Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of LaFeO$_3$ and H$_2$O$_2$

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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 m$^2$/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 LaFeO$_3$–H$_2$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$_2$O$_2$ was formed, which was important and essential for the enhanced Fenton reaction by accelerating the cycle of Fe$^{3+}$/Fe$^{2+}$. Hence, more *OH and O$_2$•−/HO$_2$•− were then produced in LaFeO$_3$–H$_2$O$_2$ system, resulting in more efficient removal of refractory organic compounds. Based on the surface interaction of LaFeO$_3$ and H$_2$O$_2$, a heterogeneous Fenton reaction mechanism was proposed.

1. Introduction

The increasing worldwide contamination of surface and ground waters caused by pharmaceuticals and pesticides is a...
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 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 (pH < 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 use 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 stimuli.

Perovskite-style metal oxides (ABO3) 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 ABO3 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 BiFeO3 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 BiFeO3 and the complex between chelating agents and Fe3+ of BiFeO3 might have positively affected the degradation. LaFeO3 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 ± 0.01 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 LaFeO3 particles [17].

In this paper, LaFeO3 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, H2O2 and LaFeO3 concentration, co-existing anions etc., on the Fenton-like activity was further studied. The interaction of LaFeO3, H2O2 and organic compound was also observed based on all the experimental results.

2. Experimental

2.1. Chemicals and materials

Citric acid, La(NO3)3·6H2O, Fe(NO3)3·9H2O and H2O2 (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. Acetylsalicylic acid (ACV), 5-tert-butoxycarbonyl 5-methyl-1-pyrrolone 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 LaFeO3 perovskite

LaFeO3 perovskite was prepared via a previously reported sol–gel method [18]. In a typical procedure, 1.3 g La(NO3)3·6H2O and 1.6 g Fe(NO3)3·9H2O 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 LaFeO3 was recorded on a Scintag-XDS–2000 diffractometer with Cu Kα radiation (λ = 1.54059 Å). 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 (TENSOR 27). N2 adsorption/desorption experiment of LaFeO3 was carried out using a Micromeritics ASAP2020 analyzer. The specific surface area and pore volume of LaFeO3 were obtained using Barrett-Joyner-Halenda (BJH) method. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo VG ESCALAB 250Xi spectrometer. The ESR spectra were obtained with 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 LaFeO3 powders were dispersed in 50 mL SMX solution (3 mg/L, pH 6.48). Prior to the addition of H2O2, the suspension was magnetically stirred for about 15 min to establish the adsorption/desorption equilibrium. Then, 23 mmol/L H2O2 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 µm) to remove LaFeO3 for analysis. The concentration of each organic compound was measured using high-performance liquid chromatography (1200 series; Agilent, Santa Clara, CA) with an Eclipse XDB-C18 column (5 µm, 4.6 mm × 150 mm; Agilent). All of the experiments were repeated three times.

The LaFeO3 film used for in-situ flow-cell ATR–FTIR measurement was prepared as the following procedure: 1 mL of diluted LaFeO3 dispersion (0.1 g LaFeO3 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 LaFeO3 on ATR crystal. The ATR–FTIR spectra were recorded using the Nicolet 8700 FTIR spectrometer equipped with a DTGS detector and
3. Results and discussion

3.1. Characterization of LaFeO3

As shown in Fig. 1, the XRD pattern of LaFeO3 showed a highly crystalline and single-phase orthorhombic structure (JCPDS 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 FeO₆ groups in LaFeO₃. Moreover, LaFeO₃ showed isotherm of type V according to IUPAC classification with a BET area of 8.5 m²/g (Fig. 2), which was totally different from the reported one (60–70 nm, 5.2 m²/g, JCPDS 74-2494). Hence, LaFeO₃ 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 LaFeO3

The effects of concentrations of LaFeO₃, organic pollutant (SMX) and H₂O₂ on the catalytic activity of LaFeO₃ were firstly investigated (Figs. S1 and S2). It was found that the SMX removal efficiency increased with the increase of catalyst load and then reached a steady value when the LaFeO₃ 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 H₂O₂ concentration. Moreover, the H₂O₂ addition mode had almost no influence on the activity of LaFeO₃ and the SMX removal efficiency was even inhibited to some extent when the same amount of H₂O₂ was added by three times. Therefore, the catalyst load and initial SMX and H₂O₂ 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 H₂O₂, but the complete degradation could be obtained in the presence of LaFeO₃ and H₂O₂ simultaneously. Besides, compared with H₂O₂ alone in Fig. 4, LaFeO₃ 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 LaFeO₃–H₂O₂ 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 LaFeO₃ 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).
Removal of typical pharmaceuticals and herbicides under different conditions. Reaction conditions: initial H$_2$O$_2$ concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48. Initial SMX concentration 3 mg/L, initial PhZ concentration 10 mg/L, initial PhT concentration 10 mg/L, initial solution pH 6.48, initial ACV concentration 3 mg/L, initial PhZ, CPh and 2,4-D concentration 5 mg/L.

The stability of LaFeO$_3$ for the Fenton-like degradation of SMX. Reaction conditions: initial H$_2$O$_2$ concentration 23 mmol/L, catalyst load 1.4 g/L, and initial solution pH 6.48. 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 also decreased with the above order: $0.017/0.022<0.023<0.026<0.027 <0.029$ 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 *OH radicals [22,23].

