally, solid materials obtained were dried at 80 °C to get the final product, MgFe-LDHs, which were kept sealed after grinding.

Catalytic oxidation experiments

The catalytic oxidation experiments were conducted in a 500 mL glass reactor with constant stirring at room temperature (20 ± 2 °C). Initial solution pH was adjusted by NaOH

(0.5 mol/L) and H_2SO_4 (1 mol/L), H_2O_2 were added into 200 mL 10 mg/L MB solutions containing given amounts of MgFe-LDHs to start the reaction. Samples were withdrawn at predetermined intervals and filtered immediately for analysis. The used catalysts were recovered and washed for the next cycling use.

Characterization of MgFe-LDH materials

The crystalline phases of MgFe-LDHs were identified by X-ray diffraction (XRD) patterns on a XRD-6000 diffractometer (Shimadzu, Japan) with $\text{Cu-K}\alpha$ radiation (40 kV, 30 mA) at a scanning speed of 4°/min in the range of 4–70°. Fourier transform infrared spectroscopy (FTIR) was recorded in the range of 500–4,000 cm^{-1} using a Nexus spectrometer (Thermo Nicolet, America). Thermo-stability of as-prepared materials was detected by a TGA/DSC1 thermogravimetric analyzer (Mettler Toledo, Switzerland) from 30 to 600 °C at a heating rate of 15 °C/min under air atmosphere. The scanning electron microscopy (SEM) images were recorded by field emission scanning electron microscopy (Rigaku S4800). X-band ESR spectra were recorded by a Bruker EMX-10/12 microspectrometer at 90 K. The operating frequency and power are 9.43 GHz and 19.83 mW, respectively.

Analysis

Concentration of MB in solution was determined at 660 nm using a UV-vis spectrophotometer (UV755B, Youke, Shanghai). Concentration of H_2O_2 was measured using the potassium titanyl oxalate method at 410 nm (Chen *et al.* 2012). The apparent generation efficiency of $\cdot\text{OH}$ was detected by $\text{Fe}(\text{phen})_3^{2+}$ method at 508 nm (Zhou *et al.* 2018a, 2018b), and concentrations of ferrous ion and total iron ions were determined by 1,10-phenanthroline method at 510 nm (Zhou *et al.* 2012).

RESULTS AND DISCUSSION

Characterization

Figure 1(a) shows XRD patterns of the as-prepared MgFe-LDH materials. All LDHx materials have a crystalline structure showing prominent and sharp diffraction peaks centered at $2\theta = 11.46^\circ$, 23.12° and 34.12° , corresponding to the reflections of (003), (006), (009). Only LDH2 and LDH3 show clear symmetrical diffraction peaks at $2\theta = 58^\circ$ to 63° (Wang *et al.* 2015), indicating the single phase of

