



## Degradations of acetaminophen via a $K_2S_2O_8$ -doped $TiO_2$ photocatalyst under visible light irradiation



Justin Chun-Te Lin<sup>a</sup>, Mark Daniel G. de Luna<sup>b</sup>, Graziel L. Aranzamendez<sup>b</sup>, Ming-Chun Lu<sup>c,\*</sup>

<sup>a</sup> Department of Environmental Engineering and Science, Feng Chia University, Taichung 407, Taiwan

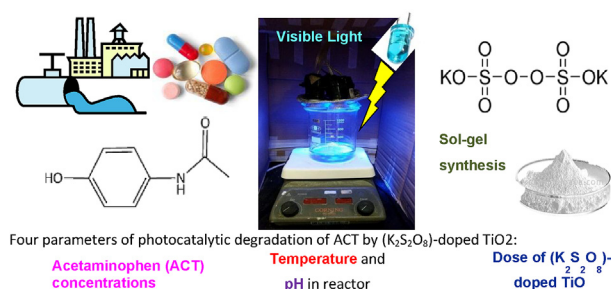
<sup>b</sup> Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines

<sup>c</sup> Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

### HIGHLIGHTS

- Doping  $TiO_2$  with  $K_2S_2O_8$  extends visible-light activity and facilitates to degrade ACT.
- Four parameters utilizing as-doped photocatalyst were systematically examined.
- Optimal conditions can achieve 100% ACT degradation efficiently.
- Three types of degradation kinetic models were computed and studied.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 31 December 2015

Received in revised form

13 April 2016

Accepted 15 April 2016

Available online 30 April 2016

Handling Editor: Shane Snyder

#### Keywords:

Potassium persulfate

$TiO_2$

Visible light active catalyst

Acetaminophen

Doping

Photocatalytic degradation parameters

### ABSTRACT

Acetaminophen (ACT) is a mild analgesic commonly used for relief of fever, headache and some minor pains. It had been detected in both fixed factory-discharged wastewaters, and diverse sources, e.g. surface waters during festival events. Degradation of such trace emergent pollutants by titanium dioxide ( $TiO_2$ ) photocatalysts is a common approach; however, the band gap that can be utilized in the UV range is limited. In order to extend downward the energy required to excite the photocatalytic material, doping with potassium persulfate ( $K_2S_2O_8$ ) by a sol-gel method was done in this work. The visible-light active photocatalyst was tested on the degradation of ACT under four parameters including: initial ACT concentration, catalyst dose, initial pH, and system temperature. Optimal conditions, which achieved 100% ACT degradation, were obtained by using 0.1 mM ACT initial concentration, catalyst dose of  $1\text{ g L}^{-1}$ , initial pH of 9.0 and system temperature of  $22\text{ }^\circ\text{C}$  at the end of 9-h irradiation. Meanwhile, three types of degradation kinetic models (i.e. zero, pseudo first and second order) were tested. The feasible model followed a pseudo-first order model with the computed constant ( $k_{app}$ ) of  $7.29 \times 10^{-3}\text{ min}^{-1}$ . The present study provides a better photocatalytic degradation route by  $K_2S_2O_8$ -modified  $TiO_2$  in comparison with pristine  $TiO_2$ , in wastewater treatment dealing with ACT and other persistent organic pollutants.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pharmaceuticals and their metabolites are regarded as one of persistent organic pollutants (POPs) with impacts on the

\* Corresponding author.

E-mail address: [mmclu@mail.cnu.edu.tw](mailto:mmclu@mail.cnu.edu.tw) (M.-C. Lu).

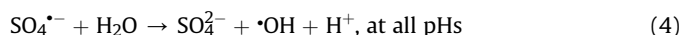
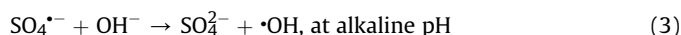
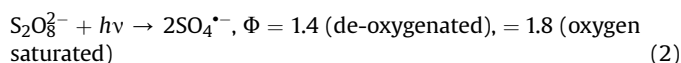
morphological, metabolic and sex alterations of aquatic organisms (Andreozzi et al., 2003). Acetaminophen (ACT, *a.k.s.* paracetamol, 4-hydroxyacetanilide and 4-acetamidophenol) is a mild analgesic commonly used for relief of fever, headache and some minor pains. It is popular in the drug market due to its higher tolerability and lower risks of gastrointestinal toxicity (Schilling et al., 2010). It had been detected in both fixed factory-discharged wastewaters, and diverse sources, e.g. surface waters during festival events (Cardoso et al., 2014; Jiang et al., 2015), sewage treatment plant effluents, (De Gussemme et al., 2011; Huguet et al., 2014; Tan et al., 2014).

