Modified ilmenite as catalyst for CWPO-Photoassisted process under LED light

P. García-Muñoz, G. Pliego, J.A. Zazo, B. Barbero, A. Bahamonde, J.A. Casas, Línea en blanco, 1

Sección departamental de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

Instituto de Investigaciones en Tecnología Química (INTEQUI), UNSL–CONICET, Chacabuco 917, D5700BWS San Luis, Argentina

Instituto de Catálisis y Petroquímica (CSIC), C/Marie Curie, 2, 28049 Madrid, Spain

Highlights

- Raw ilmenite was treated to evaluate the influence of iron oxidation state.
- The co-presence of different iron oxidation states led to a faster mineralization.
- Phenol total conversion and 95% of TOC removal was reached in all cases.
- Long-term experiments confirmed the stability of these materials.

Abstract

The influence of the iron chemical nature contained in ilmenite (FeTiO₃) upon the activity and stability of these materials as catalysts for CWPO-Photoassisted process under LED light (λ: 405 nm) were evaluated. Raw ilmenite was treated with H₂ within the range 25–1000 °C in order to partially reduce iron oxides to Fe(0). The catalysts were characterized by N₂ adsorption/desorption, TXRF, XRD and XPS analysis. The co-presence of different iron species (Fe(0), Fe(II) and Fe(III)) along with the light effect over material surface, led to an increase of H₂O₂ decomposition rate into HO⁻ and, therefore, a higher oxidation rate. In all case, after total H₂O₂ depletion, a complete phenol degradation and a 95% TOC conversion was reached in batch at pH = 3 and 50 °C using the stoichiometric H₂O₂ dose (14 mol H₂O₂/mol phenol) and 10 W m⁻² LED light. Long-term continuous experiments were carried out to assess the stability and the lifetime of the catalyst. The higher reduction degree led to a higher organic matter mineralization but also to a higher leaching of active phase around 3% of the total iron amount in ilmenite. Nevertheless, catalyst deactivation seems to be related to the oxidation of iron on the catalyst surface.

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1. Introduction

Nowadays, water pollution concerns a major issue of increasing importance. The water scarcity beside to the increasingly presence of refractory pollutants force the policymakers to enact stringent wastewater regulation to control the discharge of toxic and non-biodegradable organic compounds in waterbodies.

The EU Water Framework Directive [1] establishes a list of priority pollutants that must receive a special attention to be removed from water because their variety, toxicity and persistence impact the health of ecosystems. Among them, phenols are well known for their bio-recalcitrant and toxicity. They are continuously introduced into the aquatic environment as a result of several industries activities such as the manufacture of pesticides, biocides, resins,
dyes, pharmaceuticals. Due to their importance, it has become a challenge to achieve the effective removal of persistent organic pollutants from wastewaters to minimize the risk of pollution problems [2–6].

Advanced Oxidation Processes (AOPs) have been successfully applied for the removal or degradation of a wide variety of recalcitrant pollutants in water. AOPs involve the generation of HO· radicals that are able to oxidise the organic chemical compounds up to CO₂ and H₂O. Among these processes, Catalytic Wet Peroxide Oxidation (CWPO) and photocatalysis have demonstrated their effective to remove pollutants. Because of its iron and titanium content, ilmenite results a promising solid for CWPO and photocatalysis treatments [3,7–10]. Nevertheless, it shows significant drawbacks related to a high induction period (in CWPO) and lower activity, due to a high electron-hole recombination (in photocatalysis). A previous work [10] proved the combination of both technologies, in the so-called CWPO-Photoassisted process, decreases the induction period, because of the role of UV in the Fe(II)/Fe(III) cycle. Despite this, the catalytic activity of ilmenite was lower when compared to other heterogeneous catalysts [11,12]. In this work, Temperature Programmed Reduction (TPR) is proposed to vary the Fe(II)/Fe(III) ratio on ilmenite surface, increasing the percentage of reduced iron species, which could enhance its catalytic activity.

In addition, light source is the other key point on CWPO-Photoassisted processes. In this sense, Light Emitting Diodes (LEDs) represent a reliable and feasible choice to replace conventional light sources in many applications. The main advantages include high photon efficiency, low voltage electrical power source, power stability, emission in broader spectral wavelength, and no need for cooling during long time operation for complete photocatalytic reactions [13,14].