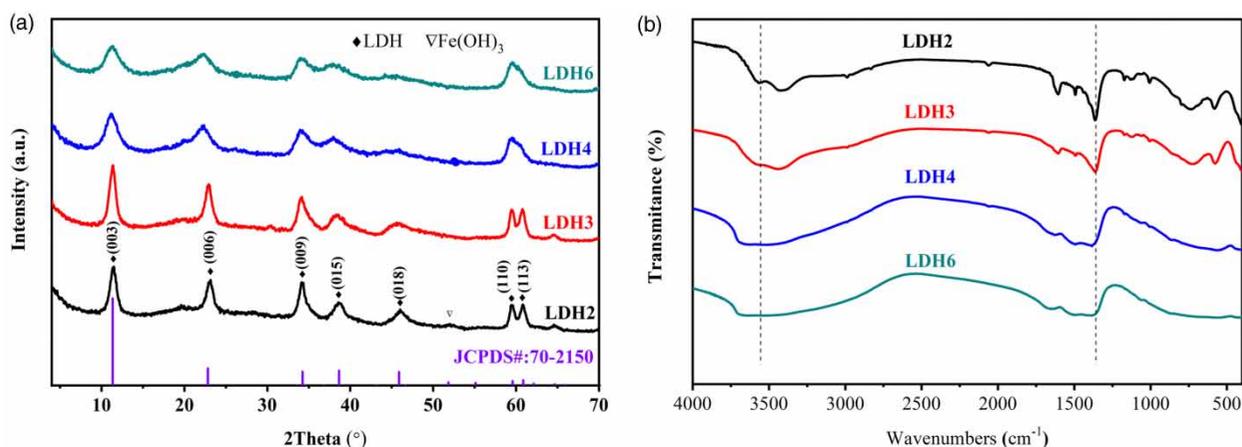


Figure 1 | (a) XRD patterns of the as-prepared LDHx; (b) FT-IR spectra of LDHx.

Rhombohedral structure (Thomas & Kamath 2006). The peak at $2\theta = 52.43$ presented in the pattern of LDH2 was determined to be $\text{Fe}(\text{OH})_3$ (JCPDS#46-1436), and LDH3 is in good agreement with standard Pyroaurite diffraction peak (JCPDS#70-2150, $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot (\text{H}_2\text{O})_{4.5}0.375$). Lattice parameters a and $d(110)$ reflect laminate and (110) crystal atoms density, and all samples were analyzed similarly, as well as $d(003)$. The influences of the ratio of $[\text{Mg}^{2+}]/[\text{Fe}^{3+}]$ on the density of crystal atoms are not obvious (Thomas & Kamath 2006).

FT-IR spectra of LDHx were recorded in the range of $4,000\text{--}400\text{ cm}^{-1}$ as shown in Figure 1(b). The absorption peak at around $3,500\text{ cm}^{-1}$ is attributed to the stretching vibration of hydroxyl groups in brucite-like layers (Wei *et al.* 2011; Gong *et al.* 2017). The absorption peak at about $1,600\text{ cm}^{-1}$ can be designated to the hydroxyl bending vibration of crystallization water interlayered (Yang *et al.* 2015; Gong *et al.* 2017). The characteristic absorption peak at about $1,360\text{ cm}^{-1}$ is attributed to the vibration of CO_3^{2-} (Yang *et al.* 2015; Gong *et al.* 2017). The group bands characteristic for LDHs in the range of $500\text{--}1,000\text{ cm}^{-1}$ are interpreted as the vibration of metal-oxygen (M-O) or metal-hydroxyl (M-OH) in the host layer. Note that absorption peaks of LDHx shifted to high wavenumber as x increased from 2 to 6, indicated that the bonding interaction between interlayered water molecules and CO_3^{2-} or hydroxyl are weakened (Wei *et al.* 2011). Characteristic bands in the range of $500\text{--}1,000\text{ cm}^{-1}$ in LDH4 and LDH6 were fuzzy.

Thermogravimetric analyses were performed to reveal the thermostability of LDHx. As shown in Figure S1(a) and S1(b) (Supporting Information), two major endothermic peaks and the corresponding weight loss stages can be observed in LDH2 and LDH3 materials. Approximately

12.56% and 14.55% weight-losses ascribed to crystal water were observed at around $193\text{ }^\circ\text{C}$ respectively. Weak endothermic peaks at around $99\text{ }^\circ\text{C}$ were due to the existence of $x\text{Fe}(\text{OH})_3 \cdot y\text{Fe}_2(\text{CO}_3)_3$. Weight losses ascribed to dehydroxylation at around $365\text{ }^\circ\text{C}$ were calculated to be 14.2% and 18.4% (Bai *et al.* 2017). The endothermic peaks at around $60\text{ }^\circ\text{C}$ in LDH4 and LDH6 (Figure S1(c) and S1(d)) may be caused by the thermal decomposition of Magnesium carbonate basic (Chaturvedi *et al.* 2019; Erlund & Zevenhoven 2018), and endothermic peaks occurred at higher temperatures as x increased. This was in accordance with XRD analysis, indicating that MgFe-LDH 3 was of high purity.

