

Photo-degradation of Methyl Orange by Polysaccharides/LaFe_{0.8}Cu_{0.2}O₃ Composite Films

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The objective of this work was to prepare a series of composite films (polysaccharides with LaFe_{0.8}Cu_{0.2}O₃) for the degradation of methyl orange under ultraviolet irradiation. LaFe_{0.8}Cu_{0.2}O₃ was prepared by a sol-gel method, and the composite films were obtained by cross-linking reactions between polysaccharides (xylan and chitosan) and LaFe_{0.8}Cu_{0.2}O₃. Physical and chemical properties of the composite films were investigated by XRD, FTIR, SEM, and BET. Moreover, the influence of the weight ratio of polysaccharide to LaFe_{0.8}Cu_{0.2}O₃ on the methyl orange degradation reaction was also studied. Results showed that 67% of the degradation efficiency was achieved within 480 min using chitosan/LaFe_{0.8}Cu_{0.2}O₃ (2:1) as photocatalysts, while 58% was for xylan/LaFe_{0.8}Cu_{0.2}O₃ (1:1). The difference was due to the variety in the structure of chitosan and xylan.

Keywords: Polysaccharides/LaFe_{0.8}Cu_{0.2}O₃ composite films; Photocatalytic degradation; Methyl orange

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INTRODUCTION

Dyes are significant pollutants in the textile industry. About 10% of the total produced dyes used up during dyeing processes may be released as effluents, leading to environmental pollution (Vijayaraghavan and Yun 2008). Seeking for efficient treatments for industrial wastewater has attracted lots of attention in recent years.

It is difficult to handle wastewater from dyeing because of its high emission, high levels of organic pollutant, deep chroma, great variation of pH, dramatic changes in water quality, and difficulty in biodegradation. Organic dyes, one of the key pollutant sources, are widely used in light industries such as textiles, cosmetics, printing, and paper making (Aksu and Yener 2001; Hameed and Ahmad 2009; Shannon *et al.* 2008). Therefore, finding an efficient degradation approach for dyeing wastewater becomes an important issue in environmental protection.

Various techniques have been applied to remove organic dyes in industrial effluents such as sedimentation, filtration, coagulation, oxidation, adsorption, ion exchange, and biological treatments (Gouvea *et al.* 2000; Neill *et al.* 2000; Swaminathan and Sandhya 2003.) One attractive approach is photo-degradation using photocatalysts (Linsebigle *et al.* 1995; Ejhieh and Khorsandi 2010a, 2010b; Ejhieh and Shamsabadi 2010; Ejhieh and Moazzeni 2013; Ejhieh and Hushmandrad 2010).

Among various photocatalysts, TiO₂-based materials and other composite materials have been found to be efficient photocatalysts. (Yang *et al.* 2013) reported that up to 75% of degradation rate was achieved using TiO₂ modified with 3 wt% alkali ions. (Zhu *et al.* 2012, 2013) used CdS/TiO₂/chitosan and TiO₂/ZnO/chitosan as catalysts to decolorize methyl orange solution under visible light. However, some drawbacks still exist, including high cost and limitations in photocatalytic activity, which greatly limits the industrial application of TiO₂ for water treatment.

Novel efficient photocatalysts have been under development in recent years. Compared with TiO₂, perovskite-type oxides are much more suitable for photocatalysis under various light sources and reaction conditions due to their multiple band energies and favorable stability in acidic and basic solutions (Tian *et al.* 2013). Perovskite-type LaCoO₃ hollow spheres, nanosized perovskite-type oxides (LaCoO₃), ultrafine perovskite-type LaCoO₃, LaCoO_{3-x} porous powder, and LaCoO₃ nanoparticles prepared by different methods have exhibited high photocatalytic activity under different light irradiation due to the high chemisorbed oxygen, and hence they could be promising candidate materials for photocatalytic application (Fu *et al.* 2013; Fu *et al.* 2011; Ha *et al.* 2013; Jung and Hong 2013; Sun *et al.* 2010a;). The perovskite-type composite oxide La_{0.5}Pb_{0.5}MnO₃ with specific surface area was successfully synthesized by the stearic acid method, and it showed excellent catalytic activity (Chen *et al.* 2013). La-loaded perovskite oxides containing metal of iron such as LaFeO₃ and LaFe_{0.5}Mn_{0.5-x}O_{3-delta} have photocatalytic performance; LaFe_{0.5}Mn_{0.5}O_{3-delta} exhibited much higher activity than that of LaFeO₃ due to its higher oxygen vacancies, variable valency Mn ions, and the strong absorption in visible light (Wei *et al.* 2012). Moreover, the dye degradation activity of oxygen-defective BaFeO_{3-x} was studied by (Sun *et al.* 2010b), who reported that BaFeO_{3-x} could degrade methyl orange in the dark, and the degradation rate can be improved under visible light due to the optical property of BaFeO_{3-x} (Sun *et al.* 2010b; Yang *et al.* 2006) studied the photodegradation of methyl orange under UV light irradiation by perovskite SrFeO₃ and brownmillerite Ca₂Fe₂O₅. Therefore, perovskite-type oxides have the potential application as the photocatalyst for the dye degradation.

