Journal of the Taiwan Institute of Chemical Engineers 62 (2016) 187–191

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Rapid photodegradation of methyl orange by oxalic acid assisted with cathode material of lithium ion batteries $LiFePO_4$

Jing Guo, Jiao Zhang, Cheng Chen, Yeqing Lan*

College of Sciences, Nanjing Agricultural University, Nanjing 210095, PR China

ARTICLE INFO

Article history:
Received 17 August 2015
Revised 26 January 2016
Accepted 2 February 2016
Available online 28 February 2016

Keywords:
Lithium iron phosphate
Oxalic acid
Photocatalytic degradation
Methyl orange

ABSTRACT

The present study investigated the application of the $LiFePO_4$ (LFP) cathode material for lithium ion batteries as a photocatalyst in the photodegradation of methyl orange (MO) by oxalic acid (Oxa, $H_2C_2O_4$). The photocatalytic role of LFP for different initial pH values as well as different concentrations of LFP, Oxa, and MO was examined. The results show that, while the decomposition of MO by either LFP or Oxa under ultraviolet light is difficult, MO removal is significantly enhanced when both LFP and Oxa coexist in the reaction system. In particular, high initial concentrations of Oxa and LFP appear to be beneficial for the degradation of MO. The optimal MO degradation efficiency was achieved at pH 4. The role of photoproduction intermediates was also investigated. Scavenging experiments using tertiary butyl alcohol, an $^\cdot OH$-specific radical scavenger, and L-histidine, a universal radical scavenger, corroborated the suggestion that other oxidative free radicals besides $^\cdot OH$ are also involved in the MO degradation. A possible reaction mechanism for the photocatalytic degradation of MO by LFP and Oxa was proposed. This study thus provides a direct route for the reutilization of the cathode material LFP as a photocatalyst in the photodegradation of organic contaminants by low-molecular weight organic acids.

1. Introduction

The recent years have witnessed a vast increase in the use of lithium ion batteries (LIBs), which have become the main power supplies in electric vehicles and portable electronics such as laptops and mobile phones [1]. In line with the increasing demand from the electronics industry and the rapid replacement of electronic products, the production of LIBs is in continuous expansion, with a corresponding growth in the number of spent batteries disposed in landfills, which in turn leads to serious environmental contamination from metals leaching from the batteries. Therefore, the recovery and reutilization of battery components, especially the highly valuable cathode materials of the discarded LIBs, has become an important and urgent issue.

Lithium iron phosphate ($LiFePO_4$, LFP) has been widely adopted as the cathode material in the LIBs of electric vehicles [2,3], because of favorable properties, such as significant theoretical capacity, thermal stability, excellent reversibility, low cost, and environmental benignity [4]. Spent LIBs must be fully discharged before any recycling process. However, after hundreds of charging and discharging cycles, the cathode material cannot be directly reused for battery fabrication, but must be first recycled as metal salts and then resynthesized as cathode material. The two main steps to obtain the metal salts from insoluble LFP, *i.e.*, dissolution under specific conditions and selective chemical precipitation, require large quantities of chemicals [1,5].

The photodegradation of organic compounds is one of the most promising advanced oxidation processes (AOPs). These processes have emerged and become accepted over the past decades as efficient means for the degradation of toxic and recalcitrant organic compounds [6–9]. These reactions involve the generation of hydroxyl radicals ($^\cdot OH$, $E^0 = +2.80$ V versus NHE), which can quickly and non-selectively oxidize most organic molecules, mineralizing them to CO_2, H_2O and inorganic species [10,11].

