

Removal of trichloroethylene from water with LaFeO₃ as photocatalyst

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Introduction

Anthropogenic discharge of organic compounds has resulted in serious water pollution. In Taiwan, trichloroethylene (TCE) is ranked as second common organic pollutant in groundwater and USEPA has classified TCE as a human carcinogen. Thus, there is an urgent need to eliminate TCE from water bodies. Photocatalytic oxidation is one of the advanced oxidation processes (AOPs) and TiO₂ is the most commonly applied photocatalyst. However, due to the limitation of TiO₂ absorption edge, its development and applicability are strictly limited. Recently, perovskite-type photocatalysts have been found with high photocatalytic activity under visible light irradiation. LaFeO₃ has many applications, such as for photocatalysis, catalytic oxidation and surface electronic states (Stoerzinger et al., 2017). Peng et al. (2016) evaluated the photocatalytic activity of LaFeO₃/montmorillonite for degradation of Rhodamine B under visible light irradiation and indicated that overall removal efficiency of Rhodamine B was up to 99.34% with 90 min of irradiation. LaFeO₃ could overcome the disadvantages of the TiO₂ and expand its applicability in environmental engineering field.

The aim of this study is to evaluate the feasibility of LaFeO₃, a perovskite-type photocatalyst, for the degradation of aqueous-phase TCE via heterogeneous oxidation. Besides, the stability of the system and the effects of the initial TCE concentration, photocatalyst loading, light intensity and pH value on TCE removal are investigated in detail. Structure of LaFeO₃ is characterized and the possible TCE degradation mechanism will be elucidated in the research.

Materials and methods

LaFeO₃ catalysts were prepared by a sol-gel method. Characterization of LaFeO₃ was conducted with N₂-ASAP, SEM and TEM, and UV-vis. The E_g (Eq 1) represents the optical band gap energy (eV) of LaFeO₃, 1240 is the product of Plank constant and light speed while λ is the absorption edge wavelength (nm).

$$E_g = 1240 / \lambda \dots\dots\dots(1)$$

The photocatalytic experiment was carried out with a quartz reactor as shown in **Figure. 1**. A water circulation jacket was coupled to maintain constant temperature ($22 \pm 2^\circ\text{C}$) of the reactor. Photocatalytic activities of the LaFeO_3 were evaluated by the photocatalytic degradation of TCE in aqueous solution with a Xenon lamp which was located in the center of the reactor. The TCE removal efficiency was evaluated by setting various initial TCE concentrations (i.e., 0.5, 1, 5, 10, 20, 50 mg/L), photocatalyst loadings (i.e., 0.5, 1 and 2 g/L) and pH value (i.e., pH 4, pH 7 and pH 11) as operating parameters. Additionally, the removal efficiency of TCE contributed by light photolysis is evaluated in the operating conditions of 15 mg/L TCE with a 250W Xenon lamp. Each batch experiment was triplicated. The aqueous sample was filtered with a membrane and extracted by liquid-liquid extraction with DCM with fluorobenzene as internal standard then analyzed by GC/MS. The removal efficiency, the photocatalytic degradation efficiency and photodegradation efficiency are calculated by Equation 2 (**Eq 2**), Equation 3 (**Eq 3**) and Equation 4 (**Eq 4**), respectively where C_0 and C_t represent the concentration of TCE (mg/L) at time 0 and time t, respectively, and C_a denotes the concentration of TCE (mg/L) adsorbed on the LaFeO_3 photocatalysts during photocatalytic degradation experiment. C_t' represents the concentration of TCE (mg/L) at time t with the direct photodegradation (i.e., without photocatalyst).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \dots\dots\dots(\text{Eq 2})$$

$$\text{Photocatalytic degradation efficiency (\%)} = \frac{C_0 - C_a - C_t}{C_0} \times 100\% \dots\dots\dots(\text{Eq 3})$$

$$\text{Photodegradation efficiency (\%)} = \frac{C_0 - C_t'}{C_0} \times 100\% \dots\dots\dots(\text{Eq 4})$$

