Journal of Photochemistry and Photobiology A: Chemistry 322–323 (2016) 102–109

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Determination of optimum extinction wavelength for paracetamol removal through energy efficient thin film reactor

Deniz İzlen Çifçi[a], Tolga Tunçal[a,*], Ayşegul Pala[b], Orhan Uslu[c]

[a] Namık Kemal University, Çorlu Engineering Faculty, Environmental Engineering Department, 59860 Çorlu, Tekirdağ, Turkey
[b] Dokuz Eylul University, Engineering Faculty, Environmental Engineering Department, 35210 İzmir, Turkey
[c] Yeditepe University, Engineering Faculty, Civil Engineering Department, 34755 Kayışdağı, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 5 December 2015
Received in revised form 17 February 2016
Accepted 2 March 2016
Available online 4 March 2016

Keywords:
TiO_2 thin film
Energy optimization
Paracetamol degradation
Hole blocking
Intermediates

ABSTRACT

Paracetamol (PAM) mineralization through nano-composite thin film (TF) based photocatalytic system was investigated under variable operational conditions. The experiments were conducted using a non-stirred flow through coated tubular quartz reactor (TQR). Elimination of energy demand arising from stirring and aeration through the developed TF reactor configuration was also among the main research interests. Ag-doped Si-TiO_2 TFs were grown on Si-decorated inner surface of the TQR using sol-gel dip coating technique. The fabricated TF was characterized by SEM-EDS, TEM, AFM, XPS and UV_{vis} spectroscopy methods. TF-based PAM mineralization kinetics were observed for both UV_{vis} and UV wavelengths using pure, Si-Ti and Ag-doped Si-TiO_2 TF(s). The direct and indirect optical ban gap energies (BGE) for the Ag doped Si-TiO_2 TF were estimated to be 2.56 eV and 2.86 eV respectively. While no visible light activity was observed for pure TiO_2 TF, Ag-doped Si-TiO_2 TF exhibited significant PAM degradation activity for $\lambda > 400$ nm with a k_{obs} value of $2.1 \pm 0.1\,10^{-3}\,min^{-1}$. In addition to known phenolic and carboxylated intermediates, UV_{vis} spectroscopy, HPLC–MS and UPLC–MS/MS measurements indicated α-cyano-4-hydroxicinnamic acid (αPHC) formation as a result of photo-addition reactions under UV C irradiation. Experimental results also indicated that αPHC blocks h^+/e^- formation completely. Paracetamol could be degraded economically under UV B irradiation through the fabricated TF reactor without stirring, aeration or adding external electron acceptors.

1. Introduction

Pharmaceuticals and personal care products are among the most important emerging pollutants present in wastewater streams. Since they are recalcitrant to biodegradation these pollutants are often detected in treated effluents and natural waters as well. [1,2] Among the pharmaceuticals, paracetamol (PAM-acetaminophen) is one of the most frequently used drugs as analgesic and antipyretic worldwide [3]. PAM is one of the 25 frequently used pharmaceuticals by weight in England. Annual average PAM consumption amount is 100 tons in all over the world [4,5].

Recently, advanced oxidation processes (AOPs) have been successfully used to remove a wide range of organic and inorganic pollutants from aquatic environments [3,6,7]. Among these processes, TiO_2 photocatalysis is the most promising because of its effectiveness, stability, and degrading much of pollutants [8]. However the use of heterogenic TiO_2 photocatalysts in pollution control has several disadvantages such as requirement to complex and expensive separation methods [9]. Moreover short lifetime of produced powder catalysts (heterogenic TiO_2) limits their use in real applications. Pure or doped TiO_2 thin films (TFs) grown on different materials require no further separation and thus attracted much attention in recent years [9–11]. Although degradation of many types of pollutants, including dyes, pharmaceuticals, phenols etc have been investigated through heterogenic photocatalysis, PAM degradation characteristics and reaction intermediates of TF-based processes have not been investigated yet. Furthermore effect of different wavelengths on PAM removal has also not been studied yet. Mixing and aeration are required applications in heterogenic photocatalysis systems. Elimination of these energy requiring applications by the developed TF reactor configuration was also among the main research interests.

Abbreviations: AFM, Atomic Force Microscopy; AOPs, Advanced Oxidation Processes; αPHC, α-cyano-4-hydroxicinnamic acid; BGE, Band Gap Energy; EA, Electron Acceptor (O_2, H_2O_2); PAM, Paracetamol; pHi, Initial pH of reaction mixture; SEM, Scanning Electron Microscopy; TEM, Transmission electron Microscopy; TF, Thin Film; TOC, Total organic Carbon; TQR, Tubular Quartz Reactor; TTIP, Titanium (IV) isopropoxide.