As LDH 3 was verified of high purity, the morphologies of fresh LDH 3 and that after Fenton reaction were examined by SEM (Figure S2). The SEM image of fresh LDH 3 shows that as-prepared samples present a rock-like morphology in much larger scale with none uniform size. LDH 3 that after Fenton reaction was much smaller, its diameter was about one-tenth of fresh LDH 3.

Catalysis

Catalysis capacities of LDHx were compared at pH 1 (Figure 2(a)); the results indicated that almost 100% removal of MB can be obtained in Fenton-like systems catalyzed by LDHx. MB was removed faster when catalyzed by LDH 2 and LDH 3, but LDH 3 was more favored for its high purity. To clarify the active radicals involved in Fenton-like system catalyzed by LDH 3, ESR with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) was acquired to probe the active free radicals generated on the surface of LDH 3 (Figure 2(b)). Four characteristic peaks with an intensity ratio of 1:2:2:1 were observed, indicating that $\cdot\text{OH}$ can be

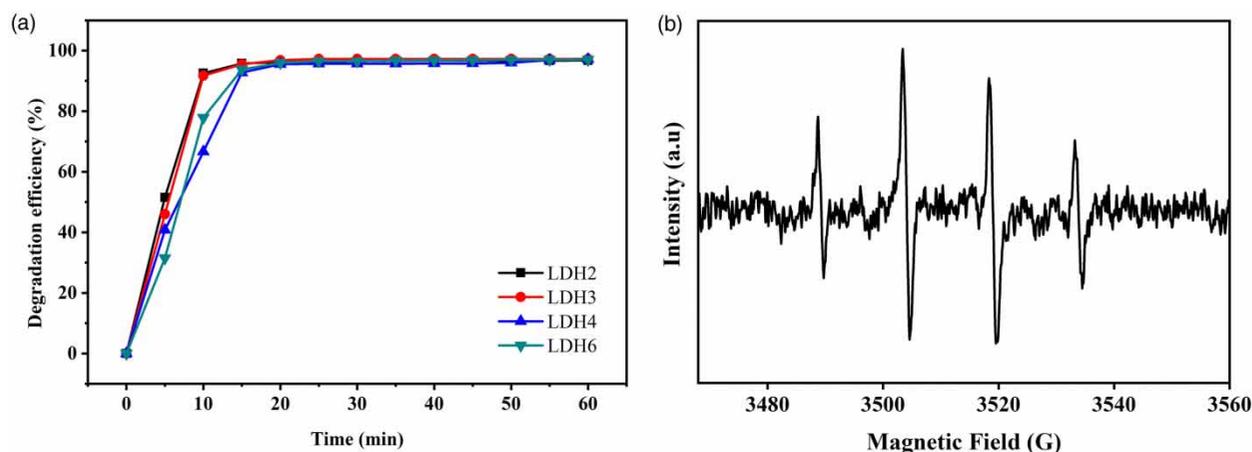


Figure 2 | (a) Catalytic activity of MgFe-LDHx ($x = 2, 3, 4, 6$); (b) DMPO spin-trapping ESR spectra recorded with MgFe-LDHs and H_2O_2 in aqueous solution (for DMPO $\cdot\text{OH}$).

generated and plays an important role in Fenton system catalyzed by LDH3 (Liu *et al.* 2016).

Influence factors

The generation of $\cdot\text{OH}$ and the degradation of target pollutants in Fenton reactions can be influenced by initial solution pH, dosages of H_2O_2 and catalyst, reaction temperature and so on; thus, influences of the factors mentioned above in an LDH-catalyzed heterogeneous Fenton system were investigated.