3.3. Reaction mechanism discussion

To ascertain the reaction mechanism, the involved reaction oxygen species (ROS) in LaFeO$_3$–H$_2$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 DMPO−*OH adduct with an intensity ratio of 1:2:2:1, and the intensity in the LaFeO$_3$–H$_2$O$_2$ system was much higher than that of H$_2$O$_2$ alone, which indicated that more *OH radicals were generated in
Besides that, the formation of HO$_2$**/O$_2$** 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 H$_2$O$_2$, while the characteristic peaks of the typical DMPO-HO$_2$**/O$_2$** adducts were observed in LaFeO$_3$ suspension with H$_2$O$_2$ [24]. The results indicated that H$_2$O$_2$ was decomposed into *OH and HO$_2$**/O$_2$** and the both radicals were the reactive oxygen species involved in the heterogeneous Fenton reaction process.

The interaction of LaFeO$_3$, H$_2$O$_2$ 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 ($\delta$(OH)) and stretching vibration ($\nu$(OH)), indicating the presence of hydroxyl groups on the surface of LaFeO$_3$ [25]. After the addition of H$_2$O$_2$, $\delta$(OH) was slightly widened, suggesting that H$_2$O$_2$ could be adsorbed on LaFeO$_3$ 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 $\nu$(O–O) frequency of superoxide [28]. While no single was detected for the O–O stretching frequency of free H$_2$O$_2$ at 880 cm$^{-1}$ [29]. These features indicated that H$_2$O$_2$ preferred to form surface complex with LaFeO$_3$ instead of direct adsorption on the catalyst. Furthermore, the FTIR spectra of LaFeO$_3$ (the $\nu$(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 LaFeO$_3$–H$_2$O$_2$ complex was essential and stable for the Fenton reaction process.

Fig. 9 further depicted H$_2$O$_2$ decomposition over LaFeO$_3$ in presence of SMX. Obviously, only 12.4 mmol/L of H$_2$O$_2$ was consumed at the reaction time 120 min and 10.6 mmol/L of H$_2$O$_2$ was still remained in the reaction system due to the initial H$_2$O$_2$ concentration 23 mmol/L. It also indicated the formation of LaFeO$_3$–H$_2$O$_2$ complex during the reaction process. Based on the experimental results and a review of the literature [30–32], a heterogeneous Fenton catalytic mechanism of LaFeO$_3$ was proposed as follows:

$$\begin{align*}
2\text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \equiv\text{Fe}^{3+}\cdots\text{O}–\text{O}–\equiv\text{Fe}^{3+} + 2\text{H}^+ \\
\equiv\text{Fe}^{3+}\cdots\text{O} – \equiv\text{Fe}^{3+} &\rightarrow 2\text{H}_2\text{O}^\cdot \rightarrow \equiv\text{Fe}^{2+}\cdots\text{O}–\equiv\text{Fe}^{2+} \\
&\rightarrow \equiv\text{HO}_2^\cdot + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^\cdot + \text{H}^+ \\
\equiv\text{Fe}^{2+}\cdots\text{O} – \equiv\text{Fe}^{2+} &\rightarrow 2\text{H}_2\text{O}^\cdot \rightarrow \equiv\text{Fe}^{3+}\cdots\text{O}–\equiv\text{Fe}^{3+} \\
&\rightarrow 2^\cdot\text{OH} + 2\text{OH}^- \\
\equiv\text{Fe}^{3+}\cdots\text{O} – \equiv\text{Fe}^{3+} &\rightarrow 2\text{O}_2^\cdot \rightarrow \equiv\text{Fe}^{2+}\cdots\text{O}–\equiv\text{Fe}^{2+} \equiv2\text{O}_2
\end{align*}$$

SMX + ^OH/\text{O}_2^\cdot \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}

Firstly, H$_2$O$_2$ was chemisorbed on the surface of LaFeO$_3$ and the LaFeO$_3$–H$_2$O$_2$ surface complex was then generated. The chemical environment of iron element in LaFeO$_3$ was changed [33], and the O–O bond in H$_2$O$_2$ was significantly weakened [14] due to the formation of LaFeO$_3$–H$_2$O$_2$ complex. Moreover, the complexed Fe$^{3+}$/Fe$^{2+}$ could decrease the Fe$^{3+}$/Fe$^{2+}$ redox potential significantly [34]. Hence, the Fe$^{3+}$/Fe$^{2+}$ cycle was greatly accelerated and more reactive oxygen species such as *OH and O$^\cdot$/HO$_2$** 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 H$_2$O$_2$ in the heterogeneous Fenton reaction process could be divided into three aspects: (1) chemically absorbed on the surface of catalyst and...
form LaFeO$_3$–H$_2$O$_2$ complex, (2) to generate $^*$OH and O$_2$•−/HO$_2$•− via radical mechanism, and (3) to enhance the Fe$^{3+}$/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. $^*$OH and O$_2$•−/HO$_2$•− 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$_2^{−}$−. The consumed H$_2$O$_2$ not only was decomposed into oxygen and $^*$OH and O$_2$•−/HO$_2$•− radicals, but also accelerated the cycle of Fe$^{3+}$/Fe$^{2+}$ by generating LaFeO$_3$–H$_2$O$_2$ complex. Moreover, the heterogeneous Fenton reaction was performed without the aid 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.

References