* Corresponding author.
E-mail address: ttuncal@nku.edu.tr (T. Tunçal).

http://dx.doi.org/10.1016/j.jphotochem.2016.03.003
1010-6030/

In this study, PAM degradation kinetics and reaction intermediates were observed through TF- based photocatalytic system for UV_{vis} and three different UV wavelengths ($\lambda \approx 450$ & 550 nm; $\lambda \approx 380$ nm; $\lambda \approx 315$ nm and $\lambda \approx 257$ nm). Pure TiO_2 and Ag-doped Si-TiO_2 TFs were successfully synthesized using a sol-gel method and characterized by SEM-EDS, AFM, XPS and UV_{vis} spectroscopy methods. Reaction kinetics and intermediate products were identified by UV_{vis} spectroscopy, Total Organic Carbon (TOC), HPLC–MS and UPLC–MS/MS methods. The experiments were repeated with using both coated and uncoated tubular quartz reactors (TQR) in order to distinguish between photolytic and photocatalytic PAM removal.

2. Materials and methods

2.1. Sol-gel synthesis and thin film coating

The Pure, Si-Ti and Ag-doped Si-TiO_2 TFs were prepared using a sol-gel dip-coating technique. Ti and Si sols were prepared using Titanium (IV) isopropoxide (TTIP) 97% (Fluka) and Tetraethyl Orthosilicate (Merck). Silver Nitrate (Merck) was used as source of Ag element and ethanol as solvent. TTIP was slowly added to the pre-acidified ethanol with stirring under nitrogen atmosphere [12]. A secondary solution was prepared mixing glacial acetic acid with deionized water in order to decrease the kinetics of the hydrolysis and polycondensation [13,14]. This secondary solution was mixed for one hour and gradually added dropwise to the TTIP solution. Si sol was prepared by dissolving Tetraethyl Orthosilicate (Merck) in diluted HNO_3 – ethanol solution. The optimum Ag:Ti atomic ratio was determined to be%3 (wt%) [15]. After being vigorously stirred for an hour, stable and homogenous Ti (pure), Ag:Ti and Si sols were obtained. The obtained sol-gels were stirred under UVC irradiation for an hour before dip-coating. The sol-gel temperature was maintained at room temperature during dip coating to control the film thickness. KSV Nima dip coater device was used to TF fabrication. The inner surface of TQR was firstly coated with one layer SiO_2 and then calcinated at 500 °C for one hour. At the second step, the SiO_2 coated inner surface was coated with four layers of TiO_2 or Ag-TiO_2 sols. After each coating cycle, the TQR was pre-annealed at 300 °C for 10 min. Finally the coated TQR was calcined in muffle furnace at 450 °C for 1 h.

2.2. Thin film characterization

The appearance and structure of TF surfaces were studied by SEM that was performed using a JEOL JSM 6060. Prior to SEM analysis, the samples were coated with gold to increase the conductivity. Electron micrographs from the surface were taken utilizing a low voltage (5 kV) charge balance. The surface morphology of the TFs was studied using a Nanosurf Easy Scan Atomic Force Microscope (AFM). The microscopic structure of the films was characterized by high-resolution transmission electron microscopy (JEOL JEM 2100F TEM). Ultraviolet–visible (UV_{vis}) absorbance spectra were obtained using a SHIMADZU UV-

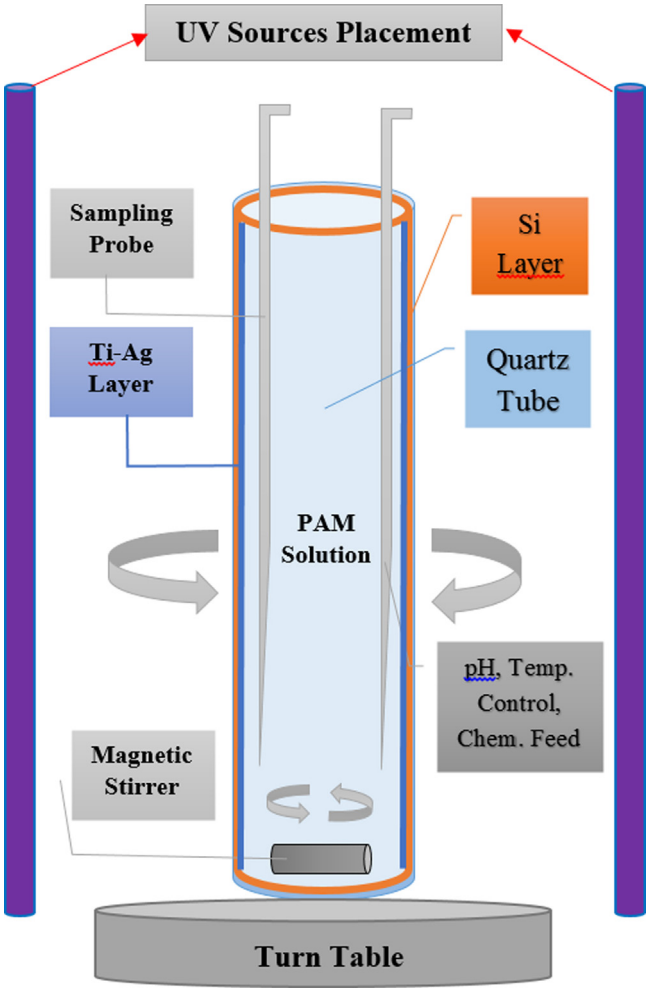

Fig. 1. The experimental set up used in photocatalytic PAM degradation.