Previous studies of the photodegradation of organic contaminants have demonstrated that the photoexcitation of Fe(III)-carboxylate complexes can result in the formation of Fe(II) and $^\cdot OH$ through a ligand-to-metal charge transfer (LMCT) path [8–10]; the Fe(III)/Fe(II) couple and organic carboxylic acids, coexisting in natural environments, can set up a photo-Fenton system [12]. Recently, we proved the feasibility of the photodegradation of an azo dye with low-molecular weight organic acids catalyzed by schwertmannite ($Fe_8O_8(OH)_x(SO_4)_y$, $x = 8 - 2y$, $1 < y < 1.75$), which is a common and often abundant Fe mineral [12,13]. These previous insights provide a compelling rationale to explore the use of discarded LFP cathode material as a photocatalyst in the photodegradation of organic contaminants by low-molecular weight organic acids.

---

* Corresponding author. Tel.: +86 25 84396697; fax: +86 25 84395255.
E-mail address: guojingjoy@outlook.com, lanyq102@njau.edu.cn (Y. Lan).

http://dx.doi.org/10.1016/j.jtice.2016.02.003

In this study, the use of LFP as a photocatalyst in the photodegradation of an azo dye by oxalic acid (Oxa, $H_2C_2O_4$) was investigated for the first time. Azo dyes, which are toxic refractory organic pollutants due to their aromatic character and the stability of their azo bonds, constitute a significant portion of the waste produced in the textile and leather industry [14,15]. Methyl orange (MO) was used as a model azo dye to monitor the photocatalytic activity of LFP and Oxa.

2. Materials and methods

2.1. Materials

MO was purchased from Beijing Chemical Reagents Company (Beijing, China), and LFP was obtained from Xiya Reagents Company (Chengdu, China). Oxa was supplied from Xilong Chemical Co., Ltd (Shantou, China). The stock solutions of MO and Oxa were prepared in deionized water. Tertiary butyl alcohol (TBA, Chengdu Kelong Chemical Reagent Factory, Chengdu, China) and L-histidine (L-h, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) served as scavengers to determine the production of relevant radicals. All the glassware used in this study was soaked in 1 M HNO_3 solution for 12 h, and thoroughly cleaned with tap water and deionized water.

2.2. Photocatalytic degradation experiments

All photocatalytic degradation experiments were conducted in an open, cylindrical 50 mL quartz tube under magnetic stirring. The reaction solutions were always freshly prepared, and the initial pH was adjusted with dilute H_2SO_4 and NaOH.

Batch photocatalytic experiments were performed in an XPA-7 photochemical reactor (Xujiang electromechanical plant, Nanjing, China). A schematic diagram of the experimental setup was shown in our previous work [16]. Ultraviolet (UV) light sources including 100, 300, and 500 W medium-pressure Hg lamps were positioned inside a cylindrical Pyrex jacket and cooled by circulating water, and the light intensities at the position of quartz tubes (reaction system) corresponding to the 100, 300, and 500 W medium-pressure Hg lamps (measured by UV-A irradiation meter, Beijing Normal University, China) were 12.7, 16.8, and 20.1 mW/cm^2, respectively.

The procedure of degradation experiments including the adsorption equilibrium of MO on LFP in dark and the photocatalytic degradation with illumination was introduced in our previous work [13].

2.3. Analytic methods

A CyberScan pH2100 Bench Meter (Eutech Instruments Pte Ltd., Ayer Rajah Crescent, Singapore), was used to measure the pH values for different reaction solutions after three-point calibration. The method of sampling and filtration was stated in our published paper [10].

The absorbance of MO solution was measured at the characteristic λ_{max} of 464 nm using a UV-VIS spectrophotometer (Alpha-1052+, Shanghai Lab-Spectrum Instruments Company, Shanghai, China). Our preliminary study showed that the λ_{max} of MO solution kept the same in a pH range of 4–8, so the filtrated MO sample was diluted with HAc-NaAc buffer (pH 5) before analysis to avoid λ_{max} shift. And the concentration of Fe(II) was quantitatively analyzed by a colorimetric method using *o*-phenanthroline [10]. To eliminate the effect of MO on the measured Fe(II)-*o*-phenanthroline absorbance, the latter was calculated according to the following equation:

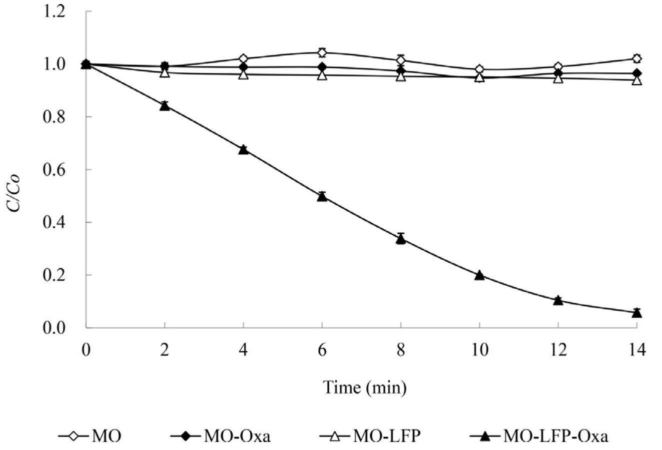

Fig. 1. Photodegradation of MO under varying experimental conditions: $[MO]_0 = 50\ mg{\cdot}L^{-1}$, $[LFP]_0 = 20\ mg{\cdot}L^{-1}$, $[Oxa]_0 = 2\ mmol{\cdot}L^{-1}$, $pH_{ini} = 4.0$, $T = 25\ °C$, under the full light of a 300 W medium-pressure Hg lamp.

$$\mathrm{Abs}(\mathrm{Fe(II)} + o\text{–phenanthroline}) = \mathrm{Abs}(\mathrm{Fe(II)} + o\text{–phenanthroline} + \mathrm{MO}) - \mathrm{Abs}(\mathrm{MO}) \qquad (1)$$

(where Abs represents the measured absorbance)

3. Results and discussion

3.1. Photodegradation of MO by LFP and Oxa

To evaluate the photodegradation performance of LFP and Oxa, MO was selected as a model organic contaminant, and its degradation in varied reaction systems was investigated. The results illustrated in Fig. 1 demonstrate that UV irradiation alone did not lead to MO removal after 14 min, whereas only slight MO degradation was observed in the UV-Oxa and UV-LFP reaction systems. On the other hand, more than 94% of the initial MO was decomposed in the UV-LFP-Oxa system, suggesting that LFP could be an excellent photocatalyst for MO degradation by Oxa.

The degradation of MO in the UV-Oxa system is attributed to the oxidants (*e.g.*, H_2O_2 and some free radicals) that are possibly produced through the photolysis of Oxa [7,13,17,18]. Possible reactions leading to the removal of MO by Oxa under UV irradiation were described as in Eqs. (2)–(7):

$$H_2C_2O_4 + O_2 + h\nu \rightarrow H_2C_2O_4^{\bullet +} + O_2^{\bullet -} \qquad (2)$$

$$MO + O_2^{\bullet -} \rightarrow \text{products} \qquad (3)$$

$$H^+ + O_2^{\bullet -} \rightarrow HO_2\bullet \qquad (4)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \qquad (5)$$

$$H_2O_2 + h\nu \rightarrow 2\bullet OH \qquad (6)$$

$$MO + \bullet OH \rightarrow \text{products} \qquad (7)$$

Some MO photodegradation in the UV-LFP system (whose efficiency was ~6% within 14 min) is due to the dissolution of Fe(II) from LFP in an acidic solution. The dark control experiment highlighted a certain amount of Fe(II) leaching out of LFP during the 30 min equilibration period, which then slightly increased upon addition of Oxa (Fig. S1). Since the reaction was carried out in an open cylindrical quartz tube, some amount of Fe(II) from LFP was oxidized to Fe(III) by dissolved oxygen. It has been reported that at least four different species of Fe(III) ions can exist in aqueous solution: Fe^{3+}, $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$, and the dimer $[Fe_2(OH)_2]^{4+}$ (Fig. S2), among which the $[Fe(OH)]^{2+}$ species possess favorable