Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of LaFeO_3 and H_2O_2

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HIGHLIGHTS

- LaFeO_3 exhibited an excellent Fenton catalytic activity and long-term stability.
- Formation of $\text{LaFeO}_3\text{--H}_2\text{O}_2$ complex is essential for the heterogeneous Fenton reaction.
- The cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ could be enhanced by the formation of $\text{LaFeO}_3\text{--H}_2\text{O}_2$ complex.

GRAPHICAL ABSTRACT

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ABSTRACT

Nanoscale LaFeO_3 was prepared via sol–gel method and characterized by XRD, FTIR and N_2 adsorption/desorption experiment. The results indicated that, LaFeO_3 had a typical perovskite structure with a BET area of $8.5 \text{ m}^2/\text{g}$. LaFeO_3 exhibited excellent Fenton activity and stability for the degradation of pharmaceuticals and herbicides in water, as demonstrated with sulfamethoxazole, phenazone, phenytoin, acyclovir and 2,4-dichlorophenoxyacetic acid, 2-chlorophenol. Among them, sulfamethoxazole (SMX) could be completely removed in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system after reaction for 120 min at neutral pH. Based on the ATR–FTIR analysis, the surface complex of LaFeO_3 and H_2O_2 was formed, which was important and essential for the enhanced Fenton reaction by accelerating the cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$. Hence, more $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot-}$ were then produced in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system, resulting in more efficient removal of refractory organic compounds. Based on the surface interaction of LaFeO_3 and H_2O_2 , a heterogeneous Fenton reaction mechanism was proposed.

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1. Introduction

The increasing worldwide contamination of surface and ground waters caused by pharmaceuticals and pesticides is a

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major environmental problem facing humanity. Their presence in waters may result in various, direct or indirect, toxicological effects on the environment and on human health. Due to their resistance to microbial degradation [1,2], a major future challenge in wastewater and drinking water treatment is to improve existing unit processes and to design new ones to remove these organic pollutants from a broad range of water matrices [3].

Advanced oxidation processes (AOPs) involving the production of highly reactive hydroxyl radicals have shown great potential for destroying various organic pollutants, in which Fenton's reagent is very attractive since its low cost, wide application range and mild operating conditions. However, the application of homogeneous Fenton reaction is limited by the narrow working pH range (<4), separation and recovery of metal ion and formation of precipitate (for example iron oxide sludge). To overcome these problems, various heterogeneous Fenton-like catalysts have recently been developed and can be used over a wide pH range for the degradation of organic pollutants, such as transition metal oxides, iron/copper immobilized zeolites, clays, and carbon materials [4,5]. However, the better catalytic performance of these catalysts often needs the aids of ultrasonic and/or UV light irradiation to accelerate the reaction. The need for specific equipment and energy consumption will increase the cost of their use in the decontamination processes [6,7]. Thus, it remains crucial to explore on other material alternative which can initiate more efficient Fenton-like process without the aids of external stimulants.

Perovskite-style metal oxides (ABO_3) has a wide application including solid oxide fuel cells [8], magnetic and electrode materials [9], chemical sensors [10] and heterogeneous catalysts in industrial reactions [11] due to the high mobility of oxygen and the stabilization of unusual oxidation states in their structure. Recently, the application of ABO_3 in adsorption [12], photocatalysis [13] and Fenton-like reaction [14–17] has been reported by changing the element at A and B site. Luo et al. demonstrated interesting catalytic properties of $BiFeO_3$ nanoparticles as Fenton-like catalyst for the degradation of Rhodamine B at pH 5.0 [14], especially for the degradation of bisphenol A in the presence of chelating agents [15]. The adsorption of organic compounds on $BiFeO_3$ and the complex between chelating agents and Fe^{3+} of $BiFeO_3$ might have positively affected the degradation. $LaFeO_3$ was also used as a heterogeneous Fenton-like catalyst and showed pseudo first order reaction kinetics for phenol degradation at pH 7 ($k=0.13 \pm 0.01 \text{ h}^{-1}$). The degradation efficiency was improved by a factor of approximately three when the pH was decreased to pH 5. However, its activity was greatly inhibited by surface re-organization [16,17] and the synthesis conditions strongly influence the structural characteristics as well as the catalytic activity of $LaFeO_3$ particles [17].

