Mechanism of Photo-Fenton Removal of Methyl Dye Orange Using Perovskite Lanthanum Orthoferrite Doped with Copper Metal

Imtiyaz Rasool Parrey

Department of Chemistry, Periyar University Salem Tamil Nadu, India

Abstract. Organic dyes are a group of major pollutants found in the wastewater, which is discharged from many textile industries. They raised a growing public concern in terms of their environmental impact. Several treatment methods have been trilled, especially advanced oxidation processes. In this paper we synthesize Copper–Lanthanum orthoferrite. The compound was further characterized by using scanning electron microscope and powdered XRD. The photo catalytic activity of lanthanum orthoferrite and Copper–Lanthanum orthoferrite were investigated for the removal of methyl orange in the presence of both hydrogen peroxide and visible light.

KEY WORDS: Lanthanum orthoferrite, Organic dyes, Environmental dyes, Advanced oxidative process.

1   Introduction

Lanthanum orthoferrite $LaFeO_3$ (LFO) is one of the gifted photo catalysts exist from perovskite material. The peculiar property consists of high stability, non-toxicity and small band gap energy (2.07 eV). Because of high band gap the perovskite of lanthanum finds use in light active photo catalyst [1]. One of the common dyes found in water wastes is methyl orange (MO). It is a carcinogenic water-soluble azo dye. Methyl orange dye is mostly used in many textile industries such as printing paper, and research laboratories. The stable nature of methyl orange shows it low biodegradability and is solvable in water, the current challenge for chemistry is how to remove these harmful compounds from the water by using common purification techniques [2]. Most of the dyes cannot get degraded in nature. The conservative methods for dye removal include biochemical and physical-chemical methods. Among the methods, some are membrane separation, ozonation and adsorption, which are not cost effective and very efficient. Therefore, the elimination of organic dyes from wastewater is a great

experiment and a persistent job [3]. The most important use of organic dyes is in textile industries. Textile industry is one of the largest industries that contribute to the growth of every financial nation. Most of the dyes used in large-scale industrial are synthetic as compared to natural dyes. The main reason is synthetic dyes have lower production cost, second benefit is they have ability to portray a broad range of colors, and third is they perform better from its fastness specification. The release of wastewater containing dyes into environment without proper treatment can cause serious water pollution [4].

In this paper, we dope Copper into the Lanthanum orthoferrite. The results shows that Copper–Lanthanum orthoferrite catalyst was recognized as a highly effective photo-Fenton catalyst when compared to one of the advantages of using over Lanthanum orthoferrite in the photo catalytic degradation [5, 6]. Experimental results shows that Cu-doped LFO produced more hydroxyl radicals, offered better stability and improved the overall performance of dye removal over LFO. Moreover, the report indicated high stability and reusability of LFO-15 Cu, which showed great potential as a catalyst for removing organic pollutants in wastewater [7, 8].

2 Materials and Methods

Lanthanum sulphate hexahydrate ($La(SO_4)_3.6H_2O$; 99.9), H_2O_2 (25wt%), citric acid $C_6H_8O_7.H_2O$, ethylamine solution (20%) and methyl orange (MO) were purchased from Sigma-Aldrich and used as the starting materials. Copper sulphate hydrated ($Cu(SO_4)_3.9H_2O$) was purchased from Alta Aesar. All of the chemicals were used without further purification. For all the experiment, the deionized (DI) water was used.

2.1 Synthesis of Lanthanum orthoferrite

The synthesis LFO was be done by mixing 0.2 mol/L of $La(SO_4)_3.6H2O$ and $Fe(SO_4)_3.9H_2O$. After nonstop stirring for about 3 hours at the room temperature, the ethylamine solution was then slowly added drop wise with the resulting solution. The formation of Precipitate started to form during the drop wise addition of ethylamine and then dissolved completely when the pH of solution reached ~ 8. The subsequent solution was then transferred into 75 mL Teflon-lined stainless steel autoclave, followed by the heating at 200°C for 24 hours. The autoclave was then cooled to room temperature gradually. The resulting particles were separated by centrifugation, washed with deionized water and ethanol, and dried in the oven at 95°C overnight. The final photo catalyst was obtained after calcination at 900°C for 7 hours (5°/min ramp rate).