Polysaccharides such as cellulose and chitosan (CS), as valuable and renewable resources, have been widely applied for the composite photocatalysts. (Zhao *et al.* 2011) used chitosan-TiO₂ as catalysts to decolorize methyl orange solution under UV light. (Obeid *et al.* 2013) used chitosan/maghemite composites as catalysts to degrade methyl orange. Moreover, xylan belongs to the hemicellulose cell wall components of all plants, and it is the most abundant polysaccharide in nature after cellulose. However, there is no report on the application of xylan and CS as composite photocatalysts with perovskite-type oxides.

From perovskite-type oxides mentioned above, metal oxides (iron oxide) as well as the rare earth metals have the good photocatalysis performance. In this work, we prepared perovskite-type oxides LaFe_{0.8}Cu_{0.2}O₃ by sol-gel method and synthesized two kinds of composite photocatalysts (xylan/LaFe_{0.8}Cu_{0.2}O₃ and CS/LaFe_{0.8}Cu_{0.2}O₃) by cross-linking reaction to form composite films. Physical and chemical properties of the composite films were investigated by X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), ultraviolet visible spectra (UV-vis), and BET method. These two composite films were evaluated relative to photocatalytic degradation of methyl orange under ultraviolet irradiation (365 nm).

EXPERIMENTAL

Materials

La(NO₃)₂·6H₂O was purchased from Aladdin. Fe(NO₃)₂·9H₂O, sodium hypophosphite (SHP), and methyl orange were obtained from Tianjin Damao Chemical Reagent CO., Ltd. Cu(NO₃)₂·3H₂O was provided by Guangzhou Chemical Reagent Factory. NaOH, ethyl alcohol, and acetic acid were purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Citric acid, ethylene glycol, and glutaric dialdehyde were bought from Shanghai Lingfeng Chemical Reagent CO., Ltd. Xylan was obtained from Sigma-aldrich CO., Ltd. Ultrapure water was used throughout the study.

Preparation of Perovskite-Type Oxides and Composite Films

LaFe_{0.8}Cu_{0.2}O₃ was prepared by sol-gel method (Li *et al.* 2013). La(NO₃)₂·6H₂O (0.1 mol), Fe(NO₃)₂·9H₂O (0.08 mol), and Cu(NO₃)₂·3H₂O (0.02 mol) were added into ultrapure water to form homogeneous solution. Then, citric acid (the molar ratio of citric acid to La³⁺ of 1.5:1) and ethyl alcohol (the ethylene glycol/citric acid ratio of 1.5:4, mL/g) were added into the solution. After that, the mixture was dried at 110 °C overnight and calcined at 700 °C for 6 h. And then desired perovskite structures were obtained.

CS/LaFe_{0.8}Cu_{0.2}O₃ composite films were prepared by the following cross-linking reaction. A certain weight ratio of chitosan and perovskite powder (1:2, 1:1 and 2:1, w/w) were added to 10-mL acetic acid solution (2%) and ultrasound for 2 h. After that, the mixture solution was poured into a glass plate to form film at 55 °C. The prepared film was congealed in the 0.2-mol/L NaOH solution and then soaked in 0.25% glutaric dialdehyde for 30 min. The composite films were washed with ethyl alcohol and water for several times and dried at 110 °C to get the target product.