In this paper, $LaFeO_3$ with different crystalline structure was prepared by sol–gel method and exhibited high efficiency and excellent long-term stability for the heterogeneous Fenton-like degradation of refractory organic compounds at neutral pH without the aids of external stimulants. The contribution of adsorption removal of organic pollutants could also be neglected. The effect of solution pH, H_2O_2 and $LaFeO_3$ concentration, co-existing anions etc., on the Fenton-like activity was further studied. The interaction of $LaFeO_3$, H_2O_2 and organic compound was also observed by in-situ flow-cell ATR–FTIR. The possible catalytic mechanism was also discussed based on all the experimental results.

2. Experimental

2.1. Chemicals and materials

Citric acid, $La(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and H_2O_2 (30%, w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2,4-Dichlorophenoxyacetic acid (2,4-D) and 2-chlorophenol (CPh) were obtained from Beijing Chemical. Acyclovir (ACV), 5-*tert*-butoxycarbonyl 5-methyl-1-pyrroline *N*-oxide (BMPO), phenazone (PhZ), phenytoin (PhT) and sulfamethoxazole (SMX) were supplied by Sigma. All reagents were analytical grade and used without further purification. Deionized water was used throughout this study. The solution pH was adjusted by a diluted aqueous solution of NaOH or HCl.

2.2. Synthesis of $LaFeO_3$ perovskite

$LaFeO_3$ perovskite was prepared via a previously reported sol–gel method [18]. In a typical procedure, 1.3 g $La(NO_3)_3 \cdot 6H_2O$ and 1.6 g $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 20 mL solvent (ethanol: deionized water = 3:1) in order to control the hydrolysis process. Citric acid was added into the nitrate precursors as the chelating agent and the molar ratio of the citric acid and metal ions was 1:1. After stirring for 17 h, the solution was heated at 100°C in open air under stirring constantly to achieve a viscous mixture, which was dried at 100°C overnight and well ground. Finally, the obtained solids were calcined in a muffle furnace at 270°C for 2 h firstly and then at 700°C for 6 h, respectively.

2.3. Characterization

The powder X-ray diffraction pattern (XRD) of $LaFeO_3$ was recorded on a Scintag-XDS-2000 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). The generator voltage and tube current used were 40 kV and 40 mA, respectively. The 2θ ranged from 10° to 80° . The crystalline size was estimated via the Scherrer equation. The infrared spectrum was recorded on a Fourier transform infrared (FTIR) spectrophotometer (SENSOR 27). N_2 adsorption/desorption experiment of $LaFeO_3$ was carried out using a Micromeritics ASAP2020 analyzer (Micromeritics, Norcross, GA). H_2O_2 concentration was determined by using the spectrophotometrically $TiCl_4$ method for $[H_2O_2] \leq 10^{-3} \text{ mol/L}$ [19]. Reactive oxygen species were detected with electron spin resonance (ESR) spectroscopy using BMPO as a spin trap agent. The ESR spectra were obtained using a Bruker A300-10/12 electron paramagnetic resonance spectrometer (center field: 3514.00 G; microwave frequency: 9.85 GHz; and power: 5.05 mW).

2.4. Procedures and analysis

The heterogeneous Fenton-like reaction was carried out under ambient conditions (at 30°C without the aids of ultrasonic and/or UV light irradiation). In a typical experiment, 70 mg $LaFeO_3$ powders were dispersed in 50 mL SMX solution (3 mg/L, pH 6.48). Prior to the addition of H_2O_2 , the suspension was magnetically stirred for about 15 min to establish the adsorption/desorption equilibrium. Then, 23 mmol/L H_2O_2 was added to the above suspension under continuous magnetic stirring. At given time intervals, 2 mL samples were withdrawn and filtered through a Millipore filter (pore size $0.45 \mu\text{m}$) to remove $LaFeO_3$ for analysis. The concentration of each organic compound was analyzed using high-performance liquid chromatography (1200 series; Agilent, Santa Clara, CA) with an Eclipse XDB-C18 column ($5 \mu\text{m}$, $4.6 \text{ mm} \times 150 \text{ mm}$; Agilent). All of the experiments were repeated three times.

The $LaFeO_3$ film used for in-situ flow-cell ATR–FTIR measurement was prepared as the following procedure: 1 mL of diluted $LaFeO_3$ dispersion (0.1 g $LaFeO_3$ was dispersed in 10 mL ethanol) was spreaded on the ATR crystal surface and allowed to dry in an oven for 3 h. The deposited film was then rinsed gently with water and dried again for the uniform dispersity of $LaFeO_3$ on ATR crystal. The ATR–FTIR spectra were recorded using the Nicolet 8700 FTIR spectrometer equipped with a DTGS detector and

ATR accessory. Infrared spectra in the range of 4000–400 cm^{-1} were obtained by averaging 128 scans with a resolution of 4 cm^{-1} under ambient temperature in dark. After the equilibration of LaFeO_3 with NaCl at a flow rate of 3.0 mL/min, a certain amount of H_2O_2 stock solution was added to start the Fenton reaction. While the oxidation experiments were subsequently performed by adding H_2O_2 and SMX simultaneously.