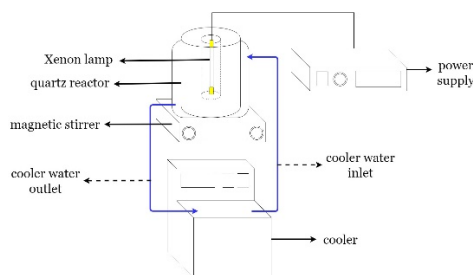


Figure 1. Schematic diagram of the photocatalytic reactor

Results and discussion

The result of XRD analysis indicates that LaFeO_3 catalyst has been successfully synthesized and is in good

agreement with that of the standard JCPDS card (No. 37-1493). The BET surface area and pore size of LaFeO_3 particles calcined at 600°C are $18.9\text{ m}^2/\text{g}$ and 13.7 nm , respectively. Compared with previous studies, the surface area of the LaFeO_3 particles prepared in this study is higher than that reported in other studies ($5.2\text{--}15.4\text{ m}^2/\text{g}$). Both higher surface area and pore volume can provide more surface active sites and make reactants transport easier, resulting in the enhancement of photocatalytic performance. Figure 2a-2c present the SEM and TEM images of LaFeO_3 particles, indicating that the pore distribution of LaFeO_3 is uniform and aggregation of the particles is not severe (Figure 2a). Besides, the diffuse reflectance spectrum of LaFeO_3 is used to calculate the band gap based on the absorption edge observed at 611 nm from the tauc plot and $E_g = 2.03\text{ eV}$ is calculated based on Eq 1. The absorption edge at 611 nm indicates that LaFeO_3 catalyst could serve as a potential visible-light-driven photocatalytic material.

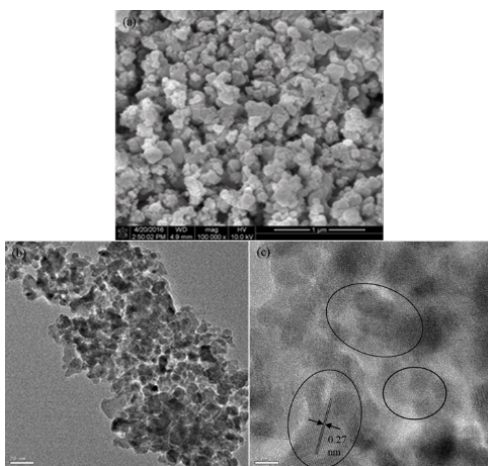


Figure 2. (a) SEM (b) TEM 100,000X (c) TEM 400,000X images of LaFeO_3 particles

The blank test was carried out by reacting 1 mg/L TCE without LaFeO_3 in dark for 2 hr . The results indicate that the TCE concentration can be maintained at 1 mg/L with the $\text{RSD} < 10\%$, indicating that TCE removal efficiency would not be overestimated in spite of vigorously stirring. The effects of initial TCE concentration, photocatalyst loading and pH value on TCE removal are evaluated and the results indicate that by increasing the photocatalyst loading and pH would favor the photocatalysis reaction, resulting in higher TCE removal efficiency. Additionally, the TCE removal efficiency decrease with increasing the initial TCE concentration since more TCE

would saturate the pore on the surface and interior of the LaFeO_3 , resulting in a dramatic reduction in the number of radical hydroxides ($\text{OH}^\cdot$) and superoxide ($\text{O}_2^{\cdot-}$). TCE removal via different mechanisms are shown in Figure 3a. The results indicate that almost 20% TCE can be adsorbed on LaFeO_3 photocatalysts. The photodegradation efficiency of TCE is 39% and it proves that TCE can be degraded directly by light. Besides, photocatalytic degradation is calculated from the removal efficiency which excludes adsorption efficiency and the results indicate that the photocatalytic degradation efficiency of TCE is 62% which is much higher than the photodegradation efficiency (39%). It proves that the LaFeO_3 prepared in this study can improve the photodegradation efficiency since more active radicals are formed in the photocatalytic process. Interestingly, the synergistic effect of photocatalyst is observed during this experiment. As shown in Figure 3, the percentage of Cl^- ions released from TCE achieves 84% and it suggests that dechlorination of TCE takes place in this system. In addition, reduction of pH value and Cl^- release prove that HCl is the main product of TCE degradation via photocatalytic process.

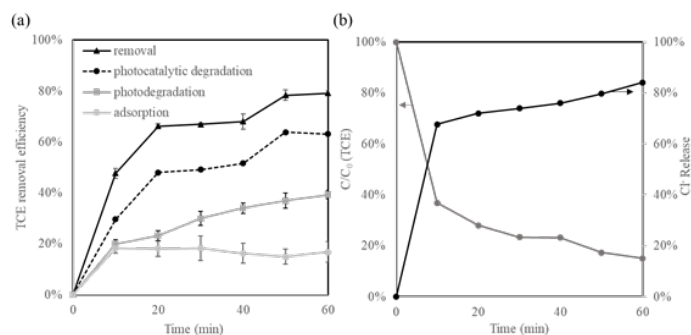


Figure 3. Comparison of (a) removal efficiencies contributed by adsorption, photodegradation and photocatalytic degradation and (b) degradation of TCE and Cl^- release of TCE over LaFeO_3 photocatalyst

Acknowledgments

This study was financially supported by Taiwan EPA and MOST (Project no. MOST-105-2221-E-008-006-MY3)

References:

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