Therefore, the aim of this work is to study the influence of reduction treatment (in H₂ atmosphere) on the physical and chemical properties of ilmenite as well as on their catalytic activity and stability for CWPO-Photoassisted process under LED light (405 nm).

2. Materials and methods

2.1. Catalysts physico-chemical characterization

The textural properties of the catalysts were determined by means of nitrogen adsorption–desorption isotherms at −196 °C using a Micromeritics Tristar 3020 apparatus. The samples were previously outgassed overnight at 150 °C to a residual pressure of 10⁻³ Torr.

The ilmenite composition was obtained by total reflection X-ray fluorescence (TXRF), using a TXRF spectrometer 8030c. The crystalline phases were analyzed by X-ray diffraction (XRD) with a diffractometer (Siemens model D-5000) with Cu Kα radiation. To determine the oxidation state of Fe and Ti, the solids were also characterized by X-ray Photoelectron Spectroscopy (XPS) using a K-Alpha – Thermo Scientific equipped with a AlKα X-ray excitation source, (1486.68 eV). XPS data was fitted by XPSpeak 4.1.

2.2. CWPO-Photoassisted runs

CWPO-Photoassisted runs were performed in a counter-flow quartz concentric tubular reactor (100 mL useful volume). The aqueous solution (phenol and H₂O₂) and the catalyst coursed through the intermediate wall. Both were continuously recirculated (with a peristaltic pump) to maintain the catalyst suspended. A commercial LED strip (SMD 5050) was placed around the external wall of the reactor. The irradiance corresponding to LED radiation was 10 W·m⁻². LED light emits at 405 nm with a power of 48 W.

All the experiments were carried out at 50 °C, an initial pH of 3 with 100 mg/L of aqueous phenol solution, 500 mg/L of H₂O₂ (that correspond to the stoichiometric amount needed for complete mineralization of phenol) and 450 mg·L⁻¹ of catalyst.

2.3. Analytical methods

Phenol and aromatic oxidation by-products were measured by HPLC (Varian Pro-Star 240) using a diode array detector (330 PDA). A Microsorb C18 5 μm column (MV 100, 15 cm long, 4.6 mm diameter) was used as stationary phase and 1 mL·min⁻¹ of 4 mM aqueous sulfuric solution was used as mobile phase. Short-chain organic acids were analyzed by an ion chromatograph (Metrohm 790 IC) using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm diameter) was employed as stationary phase, while an aqueous solution containing 3.2 mM Na₂CO₃ and 1 mM NaHCO₃ was employed as mobile phase at a flowrate of 0.7 mL·min⁻¹. Total organic carbon (TOC) was determined using a TOC analyzer (Shimadzu, model 5000A) and hydrogen peroxide concentration was measured by colorimetric titration using the TiOSO₄ method [15]. Leached iron was quantified by ortho-phenanthroline method [16].

3. Results

3.1. Ilmenite modification

Fig. 1 shows the Temperature Programmed Reduction (TPR) profile of the raw ilmenite under H₂ atmosphere in the range 25–1000 °C. As can be observed, TPR showed two reduction peaks, indicating two changes in the iron oxidation state. The first peak (around 500 °C) corresponds to the partial reduction of Fe(III) to Fe(II) (reaction 1) and the second one (around 950 °C) is related with reduction of Fe(II) to Fe(0) (reaction 2). Therefore, the catalyst obtained after reduction of raw ilmenite at 500 °C and 950 °C are named reduced ilmenite and highly reduced ilmenite.

\[
\begin{align*}
\text{ILM} & \rightarrow \text{Fe(III)}/\text{Fe(II)} \rightarrow \text{ILM} \rightarrow \text{Fe(II)} \\
(500 \, ^\circ\text{C}) & \\
\text{ILM} & \rightarrow \text{Fe(II)} \rightarrow \text{ILM} \rightarrow \text{Fe(0)} \\
(950 \, ^\circ\text{C}) & 
\end{align*}
\]

3.2. Catalysts characterization

The mineral ilmenite (FeTiO₃) has a hexagonal structure with two-third of octahedral position occupied by cations. Fe and Ti...
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