The degradation of MB in heterogeneous Fenton-like reaction catalyzed by LDH3 was performed in pH ranging from 1 to 4 and the apparent generation of $\cdot\text{OH}$ is shown in Figure 3(a) and 3(b). Degradation efficiency of MB increased immediately as the reaction initiated, without any retention time. The degradation of MB was more favored under strong acidic condition, the degradation efficiency of MB decreased as pH increased, and 97.07% degradation efficiency can be obtained in 15 min at pH 1. This result was not consistent with that optimal pH window of 2–4 as reported, for surface alkalinity of LDHs. Small declines of degradation efficiencies can be seen at around 5–10 min at pH 2–4, and this phenomenon maybe due to the influence of LDH particle suspensions and dissolved iron in solution (Chen *et al.* 2012). Higher concentrations of ferrous ion and total iron were detected as initial solution pH decreased (Figure 3(c)). Variation of $\cdot\text{OH}$ under the same conditions (Figure 3(b)) indicated that the generation of $\cdot\text{OH}$ is favored under acidic conditions and $\cdot\text{OH}$ performed with excellent oxidation potential (2.80 eV) under strong acidic conditions. But H_2O_2 was reported to be stable under strong acidic conditions ($\text{pH} < 2$) and reacted

with H^+ to form H_3O_2^+ (Daud & Hameed 2010), and ferrous ion in solution may transformed to $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ at pH 1 (Bahmani *et al.* 2013), but precipitated as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ under conditions of $\text{pH} \geq 3$ (Bahmani *et al.* 2013; Ersöz 2014), thus the apparent generation of $\cdot\text{OH}$ was detected at higher at pH 2.

With the concentration of H_2O_2 increased from 0.5 $\text{mmol}\cdot\text{L}^{-1}$ to 1.8 $\text{mmol}\cdot\text{L}^{-1}$, the degradation efficiencies of MB were almost the same (Figure 4(a)), and no obvious influence on the generation of $\cdot\text{OH}$ was observed (Figure 4(b)). This would be attributed to the reason that $\cdot\text{OH}$ was scavenged by excess H_2O_2 to form $\cdot\text{OOH}$ (Ersöz 2014), which is of much lower oxidation capability (Dutta *et al.* 2001; Singh & Tang 2013; Tian *et al.* 2013).



Ninety-seven percent degradation of MB can be approached at 15 min under all conditions investigated (Figure 5(a)), and the degradation was accelerated as the dosage of catalyst increased from 0.25 to 1.00 $\text{g}\cdot\text{L}^{-1}$ for more generation of $\cdot\text{OH}$ theoretically (Elshafei *et al.* 2010; Tian *et al.* 2013). However, the generation of $\cdot\text{OH}$ increased as the dosage of catalyst increased to 0.75 $\text{g}\cdot\text{L}^{-1}$, but decreased with further addition of catalyst (Figure 5(b)) for $\cdot\text{OH}$ was consumed by the extra catalyst (Elshafei *et al.* 2010) (Equation (2)):



Additionally, the degradation of MB and generation of $\cdot\text{OH}$ were found to be temperature-dependent and higher efficiencies were performed at higher temperatures (Figure 6(a)), for the generation rate of $\cdot\text{OH}$ is accelerated

