

## Abstract

Photocatalytic method has been considered as a cost-effective alternative for the degradation of various hazardous organic contaminants from wastewater, since the pollutants can be oxidized quickly and non-selectively. The discovery of photocatalytic effect on water splitting using  $\text{TiO}_2$  electrode, numerous researches have evolved to synthesize  $\text{TiO}_2$  catalyst of different scale, characterise its physical properties and determine its photooxidation performances to the surface-oriented nature of photocatalysis reaction. To enhance the photocatalytic performance of photocatalysts, micro- and nanoscaled particles are developed to increase the surface areas resulting in more active sites with photocatalytic performance improved and shorter distance for electrons and holes to migrate from bulk to reaction active sites. In addition, high efficiencies for the photo-generation of electron-hole pairs and high oxidizing power of photo-generated holes were achieved in semiconductor particles under supra-bandgap illumination.

Recently, electrochemical techniques have been extensively studied in organic contaminants degradation in aqueous solution due to their easy applicability including automation, high efficiency, and environmental compatibility. Although the electrochemical method could effectively degrade ChS using a  $\text{Ti}/\text{IrO}_2\text{-Pt}$  anode, the current density was relatively high. Moreover, without the presence of  $\text{NaCl}$ , the degradation efficiency was low. Therefore, a novel electrode will be explored via coating  $\text{WO}_3$  or  $\text{Ag}_3\text{PO}_4$  onto the  $\text{Ti}/\text{IrO}_2\text{-Pt}$  to form  $\text{Ti}/\text{IrO}_2\text{-Pt-WO}_3$  (TIW) and

Ti/IrO<sub>2</sub>-Pt-Ag<sub>3</sub>PO<sub>4</sub> (TIA) to exhibit a synergetic effect between the electro-oxidation and photocatalysis by sol-gel or electro-deposition methods. Chlorsulfuron (ChS) herbicide was also chosen as the model contaminant to evaluate and compare the electrochemical oxidation (EO) under low current density without the presence of NaCl, photocatalytic (PC) and photoelectrochemical (PEC) degradation of ChS herbicide using Ti/IrO<sub>2</sub>-Pt anode, WO<sub>3</sub>, Ag<sub>3</sub>PO<sub>4</sub> and TiW, TIA. Below current densities of 2 mA cm<sup>-2</sup>, the potential increases the photocatalytic degradation rate of ChS by promoting the separation and transfer of photogenerated holes and electrons. And the current density can not only separate the holes and electrons but also directly electrolyze ChS. The integrated degradation of ChS was through the direct electro-oxidation and photocatalysis. However, at current density of 4 mA cm<sup>-2</sup>, the by-product (H<sub>2</sub>) formation reaction may decrease the degradation efficiency.

Besides, magnetic separation provides a new alternative to separate and recover magnetic particles by applying external magnetic fields. Recently, magnetic core-shell photocatalysts composed of a magnetic core and a photocatalytic shell have been of great interest. Herein, another objective of this study is to develop a novel magnetically recoverable core-shell Fe<sub>3</sub>O<sub>4</sub>@Ag<sub>3</sub>PO<sub>4</sub>/AgCl photocatalyst, characterized as fast magnetic separation, stability and high photocatalytic activity under the simulated solar light. Briefly, the Ag<sub>3</sub>PO<sub>4</sub> are immobilized onto magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles through electrostatic interaction, followed by *in situ* ion-exchange process to form AgCl Shell. As we know, Fe<sub>3</sub>O<sub>4</sub> colloids show positive in slightly acidic conditions. Therefore, cationic Fe<sub>3</sub>O<sub>4</sub> nanoparticles can connect to

$\text{PO}_4^{3-}$  in  $\text{NaH}_2\text{PO}_4$  solution through electrostatic interaction. Magnetic nanoparticles enriched with phosphate functional groups react with  $\text{Ag}^+$  to form  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$ , followed by the insoluble  $\text{AgCl}$  shell ( $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$ ), making the photocatalysts more stable and reusable after multiple reaction cycles. As a result, this novel magnetically recoverable photocatalysts can effectively utilize visible light to decompose organic contaminants in aqueous solution, which was demonstrated by photocatalytic degradation of methyl blue (MB). MB was completely degraded under the simulated solar irradiation over  $\text{Ag}_3\text{PO}_4$  (30 min),  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4$  (about 42 min) and  $\text{Fe}_3\text{O}_4@\text{Ag}_3\text{PO}_4/\text{AgCl}$  (60 min). In addition, the photocatalysts can be easily separated and recovered from the reaction solution by applying a magnetic field.