Xylan/LaFe_{0.8}Cu_{0.2}O₃ composite films were prepared by the cross-linking reaction. 0.6 g of xylan and 0.2 g of SHP were added into 8-mL ultrapure water at 60 °C. 2.4 g of citric acid was dissolved in 2-mL ultrapure water, and then perovskite powder (the Xylan/LaFe_{0.8}Cu_{0.2}O₃ ratio of 1:2, 1:1, and, 2:1 w/w) was added. The above mixture was ultrasonicated for 20 min and then dried at 100 °C for 30 min. After that, temperature was elevated to 120 °C and kept for 5 h. Products were washed by 70% and 95% ethyl alcohol, respectively. Finally, the product was dried at 50 °C for 24 h.

Characterizations of Photocatalysts

Fourier transform infrared (FTIR) spectra were recorded on a TENSOR27 spectrometer (Bruker, Germany) at room temperature. The X-ray power diffraction (XRD) pattern was measured with a D8 Advance (Bruker, Germany) device. Scanning electron microscope (SEM) images were taken on an S-3700N (Hitachi, Japan) instrument. UV-visible spectra were obtained with a UV2550 ultraviolet spectrophotometer (Shimadzu, Japan). Specific surface area was measured by Gemini VII 2390 (Micromeritics, USA). Surface area (S_{BET}) of samples were measured by N₂ adsorption using a Micromeritics ASAP 2010 instrument at 77 K and calculated from the adsorption data in the relative pressure range from 0.05 to 0.30.

Photocatalytic Degradation Experiments

Photocatalytic reactions were carried out in a XH-300UL instrument (Xianghu, Beijing). 100-mL methyl orange solution (15 mg/L) was placed in a 250 mL quartz flask, and then photocatalysts were added. The photocatalytic degradation experiments were

carried out under ultraviolet irradiation (365 nm) at different intervals. After a required time, the filtrate was measured by ultraviolet spectrophotometer at 464 nm for 3 times to reduce standard errors. Concentration of methyl orange was calculated as follows:

$$\text{Concentration of methyl orange (mg/L)} = 13.49 \times \text{Abs} - 0.071 \quad (1)$$

And then, the degradation efficiency of methyl orange was calculated as follows:

$$\text{Degradation efficiency of methyl orange (\%)} = \frac{15 - C(\text{MO})}{15} \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of CS and CS/LaFe_{0.8}Cu_{0.2}O₃ composites are presented in Fig. 1a. An absorption band at 560 cm⁻¹ corresponded to the band of Fe-O in LaFe_{0.8}Cu_{0.2}O₃ (Gosavi and Biniwale 2010; Pecchi *et al.* 2008). Bands located at 1668 cm⁻¹, 2873 cm⁻¹, 3417 cm⁻¹, and 1055 cm⁻¹ were attributed to the N-H stretch, CH₂ stretch, O-H stretch, and secondary alcohol C-O stretch of chitosan, respectively (Jiang *et al.* 2012). The spectra of composite films were similar to that of chitosan, and the band of Fe-O is present in CS/LaFe_{0.8}Cu_{0.2}O₃ composite films. This indicated that the composites contained CS and LaFe_{0.8}Cu_{0.2}O₃.

The FTIR spectra of xylan/LaFe_{0.8}Cu_{0.2}O₃ are presented in Fig. 1b. Bands at 1051 cm⁻¹, 1168 cm⁻¹, 1400 cm⁻¹, 2918 cm⁻¹, and 3450 cm⁻¹ correspond to the stretches of C-O, C-C, C-O-C, and C-H in methyl and methylene, as well as CH₂ and O-H in xylan, respectively.