Samples for GC–MS analysis were prepared by the following procedure. The suspension after 30 and 120 min reaction time was filtered to remove LaFeO_3 particles. The solution was evaporated by freeze-dried method. The residue was dissolved with 1.0 mL dichloromethane, and then trimethylsilylated with 0.1 mL of hexamethyldisilazane and 0.05 mL of chlorotrimethylsilane at room temperature. The mixture was shaken vigorously for about 60 s and then allowed to stand for 5 min at room temperature. Precipitate was separated by filtration prior to chromatographic analysis. GC–MS analysis was carried out on Agilent 6890GC/5973MSD with a DB-5 MS capillary column. The chromatographic conditions were as follows: the initial column temperature was held for 20 min at 353 K, ramped at 3.5 K/min–553 K.

3. Results and discussion

3.1. Characterization of LaFeO_3

As shown in Fig. 1, the XRD pattern of LaFeO_3 showed a highly crystalline and single-phase orthorhombic structure (JCDPS 15-0148) and the main crystallite size was estimated using the XRD data evaluated with the Scherrer equation at 40 nm. The strong adsorption at 558 cm^{-1} was observed in the FTIR spectrum (inset of Fig. 1), indicating the Fe–O stretching of FeO_6 groups in LaFeO_3 . Moreover, LaFeO_3 showed isotherm of type V according to IUPAC classification with a BET area of 8.5 m^2/g (Fig. 2). The obtained results proved that the typical perovskite of LaFeO_3 has been successfully prepared (40 nm, 8.5 m^2/g , JCDPS 15-0148), which was totally different from the reported one (60–70 nm, 5.2 m^2/g , JCDPS 74-2494). Hence, LaFeO_3 with the smaller particle size, larger BET area and different crystalline structure in our study should have a promising performance in Fenton-like degradation of refractory organic compounds.

3.2. Heterogeneous Fenton catalytic activity of LaFeO_3

The effects of concentrations of LaFeO_3 , organic pollutant (SMX) and H_2O_2 on the catalytic activity of LaFeO_3 were firstly investigated (Figs. S1 and S2). It was found that the SMX removal efficiency increased with the increase of catalyst load and then

Fig. 1. XRD pattern and FTIR spectrum (inset) of LaFeO_3 .

Fig. 2. Nitrogen adsorption–desorption isotherm of LaFeO_3 .

reached a steady value when the LaFeO_3 concentration was above 1.4 g/L. While the reaction rate decreased with the increase of initial SMX concentration and increased with the increase of initial H_2O_2 concentration. Moreover, the H_2O_2 addition mode had almost no influence on the activity of LaFeO_3 and the SMX removal efficiency was even inhibited to some extent when the same amount of H_2O_2 was added by three times. Therefore, the catalyst load and initial SMX and H_2O_2 concentration were selected at 1.4 g/L, 3.0 mg/L and 23 mmol/L, respectively.

As shown in Fig. 3, 46.3% of SMX was depleted only by H_2O_2 , but the complete degradation could be obtained in the presence of LaFeO_3 and H_2O_2 simultaneously. Besides, compared with H_2O_2 alone in Fig. 4, LaFeO_3 also exhibited much higher catalytic activity for the Fenton-like degradation of other typical pharmaceuticals (ACV, PhZ and PhT) and herbicides (2,4-D and CPh). Moreover, the reaction process above followed a pseudo first order reaction in kinetics and the reaction rate constants for SMX, ACV, PhZ, PhT, 2,4-D and CPh in LaFeO_3 – H_2O_2 system were 0.029, 0.006, 0.008, 0.016, 0.011 and 0.014 min^{-1} , respectively. There was also almost no adsorption of the investigated organic pollutants on LaFeO_3 except CPh (10%). Thus, the enhanced removal of organic pollutants was attributed to the heterogeneous Fenton-like process and the degradation process was mainly occurred in the solution.

SMX was then selected as the representative to investigate its degradation process in different reaction system. The intermediates were monitored by GC–MS analysis (all the identified compounds were unequivocally identified using the NIST98 library database

Fig. 3. The degradation of SMX in the presence of (a) LaFeO_3 , (b) H_2O_2 , and (c) $\text{LaFeO}_3 + \text{H}_2\text{O}_2$. Reaction conditions: initial SMX concentration 3 mg/L, initial H_2O_2 concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48.