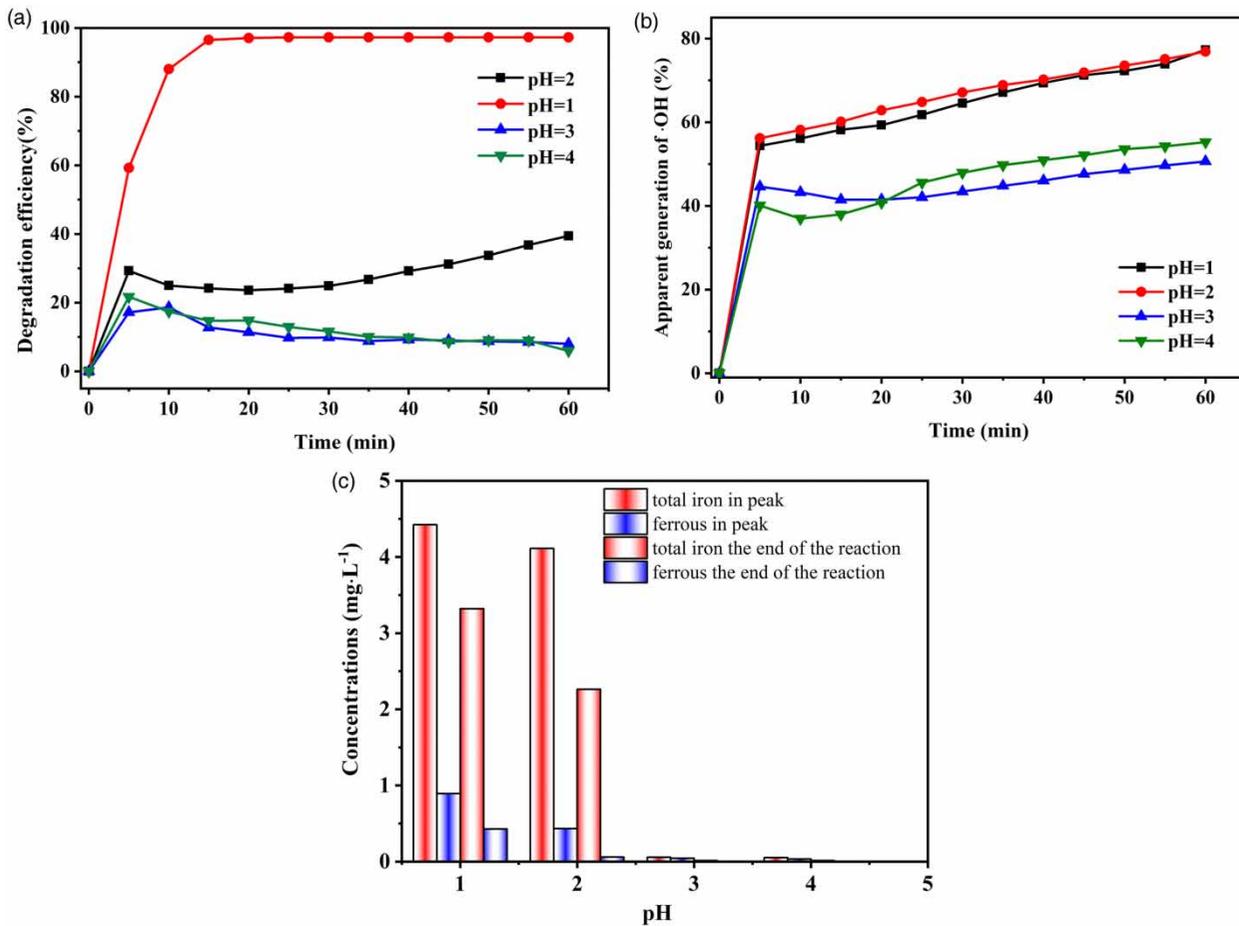


Figure 3 | Effects of initial solution pH on (a) the degradation of MB; (b) apparent generation of ·OH; (c) leaching of ferrous and total iron.