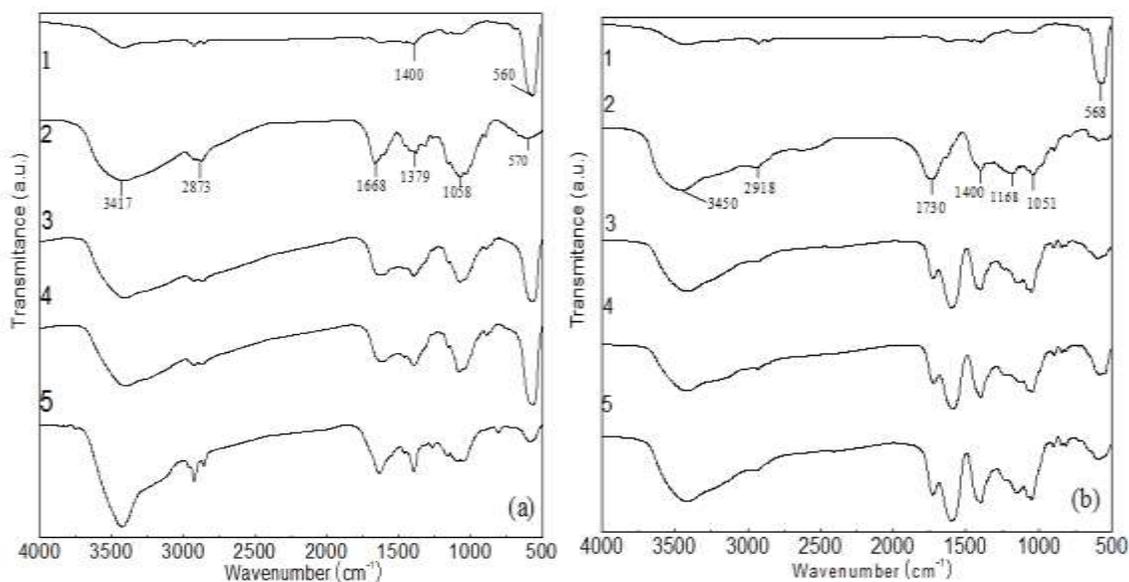


Fig. 1. FTIR spectra of composite films (a) CS/LaFe_{0.8}Cu_{0.2}O₃ (a1:LaFe_{0.8}Cu_{0.2}O₃; a2:CS; a3:CS/LaFe_{0.8}Cu_{0.2}O₃=1:1; a4:CS/LaFe_{0.8}Cu_{0.2}O₃=1:2; a5:CS/LaFe_{0.8}Cu_{0.2}O₃=2:1). Composite films (b) xylan/LaFe_{0.8}Cu_{0.2}O₃ (b1:LaFe_{0.8}Cu_{0.2}O₃; b2:xylan; b3:xylan/LaFe_{0.8}Cu_{0.2}O₃=1:1; b4:xylan/LaFe_{0.8}Cu_{0.2}O₃=1:2; b5:xylan/LaFe_{0.8}Cu_{0.2}O₃=2:1)

For spectra 3b-5b, the absorption band at 568 cm^{-1} in the spectra of xylan/perovskite composites with different weight ratios. A new signal at 1603 cm^{-1} is ascribed to the COO^- group produced by the cross-linking reaction of xylan with citric acid, and the new band around 1412 cm^{-1} is assigned to CO stretching on $-\text{COOH}$ groups (Wang *et al.* 2013). The band at around 1730 cm^{-1} is indicative of ester groups (carbonyl groups) in spectra 3b-5b. So the composites were confirmed to have cross-linked xylan and $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$.

X-ray Diffraction Analysis

The XRD patterns of samples are shown in Fig. 2. Diffraction peaks at 22.74° , 32.41° , 39.88° , 46.88° , 57.38° , 67.50° , and 76.71° were attributed to the specific diffractions of $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (Mo *et al.* 2013). Two peaks at 10.53° and 19.89° were ascribed to chitosan (Liu *et al.* 2013). Characteristic peaks of chitosan observed in $\text{CS}/\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ with different weight ratios (1:1, 1:2, and 2:1) indicated that the composite films were prepared successfully. From Fig. 2b, an obvious peak at 19.11° was attributable to xylan. For spectra 3b-5b, the diffraction peaks of $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ were present, and the crystal peak at 19.11° disappeared, indicating that the structure of xylan changed after cross-linking reaction. Those meant that the $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ had been inserted in the composite films.