Degradation studies of ACT by various advanced oxidation processes (AOP), e.g. various UV-based processes (Tan et al., 2014), ozonation and UV/H<sub>2</sub>O<sub>2</sub> system (Andreozzi et al., 2003), UV/H<sub>2</sub>O<sub>2</sub> hybrid with halides ions (Li et al., 2015) and sole TiO<sub>2</sub> photocatalysis (Yang et al., 2008) were extensively studied due to the presence of this drug in the aqueous environment which would be potentially harmful to non-target organisms if mixed with other compounds and metabolites present in the receiving waters. In contrast to hydroxyl radical ( $\cdot\text{OH}$ ) degrading ACT by UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> system, UV/persulfate (PS) system degrades ACT by sulfate radical (SO<sub>4</sub> $\cdot^-$ ). Yang et al. (2008) found that the highest removal efficiency of ACT occurred at 0.8 g L<sup>-1</sup> dosage of TiO<sub>2</sub> at pH 9.0 in the UV/TiO<sub>2</sub> alone system, while Tan et al. (2014) further compared  $\cdot\text{OH}$  (UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>) attack system and SO<sub>4</sub> $\cdot^-$  attack system. Apart from the traditionally  $\cdot\text{OH}$  attack system, the latter draws more and more attention as persulfate (S<sub>2</sub>O<sub>8</sub> $^{2-}$ , E<sup>0</sup> = 2.01 V) is generally recognized as a strong oxidant that can generate SO<sub>4</sub> $\cdot^-$  (E<sup>0</sup> = 2.6 V). Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) is commonly used in AOP as the formed SO<sub>4</sub> $\cdot^-$  free radical is extremely active and short-lived (30–40 μs) due to their high redox potentials (E<sup>0</sup> = 2.5–3.1 eV).

To treat various emergent contaminants, potassium persulfate has been widely used as a sulfate radical-generating oxidant in aqueous solutions. For example, degradation of polyvinyl alcohol was introduced by Lin et al. (2013). Gao et al. (2012) used UV light-activated persulfate oxidation to treat another drug in water, and Xie et al. (2015) used to remove odorous compounds by UV/persulfate. Antoniou et al. (2010) have used sulfate radical for Microcystin-LR with irradiation by two long-wave UVA (300 < λ < 400 nm) lamps. Yu et al. (2004) used potassium persulfate to generate S<sub>2</sub>O<sub>8</sub> $^{2-}$  ions to study free radical reactions containing Cl<sup>-</sup>(aq) in the laser photolysis. Wang and Liang (2014) elucidated oxidative degradation of tetramethylammonium hydroxide by UV/persulfate. Chen et al. (2012b) found it can accelerate TiO<sub>2</sub> photocatalytic degradation of Acid Orange 7 under visible light by peroxymonosulfate. Sánchez-Polo et al. (2013) tested photo-degradation efficiency of bisphenol A in pure water and real freshwater under UV-C light radiation in the presence of S<sub>2</sub>O<sub>8</sub> $^{2-}$ , which was generated by potassium persulfate, in comparison with the presence of another symmetrical peroxide (H<sub>2</sub>O<sub>2</sub>). Significant mineralization rate (85%) and fast removal (≤7 min) of BPA was achieved when the S<sub>2</sub>O<sub>8</sub> $^{2-}$  was irradiated by UV-C in the pure water. Antoniou and Andersen (2015) compared efficiency and cost of the same system for the removal of micropollutants, including: four antibiotics, three estrogenic steroids and one personal care product, from groundwater. Chen et al. (2012a), also applied S<sub>2</sub>O<sub>8</sub> $^{2-}$ , generated by the same potassium persulfate to facilitate UV photo-degradation of Rhodamine B in aqueous with or without the presence of other inorganic anions. Antoniou and Andersen (2015) compared UVC/S<sub>2</sub>O<sub>8</sub> $^{2-}$  and UVC/H<sub>2</sub>O<sub>2</sub> degradation efficiency of Atrazine and four volatile compounds and cost in groundwater applications. Li et al. (2015) investigated ACT degradation kinetics of a UV/H<sub>2</sub>O<sub>2</sub> process in the presence of halide ions and pointed out that the simultaneous existence of the two ions enhanced ACT degradation than with any single halide ion alone. Therefore, an ACT degradation pathway with halogen radicals in the UV/H<sub>2</sub>O<sub>2</sub>