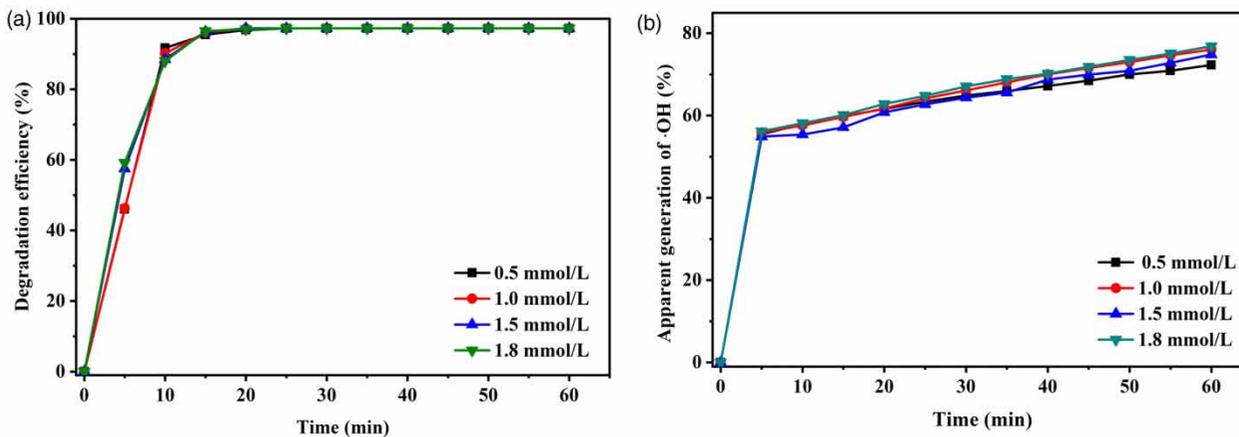


Figure 4 | Effect of H₂O₂ concentration on (a) degradation of MB; (b) apparent generation of ·OH.

(Dutta *et al.* 2001; Elshafei *et al.* 2010). The tendency of the degradation of MB is in good agreement with the production of ·OH (Figure 6(b)), inferring that ·OH played a predominant role in the MB removal process.

Possible catalytic mechanism

Variations of pH, concentrations of solution total iron and ferrous ion were detected and are shown in Figure 7(a).

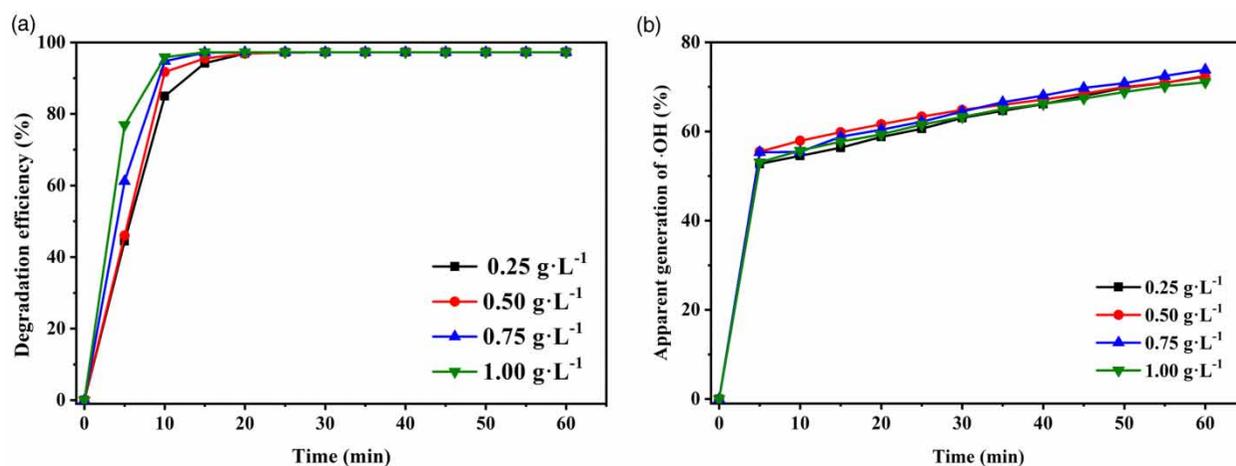


Figure 5 | Effect of catalyst dosages on (a) degradation of MB; (b) apparent generation of ·OH.