Fig. 4. Removal of typical pharmaceuticals and herbicides under different conditions. Reaction conditions: initial H_2O_2 concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48, initial SMX concentration 3 mg/L, initial PhT concentration 10 mg/L, initial concentration of ACV, PhZ, CPh and 2,4-D 5 mg/L.

with fit values higher than 90%). As shown in Tables S1–S4, either in H_2O_2 alone or in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system, almost the same products were detected at different reaction time (30 and 120 min) such as phenol, benzoic acid and dihydroxylamine except that formic acid was further generated in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system at 120 min. While the TOC removal of SMX in H_2O_2 alone and $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system was zero and 22%, respectively. The results indicated that the structure of SMX has been completely destroyed and simpler aliphatic acid was formed in heterogeneous Fenton system. Hence, the intermediates, especially in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system, are mostly biodegradable, which could be discharged for further biological treatment [20,21].

The stability and reusability of LaFeO_3 catalyst was evaluated by successive batches of SMX degradation. It was found that LaFeO_3 could be reutilized for at least 10 cycles and the reused catalyst almost retained the catalytic activity as efficient as the fresh one (Fig. 5). Moreover, LaFeO_3 exhibited a high catalytic activity at initial pH values from 5.5 to 7.14, followed by a slight decrease of SMX degradation at higher initial pH 8.05 (Fig. 6). The pseudo first order reaction rate constants for pH at 5.50, 6.48, 7.14 and 8.05 were 0.056, 0.029, 0.020 and 0.0097 min^{-1} , respectively. The leaching of Fe and La from LaFeO_3 during the reaction process was further tested using ICP-OES method and the results were shown in

Fig. 5. Stability of LaFeO_3 for the Fenton-like degradation of SMX. Reaction conditions: initial SMX concentration 3 mg/L, initial H_2O_2 concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48.

Fig. 6. Effect of initial solution pH on SMX degradation (3 mg/L) in the presence of LaFeO_3 (1.4 g/L) and H_2O_2 (23 mmol/L): (a) pH 5.50, (b) pH 6.48, (c) pH 7.14 and (d) pH 8.05.

Table S5. Obviously, there were no leaching Fe and La ions at the tested pH except 0.292 mg/L of La ion at pH 5.5. The above results indicated that LaFeO_3 had an excellent long-term stability.

Fig. 7 exhibited the investigation of the effects of co-existing anions on LaFeO_3 performance. The addition of anions had a negative influence on the efficiency of the heterogeneous Fenton system and followed the order $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{SO}_4^{2-} > \text{C}_2\text{O}_4^{2-} > \text{NO}_3^-$. The corresponding pseudo first order reaction rate constants also decreased with the above order: $0 < 0.017/0.002 < 0.022\text{--}0.023 < 0.026 < 0.027 < 0.029 \text{ min}^{-1}$ (without anion). The results indicated that most of the co-existing anions have little effect on the reaction system. While the significant retardation caused by PO_4^{3-} and CO_3^{2-} may be due to their quencher for $\cdot\text{OH}$ radicals [22,23].

3.3. Reaction mechanism discussion

To ascertain the reaction mechanism, the involved reaction oxygen species (ROS) in $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system were monitored by using DMPO spin-trap ESR. As shown in Fig. 8A, the both measured ESR spectra exhibited a 4-fold characteristic peaks of the typical $\text{DMPO}\text{--}\cdot\text{OH}$ adduct with an intensity ratio of 1:2:2:1, and the intensity in the $\text{LaFeO}_3\text{--H}_2\text{O}_2$ system was much higher than that of H_2O_2 alone, which indicated that more $\cdot\text{OH}$ radicals were generated in

Fig. 7. Effect of co-existing anions (1 mg/L) on the Fenton-like degradation of SMX over LaFeO_3 . (a) Without anions, (b) NO_3^- , (c) $\text{C}_2\text{O}_4^{2-}$, (d) SO_4^{2-} , (e) Cl^- , (f) CO_3^{2-} , (g) PO_4^{3-} . Reaction conditions: initial SMX concentration 3 mg/L, initial H_2O_2 concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48.

Fig. 8. BMPO spin trapping ESR spectra recorded in the dark at ambient conditions for BMPO-•OH (A) and BMPO-HO₂•/O₂•⁻ (B): (a) H₂O₂, (b) LaFeO₃-H₂O₂.