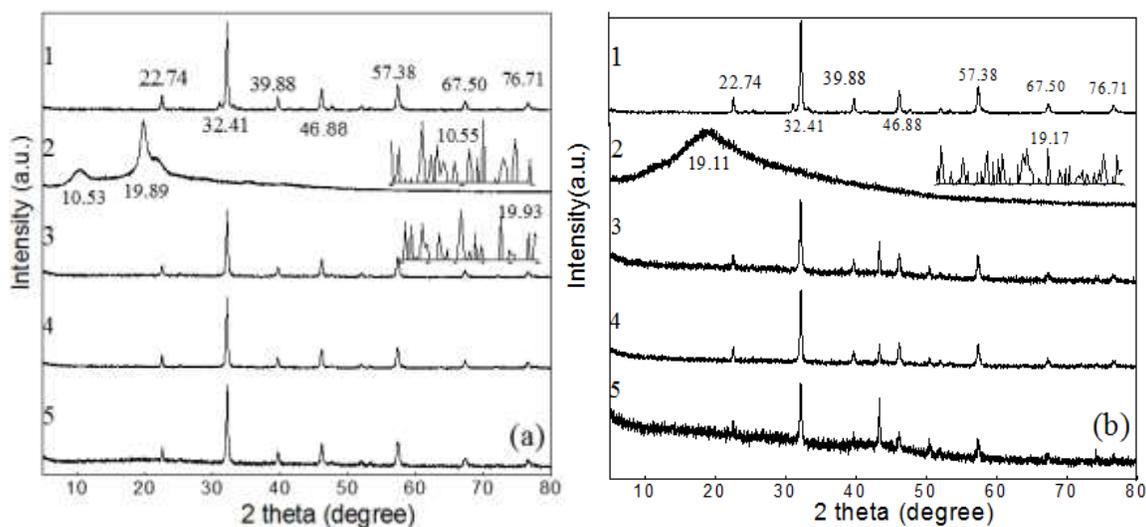


Fig. 2. XRD spectra of composite films (a) $\text{CS}/\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (a1: $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$; a2: CS; a3: $\text{CS}/\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=1:1$; a4: $\text{CS}/\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=1:2$; a5: $\text{CS}/\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=2:1$). Composite films (b) xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (b1: $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$; b2: xylan; b3: xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=1:1$; b4: xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=1:2$; b5: xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3=2:1$)

SEM and BET Analysis

Figure 3 shows the SEM images of the ground samples. Small particles of $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ and compact morphology of chitosan were observed, which implied that the $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ was likely to have had a larger surface area. Moreover, after the combination of polysaccharides (CS and xylan) with $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$, pore structure was formed, and many small particles were present at the surface of amorphous solids.

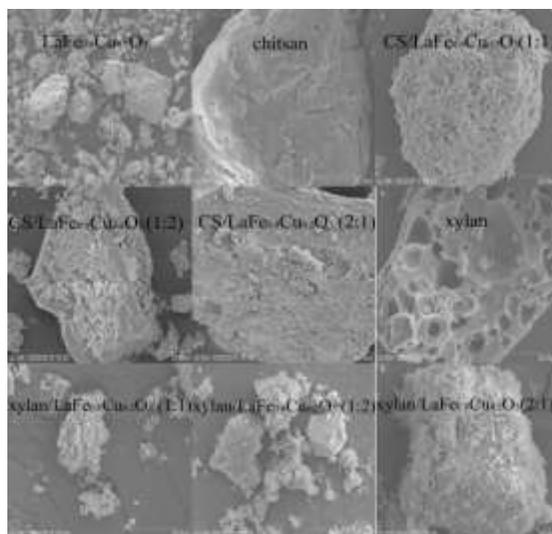


Fig. 3. SEM of prepared catalysts

The BET area of the prepared catalysts is presented in Table 1. LaFe_{0.8}Cu_{0.2}O₃ showed the largest surface area (9.37 m²/g), which was consistent with the SEM results. When the weight ratio of polysaccharides to LaFe_{0.8}Cu_{0.2}O₃ was 1:2, a higher specific surface area was obtained in composite films.

Table 1. BET of Composite Films

| Sample | w/w | Specific surface area (m ² /g) |
|---|-----|---|
| LaFe _{0.8} Cu _{0.2} O ₃ | - | 9.37 |
| chitosan film | - | 0.37 |
| CS /LaFe _{0.8} Cu _{0.2} O ₃ | 1:1 | 5.03 |
| CS /LaFe _{0.8} Cu _{0.2} O ₃ | 1:2 | 7.56 |
| CS /LaFe _{0.8} Cu _{0.2} O ₃ | 2:1 | 3.12 |
| xylan film | - | 0.88 |
| xylan /LaFe _{0.8} Cu _{0.2} O ₃ | 1:1 | 4.71 |
| xylan /LaFe _{0.8} Cu _{0.2} O ₃ | 1:2 | 7.83 |
| xylan/LaFe _{0.8} Cu _{0.2} O ₃ | 2:1 | 1.53 |