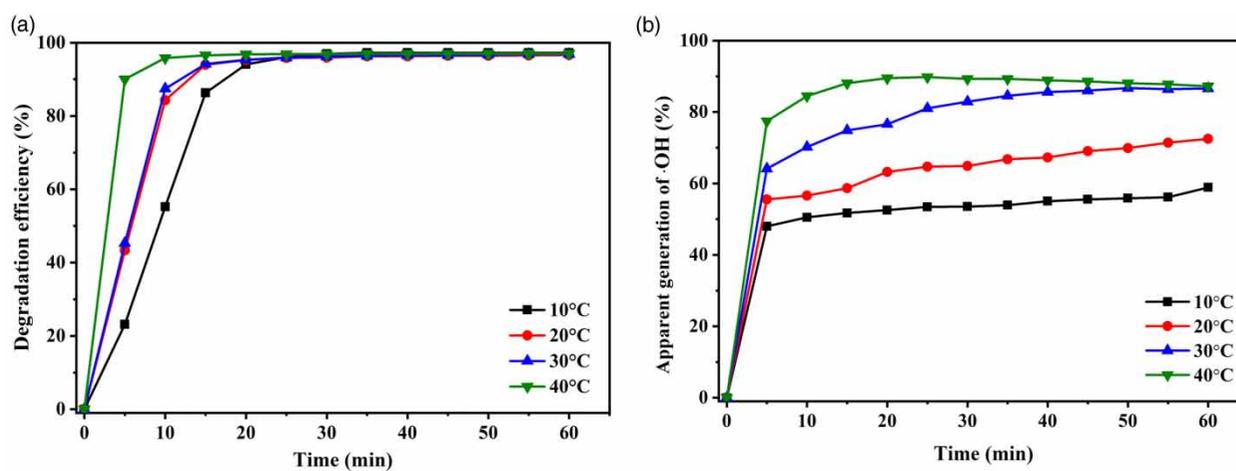


Figure 6 | Effect of temperature on (a) degradation of MB; (b) apparent generation of ·OH.

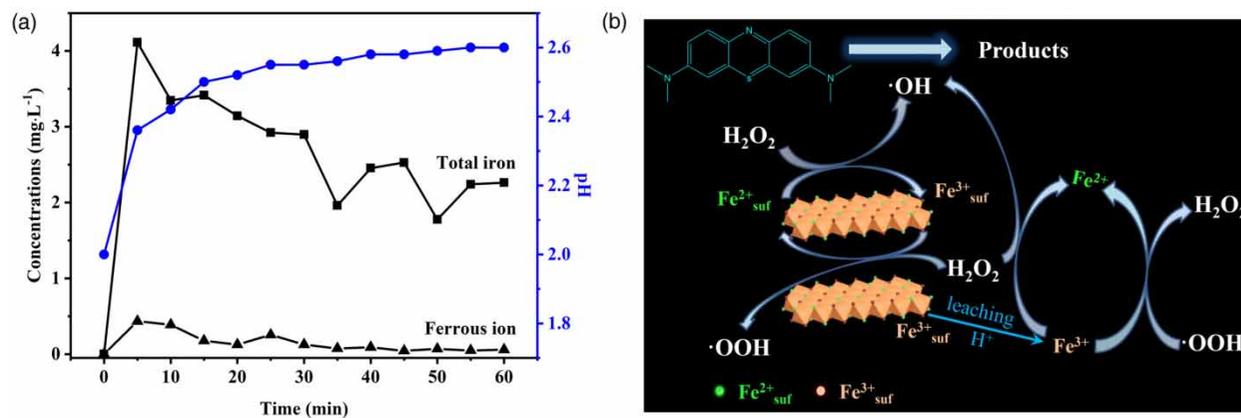


Figure 7 | (a) Variations of pH, concentrations of total iron and ferrous iron in the degradation of MB in Fenton system catalyzed by LDH3 ($[H_2O_2] = 2.5$ mmol/L, $[LDH3] = 2.50$ g/L, pH = 2, $[MB] = 10$ mg/L); (b) possible mechanism for LDH-catalyzed Fenton system.