2.2   Copper-doped Lanthanum orthoferrite

Synthesis of Coper doped LFO is done by mixing $La(NO_3)_3.6H_2O$, $Fe(SO_4)_3.9H_2O$ and $(Cu(SO_4)_3.9H_2O)$ together to prepare 1.5 mol/L of solution. The solution was then added with 1 mol/L of citrate acid and nonstop stirred for 2 hours at the room temperature. From this point, by following the same synthetic procedures of LFO, the final product 15CuLFO was produce.

3   Characterizations

3.1   X-ray powder diffraction (XRD)

In the X-ray powder diffraction (XRD) analysis, the sample was finely crushed using a grind and placed on an aluminium sample plate. Then a few drops of ethanol were applied to hold the sample on the aluminium plate, which was air dried for about 15 minutes. The XRD analysis was performed on a GBC eMMA X-ray diffractometer with Cu Kα radiation using an acceleration voltage of 35 kV and a current of 28 mA. The 2θ scan region was set to be at 10–80° with a rate of 1°/min. Based on the results of XRD analysis, the average crystal sizes of the samples were estimated based on Scherrer's formula. The cell volume and the lattice parameters of the samples can be determined using Bragg's law.

3.2   Scanning electron microscope

The external Morphology and of 15CuFLO and LFO were studies by using scanning electron microscope (SEM) (5 kV; Zeiss 1555 VP-FESEM) from the University of Periyar University Salem India. Before SEM analysis, the sample was coated with a thin layer of platinum. On the other side, the carbon coating was used when determining the composition of the samples by using SEM (20)KV; JCM-6000) which is equipped with energy dispersive X-rays spectroscopy (EDS) detector.

3.3   Photo-Fenton removal of methyl orange

The photo degradation removal of catalyst 15CuLFO was analyzed using Photo Fenton instrument, which contains cylindrical Pyrex reactor equipped with a circulating water jacket and was capable to maintain the reaction temperature at 18°C. 0.1 g of the 15CuLFO was added into the reactor, followed by the addition of 80 mL of MO aqueous solution.

The solution was then preserved in the dark for 340 minutes with constant stirring to reach the adsorption-desorption equilibrium between MO and the photo catalyst. Afterwards, the photo-Fenton reaction was quickly initiated by introducing 2 mL of 35 w/v% H_2O_2 to the solution and using a xenon lamp (CEL-HX

F300, IIT Kanpur India) with a 400 nm cut-off filter. The reaction solution was exposed to the visible light for approximately 3 hours, during which approximately 3 mL of the suspension was taken from the system at an interval of every 15 minutes. Then the extracted suspension was centrifuged to separate the residual catalyst particles, and then monitored by using Perkin Elmer Lambda 750 UV/vis spectrometer.

4   Results and Discussion

The characteristic peaks shown in Figures 1 and 2 were observed at 22.76, 32.36, 38.56, 72.32 and 76.96 a.u can be indexed as (101) (121) (121) (143) and (204), respectively [9]. These results indicate well-crystallized orthorhombic structure of LFO and 15CuLFO. Moreover, both metal-doped LFO samples exhibited similar intensity of peaks as compared to that of the pristine LFO. Hence, the crystal structure of LFO was not affected by the doping with Copper. The XRD result also indicates the calcination at 900°C can lead to the formation of well-crystallized perovskite particles, which coincide with the literature. [9, 10].
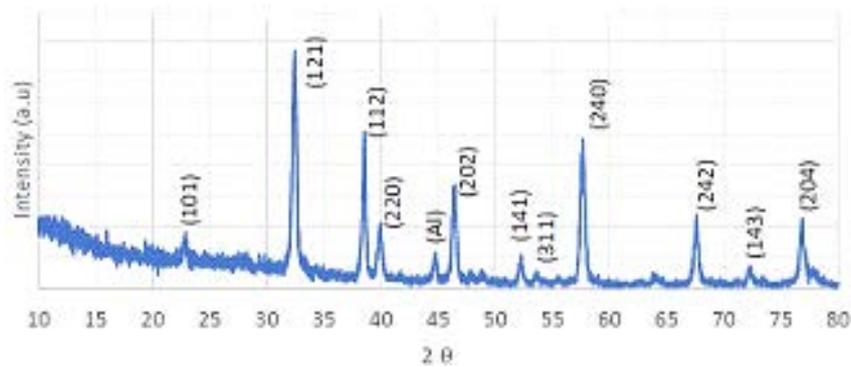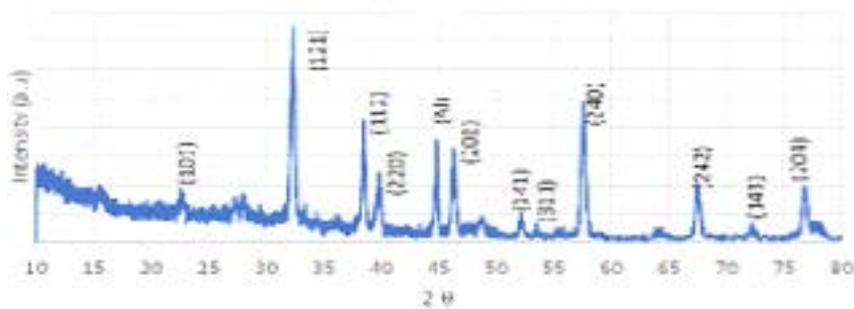