Photocatalytic Activities of Catalysts

The photo-degradation experiments were carried out under UV irradiation as shown in Fig. 4. 50 mg of catalysts were added into 100 mL methyl orange solution (15 mg/L). The degradation rate increased with the increasing irradiation time. In comparison with xylan/LaFe_{0.8}Cu_{0.2}O₃ composite films, the chitosan/LaFe_{0.8}Cu_{0.2}O₃ system showed better catalytic ability for the degradation of methyl orange. The rate of degradation increased dramatically with growth in photocatalytic reaction time. When the ratio of CS to LaFe_{0.8}Cu_{0.2}O₃ was 2:1, the largest degradation rate of 67% was achieved in 480 min, and then it flattened out with prolonging irradiation time. For xylan/LaFe_{0.8}Cu_{0.2}O₃, increasing irradiation time led to an increment of the degradation rate. When the weight ratio of xylan and LaFe_{0.8}Cu_{0.2}O₃ was 1:1, the maximum degradation rate of 58% was obtained in 480 min. The difference in the methyl orange degradation rate for CS/

$\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ and xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ was due to the various structure of nature macromolecules. Chitosan is a natural resource with positive charge and high molecular weight (Cestari *et al.* 2004). $-\text{OH}$ and $-\text{NH}_2$ groups endow chitosan with the ability to adsorb and to engage in chelation. Compared with xylan, chitosan is a more suitable material for preparing the composite photocatalysts.

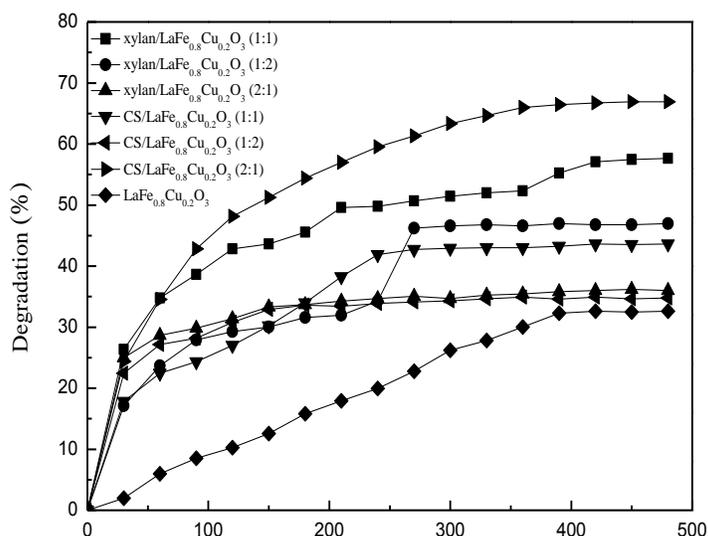


Fig. 4. Photo-degradation performance of different photocatalysts

The photocatalytic efficiency of a catalyst is based on three aspects: adsorption ability, quantum efficiency of the photo-generation of the electron-hole pair, and the separation speed of electron-hole pair. Under UV irradiation, electrons in Fe_2O_3 and CuO may transfer from valence band (VB) to conduction band (CB), which forms large number of active electrons and holes with high reducibility and oxidability. The co-operation of Fe_2O_3 , CuO , and La_2O_3 benefits the transformation of electrons and holes so that they could shift to the surface of catalysts to react with methyl orange. Hence, the decomposition of methyl orange occurs.

CONCLUSIONS

1. In summary, the two described polysaccharides/perovskite-type oxides composite films ($\text{CS/LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ and $\text{xylan/LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$) were synthesized successfully via cross-linking reactions, and the photo-degradation ability of each for methyl orange was investigated under UV irradiation.
2. Results showed that the addition of polysaccharides could greatly enhance the catalytic ability of $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$. When the weight ratio of CS to $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ was 2:1, the highest degradation rate of 67% was obtained in 480 min. And the maximum degradation rate of 58% for xylan/ $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ (1:1) was achieved in 480 min.

- This study provides an efficient strategy to solve dyeing pollution problems using new photocatalysts for industrial applications.

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