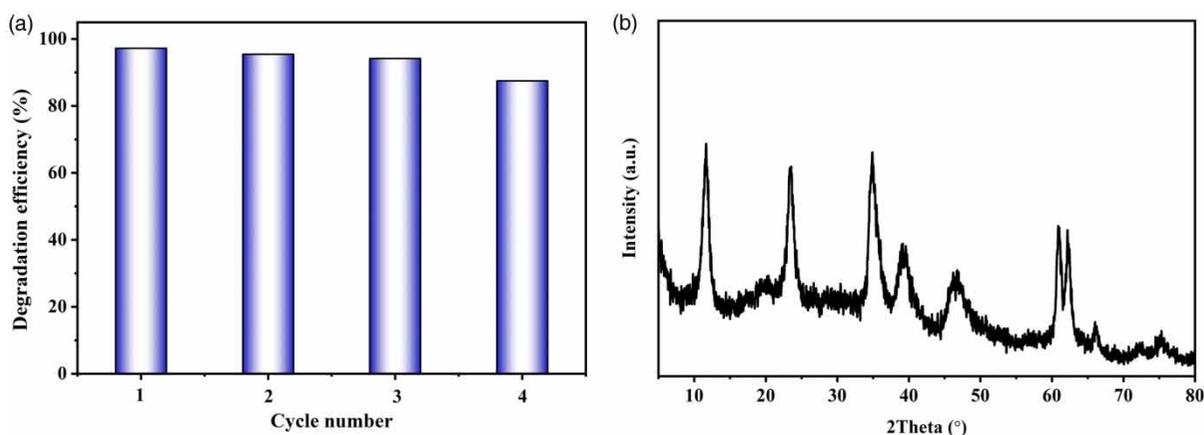
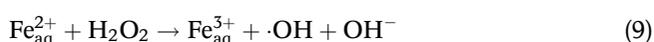
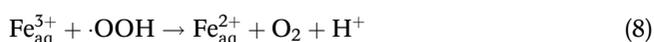
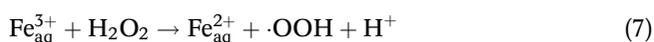
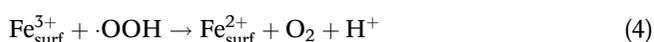


Figure 8 | (a) Recycling use of LDH3 for the degradation of MB (Reaction conditions: $[\text{H}_2\text{O}_2] = 0.5 \text{ mmol/L}$, $[\text{LDH3}] = 0.50 \text{ g/L}$, $\text{pH} = 2$, $200 \text{ mL } 10 \text{ mg/L MB}$); (b) XRD pattern of LDH after four cycles of utilization.

pH increased from 2.0 to 2.6, and concentrations of total iron and ferrous ion increased immediately as the reaction initiated, especially sharply in the first 5 min. Increase of pH was reported for the progress of Fenton reaction, but also for the dissolution of LDH in study. The concentrations of ferrous and total iron first increased as LDH dissolved and then decreased for the adsorption of MgFe-LDHs (Chen *et al.* 2012) and their precipitation at higher pH. Based on all results mentioned above, the mechanism of Fenton catalyzed by MgFe-LDH was revealed, the reactions involved are listed as follows (Equations (3)–(10)) with the possible reaction mechanism depicted in Figure 7(b).



Stability of catalyst

Four recycling uses of LDH3 were performed (Figure 8(a)) and the XRD pattern of LDH after four cycles of use are shown in Figure 8(b) to investigate its stability. LDH

exhibited good catalytic activity in the fourth cycle and 88.93% degradation of MB was obtained. The XRD pattern of LDH after four times use still followed JCPDS#70-2150, without impurities, indicating excellent stability of LDH.

CONCLUSIONS

In this study, LDHx were prepared using the co-precipitation method with the ratio of $[\text{Mg}^{2+}]/[\text{Fe}^{3+}]$ varied in the range of 2:1–6:1. LDHx as-prepared were characterized with XRD, FTIR, TGA/DSC methods, and occupied as catalysts to establish heterogeneous Fenton systems for the degradation of MB. The results indicated that LDH3 is of high purity, and more than 97% degradation of MB can be obtained in 20 min under optimal condition. $\cdot\text{OH}$ was catalytically generated, and a reaction mechanism was proposed. LDH3 was still of excellent catalytic activity and good stability after four cycling use.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/wst.2020.161>.

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