Fig. 9. Evolution of ATR-FTIR spectra as a function of reaction time at a flow rate 3.0 mL/min. (A) LaFeO₃-H₂O₂; (B) LaFeO₃-H₂O₂-SMX.

the former system. Besides that, the formation of HO₂•/O₂•⁻ radical was also detected and the results were shown in Fig. 8B. Obviously, no significant signals attributed to ROS were found only in the presence of H₂O₂, while the characteristic peaks of the typical DMPO-HO₂•/O₂•⁻ adducts were observed in LaFeO₃ suspension with H₂O₂ [24]. The results indicated that H₂O₂ was decomposed into •OH and HO₂•/O₂•⁻ and the both radicals were the reactive oxygen species involved in the heterogeneous Fenton reaction process.

The interaction of LaFeO₃, H₂O₂ and SMX was further examined with ATR-FTIR. As shown in Fig. 9A, the peak of 1637 cm⁻¹, characterized as O–H bending vibration (δ_{OH}) and stretching vibration (ν_{OH}), indicating the presence of hydroxyl groups on the surface of LaFeO₃ [25]. After the addition of H₂O₂, δ_{OH} was slightly widened, suggesting that H₂O₂ could be adsorbed on LaFeO₃ surface via either directly bound to the surface Fe or by hydrogen bonding to form the surface complex [26,27].

Moreover, the new peaks centered at 1400 cm⁻¹, 1195 cm⁻¹ and 1080 cm⁻¹ were observed and the intensity also increased with reaction time, which could be attributed to the ν(O–O) frequency of superoxide [28]. While no single was detected for the O–O stretching frequency of free H₂O₂ at 880 cm⁻¹ [29]. These features indicated that H₂O₂ preferred to form surface complex with LaFeO₃ instead of direct adsorption on the catalyst. Furthermore, the FTIR spectra of LaFeO₃ (the ν(O–O) peak intensity) did not change with the reaction time during the heterogeneous Fenton degradation of SMX (Fig. 9B), which implied that the formation of LaFeO₃-H₂O₂ complex was essential and stable for the Fenton reaction process.

Fig. S3 further depicted H₂O₂ decomposition over LaFeO₃ in presence of SMX. Obviously, only 12.4 mmol/L of H₂O₂ was consumed at the reaction time 120 min and 10.6 mmol/L of H₂O₂ was still remained in the reaction system due to the initial H₂O₂

concentration 23 mmol/L. It also indicated the formation of LaFeO₃-H₂O₂ complex during the reaction process. Based on the experimental results and a review of the literature [30–32], a heterogeneous Fenton catalytic mechanism of LaFeO₃ was proposed as follows:

Firstly, H₂O₂ was chemisorbed on the surface of LaFeO₃ and the LaFeO₃-H₂O₂ surface complex was then generated. The chemical environment of iron element in LaFeO₃ was changed [33], and the O–O bond in H₂O₂ was significantly weakened [14] due to the formation of LaFeO₃-H₂O₂ complex. Moreover, the complexed Fe³⁺/Fe²⁺ could decrease the Fe³⁺/Fe²⁺ redox potential significantly [34]. Hence, the Fe³⁺/Fe²⁺ cycle was greatly accelerated and more reactive oxygen species such as •OH and O₂•⁻/HO₂• were then produced according to the Haber–Weiss mechanism, which was responsible for the efficient degradation of aqueous organic pollutants at neutral pH. Hence, the role of H₂O₂ in the heterogeneous Fenton reaction process could be divided into three aspects: (1) chemically absorbed on the surface of catalyst and

form $\text{LaFeO}_3\text{--H}_2\text{O}_2$ complex, (2) to generate $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet-}$ via radical mechanism, and (3) to enhance the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle and convert into oxygen via the surface oxygen vacancies mechanism [35].

4. Conclusion

Nanoscale LaFeO_3 with a typical perovskite structure was prepared and exhibited excellent Fenton activity and stability for the degradation of typical pharmaceuticals and herbicides in water. The organic pollutants could be almost completely degraded at neutral pH after 120 min of reaction time. $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet-}$ were the main reactive oxygen species involved in the degradation process. The initial solution pH (5.5–8.05) and co-existing anions had no significant negative influence on the Fenton activity of LaFeO_3 except PO_4^{3-} and CO_3^{2-} . The consumed H_2O_2 not only was decomposed into oxygen and $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet-}$ radicals, but also accelerated the cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ by generating $\text{LaFeO}_3\text{--H}_2\text{O}_2$ complex. Moreover, the heterogeneous Fenton reaction was performed without the aids of external stimulants, such as ultrasonic and UV light irradiation, which would greatly decrease the operation cost and accelerate its application in practical wastewater treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2015.03.065>.

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