Figure 1. XRD graph of Lanthanum orthoferrite.

Figure 2. XRD graph of metal doped Lanthanum orthoferrite.

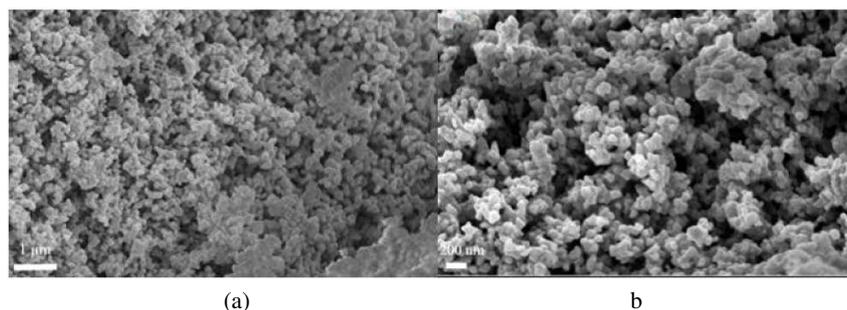(a)   b

Figure 3. SEM images of: (a) Lanthanum orthoferrite; and (b) Cu doped Lanthanum orthoferrite.

Table 1 shows corresponding values of BET explain the significance surface area, pore volume and pore size of all samples. The specific surface areas (SBET) of Lanthanum orthoferrite, Cu FLO are 11.8, and 16.54 m^2/g, respectively. As can be seen, the 15 Copper Lanthanum orthoferrite is slightly larger surface areas when compared to that of Lanthanum orthoferrite. The pore volumes of Lanthanum orthoferrite, and 15 Cu Lanthanum orthoferrite 0.18 cm^3/g and 0.09 cm^3/g, respectively; whilst the average pore sizes of Lanthanum orthoferrite, and 15Cu-Lanthanum orthoferrite are 191.03 and 339.2 Å. These pores might be formed caused by the agglomeration of small particles, which have been evidence in the SEM images (Figure 3). These data, as summarized in Table 1, suggest that the Lanthanum orthoferrite samples doped with Cu only improves the surface area but not the pore volume and pore size of the sample. The increase of surface area may lead to enhancement in the photo catalytic activity as it is stated in literature [11].

Table 1. BET surface area, pore volume and pore size of Lanthanum orthoferrite and Copper doped Lanthanum orthoferrite

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (Å)
Lanthanum orthoferrite	11.8	0.18	191.03
Cu doped Lanthanum orthoferrite	16.54	0.09	339.2

4.1 Removal of methyl orange by Lanthanum othoferrite and Copper-doped Lanthanum othoferrite

The photo catalytic activity of Lanthanum othoferrite and Copper–Lanthanum orthoferrite were investigated for the removal of MO in the presence of both hydrogen peroxide and visible light (Figure 4); the summary of the reaction constants k and R^2 is the correlation coefficient is the degree relationship between

two variables of photo degradation results indicates ~30% of MO removal is observed for Lanthanum orthoferrite sample alone as compared to the literature results of Lanthanum othoferrite samples performed under same condition such as amount of H_2O_2 dosage, catalyst loading, MO dye concentration and same light source. [12]. However, for metal-doped Lanthanum orthoferrite samples only ~20% of MO removal for 15 Copper Lanthanum othoferrite for one hour.