system was suggested.

Photocatalysis also effectively oxidizes many organic compounds to CO<sub>2</sub>, water and mineral acids. They are more efficient in generating active oxygen species such as  $\cdot\text{OH}$  radicals as compared to other metal oxides. A typical photocatalyst is titanium dioxide (TiO<sub>2</sub>) with advantages of being chemically stable, non-toxic, less resistant, less corrosive, easy to produce and use, and inexpensive. However, TiO<sub>2</sub> alone is ineffective under visible-light irradiation since it requires excitation wavelengths of <387.5 nm. Doping is one of the common approaches to reduce the absorption threshold of bare TiO<sub>2</sub> and extends its optical absorption range towards the visible light region. Tan et al. (2014) investigated ACT degradation kinetics of three UV-based AOP processes enhanced by various oxidants in various conditions including: initial concentration of ACT, dosage of adding oxidants or catalyst, pH<sub>0</sub> and two common anions in the groundwater. They found that hydroxyl radicals ( $\cdot\text{OH}$ ) were predominant in the UV/TiO<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> system, while sulfate radical (SO<sub>4</sub> $\cdot^-$ ) is predominant in the UV/persulfate system. Moreover, a triple system of UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was introduced by Hazime et al. (2014) to compare with previous double system (i.e. UV/TiO<sub>2</sub> and UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) in order to degrade imazalil. Persulfate ions suspended with TiO<sub>2</sub> could be activated by electron transfer and photolysis according to following equations.



Ahmed (2012) reviewed the influence of a number of operating parameters on the photocatalytic degradation of organic compounds, and concluded that it is crucial to study the nature of the pollutants to be degraded and to determine the optimum pH.

In addition to direct use in the suspension system, potassium persulfate was used as sulphur source to synthesize S-doped and Fe–S co-doped TiO<sub>2</sub> photocatalysts by Niu et al. (2013). Their post-treatment was a solvothermal method (kept in an autoclave under 120 °C for 12 h in contrast to the authors' method which involved calcination in an oven at 300 °C for 3 h – the optimum synthetic conditions, in terms of calcination temperature and calcination time, of photodegradation for the same target pollutants). Niu et al. (2012) pointed out that S was not only incorporated into the crystal lattice of TiO<sub>2</sub> replacing Ti<sup>4+</sup> but also anchored on its surface in the form of SO<sub>4</sub> $^{2-}$ . Hazime et al. (2013) applied an integrated TiO<sub>2</sub> photocatalytic degradation system irradiated by UV in the presence of persulfate, which has a double role: 'an electron scavenger and it promotes the formation of sulfate radicals which allow accelerating the removal of imazalil'. They further compared three systems with and without UV or K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, while constant UV irradiation to degrade imazalil (Hazime et al., 2014).

Friedmann et al. (2010) elucidated parameters affecting the kinetics and mechanisms of TiO<sub>2</sub> photocatalytic degradation in water treatment. Visible light active photocatalyst for environmental applications was reviewed by Pelaez et al. (2012) which highlighted on different light sources affecting photocatalytic efficiencies and emphasis on the origin of visible light absorption. This study utilized K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as a dopant into TiO<sub>2</sub> via a sol-gel method. Four key extrinsic parameters (including initial concentration of the model pollutant, catalyst dosage applied, initial pH and temperature in the reactor) affecting efficiency of the new visible light active photocatalyst on the degradation of ACT were systematically

Download English Version:

<https://daneshyari.com/en/article/4407560>

Download Persian Version:

<https://daneshyari.com/article/4407560>

[Daneshyari.com](https://daneshyari.com)