After 2-hour exposure to the visible light, the following photo catalytic efficiency of Copper Lanthanum othoferrite showed 70% removal of MO were recorded [13]. The pseudo-first-order kinetic was observed on Figure 4 for 15Copper Lanthanum orthoferrite have similar photo catalytic activity with a kinetic constant k value of approximately 0.003/min and R^2 value of 0.99.
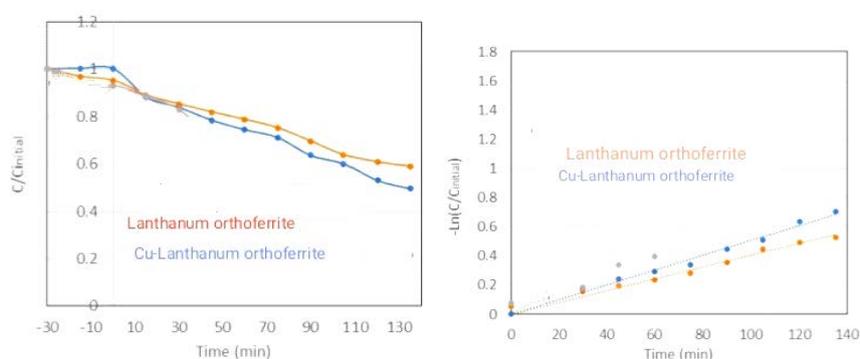

Figure 4. Photo degradation of methyl orange using Lanthanum orthoferrite doped with Copper. (The pseudo-first-order kinetic was observed for Lanthanum orthoferrite and 15 Cu Lanthanum orthoferrite both of which have similar photo catalytic activity with a kinetic constant k value of approximately 0.003/min and R^2 value of 0.99. Lanthanum orthoferrite only displays with a R^2 value of 0.98 with the apparent k value of 0.0064/min.)

4.2 Photo-Fenton mechanism of removal of methyl orange

In Figure 5, when Lanthanum orthoferrite is exposed to visible light, it is promoted to an electronically excited state, characterized by the generation of electron-hole pairs (e^-, h^+), due to the promotion of electrons from the valence band (VB) to the conduction band (CB) by photon absorption. The energy difference between the two bands corresponds to the band gap energy (E_g). When the electrons are promoted to the CB, the holes (h^+) are generated in VB with a strongly oxidizing agent such as hydrogen peroxide, reducing and oxidizing sites are created respectively [8]. These sites are capable to induce chemical reactions with adsorbed species such as MO. Secondly, Fe(III) from undergo series of steps to produce hydroxyl radical through interaction between the surface
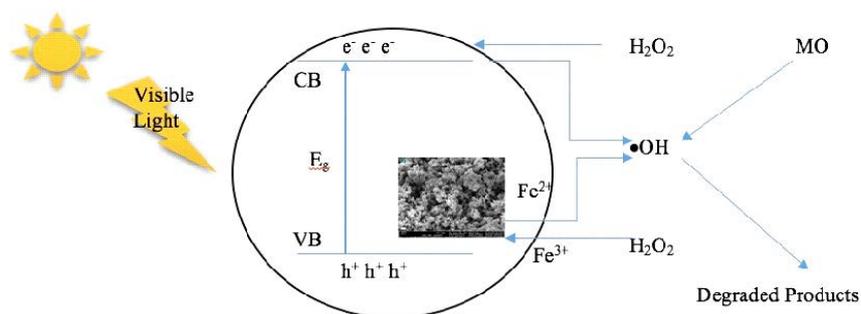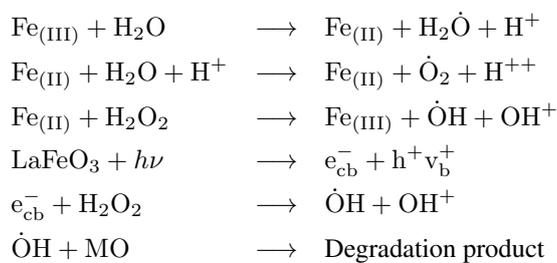
Figure 5. Diagram showing the mechanism of degradation of methyl orange using photo-fenten mechanism.

of the catalyst and hydrogen peroxide [1, 5, 11].

$$Fe_{(III)} + H_2O \longrightarrow Fe_{(II)} + H_2\dot{O} + H^+$$
$$Fe_{(II)} + H_2O + H^+ \longrightarrow Fe_{(II)} + \dot{O}_2 + H^{++}$$
$$Fe_{(II)} + H_2O_2 \longrightarrow Fe_{(III)} + \dot{O}H + OH^+$$
$$LaFeO_3 + h\nu \longrightarrow e_{cb}^- + h^+v_b^+$$
$$e_{cb}^- + H_2O_2 \longrightarrow \dot{O}H + OH^+$$
$$\dot{O}H + MO \longrightarrow \text{Degradation product}$$

5 Conclusion

LaFeO$_3$, doped with copper catalyst were successfully prepared using an efficient synthesis procedure via a hydrothermal method. The produced LaFeO$_3$ material presents high crystallinity and possesses spherical symmetry with well uniform structure, which are essential characteristics for catalytic purposes. However, formation of clusters and aggregation were observed on SEM image of Lanthanum orthoferrite and 15 Copper Lanthanum orthoferrite and increased pore volume and pore size in N$_2$ adsorption-absorption test. Heterogeneous photo-Fenton process using LaFeO$_3$ as a catalyst demonstrated a satisfactory ability for degradation of the methyl orange dye from aqueous solution under the best reaction conditions, around 70% degradation was achieved compare to 39% and 49% degradation by Lanthanum orthoferrite and 15 Copper Lanthanum orthoferrite respectively under 2 hours of irradiation.

References

[1] R. Köferstein, L. Jäger, S. Ebbinghaus (2013) Magnetic and optical investigations on LaFeO$_3$ powders with different particle sizes and corresponding ceramics. *Solid State Ionics* **5** 249-250.

[2] V. Vaiano, G. Iervolino, D. Sannino, J.J. Murcia, M.C. Hidalgo, P. Ciambelli, J.A. Navío (2016) Photocatalytic removal of patent blue V dye on Au-TiO2 and Pt-TiO2 catalysts. *Appl. Catal. B-Environ.* **188** 134-146.

[3] K.K. Nanda, S. Swain, B. Satpati, L. Besra (2015) Electronic supplementary material (ESI) for RSC advances. *Royal Society of Chemistry* **3** 15-18.

[4] I. Oller, W. Gernjak, M.I. Maldonado, L.A. Pérez-Estrada, J.A. Sánchez-Pérez, S. Malato (2006) Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *J. Hazard. Mater.* **138** 507-517.

[5] T.T.N. Phan, A.N. Nikoloski, P.A. Bahri, D. Li (2018) Heterogeneous photo-Fenton degradation of organics using highly efficient Cu-doped LaFeO$_3$ under visible light. *J. Ind. Eng. Chem.* **61** 53-64.

[6] T.T.N. Phan, A.N. Nikoloski, P.A. Bahri, D. Li (2018) Optimizing photocatalytic performance of hydrothermally synthesized LaFeO$_3$ by tuning material properties and operating conditions. *J. Environ. Chem. Eng.* **6** 1209-1218.

[7] F.P. Sejie, M.S. Nadiye-Tabbiruka (2016) Removal of Methyl Orange (MO) from Water by adsorption onto Modified Local Clay (Kaolinite). *Phys. Chem.* **6**(2) 39-48; doi: 10.5923/j.pc.20160602.02.

[8] E.M. Saggioro, A.S. Oliveira, T. Pavesi, M.J. Tototzintle, M.I. Maldonado, F.V. Correia, J.C. Moreira (2015) SSolar CPC Pilot Plant Photocatalytic Degradation of Indigo Carmine Dye in Waters and Wastewaters Using Supported-TiO$_2$: Influence of Photodegradation Parameters. *Int. J. Photoenergy* **2015** Article ID 656153

[9] K. Sornalingam, A. McDonagh, J.L. Zhou, Md A.H. Johir, M.B. Ahmed (2018) Photocatalysis of estrone in water and wastewater: Comparison between Au-TiO$_2$ nanocomposite and TiO$_2$, and degradation by-products. *Sci. Total Environ.* **610-611** 521-530.

[10] G. Tchobanoglous, H.D. Stensel, R. Tsuchihashi, F.L. Burton. M. Abu-Orf, G. Bowden, W. Pfrang, Metcalf & Eddy (2014) "*Wastewater Engineering: Treatment and Resource Recovery*" (New York, NY: McGraw-Hill Education).

[11] V. Vaiano, L.A. Isupova, P. Ciambelli, D. Sannino (2014) Photo-fenton Oxidation of t-Butyl methyl ether in Presence of LaFeO$_3$ Supported on Monolithic Structure. *J. Adv. Oxid. Technol.* **17** 187-192.

[12] B. Viswanathan, S. Sivasanker, A.V. Ramaswamy (2002) "*Catalysis: Principles and Applications*" (CRC Press).

[13] H. Zhao, F. Pan, Y. Li (2017) A review on the effects of TiO$_2$ surface point defects on CO$_2$ photoreduction with H$_2$O. *J. Materiomics* **3** 17-32.