Photocatalytic Oxidation of Emerging Pollutants by Nano TiO_2

By

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Certificate of authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

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Abbreviations

AOP: Advanced Oxidation Processes

BET: Brunauer, Emmet and Teller

C_o: Initial Concentration

CB: Conduction Band

COD: Chemical Oxygen Demand

DC: Direct Current

DP: Deposition-Precipitation

DO: Dissolved Oxygen

DOC: Dissolved Organic Carbon

DOM: Dissolved Organic Matter

E1: Estrone

E2: 17β-estradiol

E3: Estriol

EDC: Endocrine Disrupting Chemicals

EDS: Energy Dispersive X-ray Spectroscopy

EE2: 17α-ethynylestradiol

ESI: Electrospray Ionisation

e^-: electrons

HA: Humic Acid

HP: High Pressure

h^+: holes

I: Light Intensity

IC: Inorganic Carbon

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

k: rate constant

LC-MS-QQQ: Liquid Chromatography - Mass Spectrometry - Triple Quadrupole

L-H: Langmuir-Hinshelwood

LP: Low Pressure

LSPR: Localised Surface Plasmon Resonance

MP: Medium Pressure

MPC: Midpolar Compounds

MP-AES: Microwave Plasma - Atomic Emission Spectroscopy

m/z: mass / charge

NPC: Nonpolar Compounds

PC: Polar Compounds

PPCPs: Pharmaceutical and Personal Care Products

PTFE: Polytetrafluoroethylene

PZC: Point of Zero Charge

QTOF-LC-MS: Quadrupole Time-Of-Flight Liquid Chromatography - Mass Spectrometry

r: reaction rate

RT: Retention Time

SEM: Scanning Electron Microscope

SIM: Selective Ion Monitoring

STP: Sewage Treatment Plant

SWW: Synthetic Wastewater

$t_{1/2}$: Half-life

TEM: Transmission Electron Microscope

TGA: Thermogravimetric analysis

TIC: Total Ion Chromatogram

TOC: Total Organic Carbon

UHPLC: Ultra-High Performance Liquid Chromatography

UPW: Ultrapure Water

UV: Ultra Violet

VB: Valence Band

WW: Waste Water effluent from membrane bio-reactor

XRD: X-ray Diffraction

YES: Yeast Estrogen Screen

λ: Wavelength

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Publications and conference presentations

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Sornalingam K, McDonagh A, Zhou JL. Photocatalytic Oxidation of emerging pollutants by nano TiO_2. CEE Research Showcase 2017, UTS, Sydney, Australia, 28 August, 2017.

Sornalingam K, Canning J, Cook K, McDonagh A, Zhou JL. Air-clad optical fibres for the photocatalytic degradation of emerging contaminants. The 3rd Australian New Zealand Conference on Optics (ANZCOP), 4-7 December 2017, Queenstown, New Zealand.

Abstract

Emerging contaminants pose health threats to flora and fauna even at trace level concentrations. Among these pollutants, estrogenic steroidal hormones such as estrone (E1), 17β-estradiol (E2), estriol (E3) and 17α-ethynylestradiol (EE2) are known to cause endocrine disruption, especially in aquatic systems. The successful treatment of these chemicals in water requires advanced oxidation processes (AOPs) in addition to the conventional treatment methods. Photocatalysis by TiO_2 that utilises free radicals for the photodegradation of organic pollutants is an AOP that has attracted recent research interest.

TiO_2 photocatalysis face challenges such as its inability to degrade pollutants under visible light irradiation, the requirement for suitable immobilisation techniques for catalyst reuse and the need for appropriate methods to transmit light over long distances including under water. Each of the aforementioned shortcomings should be addressed for TiO_2 to be successfully applied.

This study focusses on addressing the challenges to effectively degrade estrogenic steroidal hormones using TiO_2 photocatalysis. Commercial Aeroxide P25 TiO_2 was modified with gold nanoparticles to achieve visible light photocatalytic activity. Au-TiO_2 photocatalysts were synthesised using deposition-precipitation (DP) method and characterised using thermogravimetric analysis (TGA), X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectroscopy, scanning electron microscopy (SEM), inductively coupled plasma mass spectrometer (ICP-MS), zeta potential and particle size analysis.

The performance of the new catalysts was compared to that of commercial P25 TiO_2 under different LED light sources: UVA, cool white and green. For the degradation of E1, E2, E3 and EE2, 0 – 8 *wt.*% gold loadings to P25 TiO_2 were studied, where 4 wt.% Au-TiO_2 was found to provide the fastest degradation rate of the pollutants. The catalysts' performance decreased for the light sources in the order, UVA > cool white > green light. Photocatalysis of E1 (1 mg l^{-1}) was found to follow pseudo 1st order kinetics. E1 degradation was significantly more efficient by using 4 *wt.%* Au-TiO_2 than P25 TiO_2 under UVA ($k = 0.28 \pm 0.01$ min^{-1} vs. 0.01 min^{-1}) and cool white light ($k = 2.44 \pm 0.36$ h^{-1} vs. 0.06 ± 0.01 h^{-1}). The photocatalytic activity under visible light decreased in the order: 4 *wt.%* Au-TiO_2 > 8 *wt.%* Au-TiO_2 > 2 *wt.%* Au-TiO_2 > 1 *wt.%* Au-TiO_2 > P25 TiO_2. The enhanced activity of the Au-TiO_2 catalysts was attributed to the gold nanoparticles acting as electron sinks to minimise electron-hole recombination under UVA and due to increased absorption of light in the 500-600 nm wavelength as a result of localised surface plasmon resonance (LSPR).

The stability of the catalysts for reuse is an important factor for consideration in photocatalysis. This was studied by reusing the catalysts over three cycles, for the photodegradation of E1. After three cycles of photocatalysis, the activity did not diminish by any significant amount (< 3%), showing the reusability of the photocatalysts. The detection and identification of photodegradation by products is important to understand the degradation mechanism of the pollutants. The photodegradation by-products of E1 were identified using QTOF-LC-MS and a possible degradation pathway was proposed. Four E1 by-products were identified, of which one was lumiestrone and the other three were hydroxylated forms of E1. In addition, the photoproducts were also degraded with further photocatalysis.

The constituents of water influence the rate of photodegradation of pollutants. The photocatalytic rate of E1 were studied using three different water matrices – ultrapure water (UPW), synthetic waste water (SWW) and wastewater effluent from membrane bio-reactor (WW). The photodegradation rate of E1 decreased for the water matrices in the order, UPW > SWW ≈ WW. This may be due to the negative effects of the constituents present in wastewater.

The recycling of photocatalysts is a major challenge faced by TiO_2 suspended catalysts, since the costs of separating the catalysts from the water is not economical. The immobilisation of the catalysts onto different substrates is considered as an alternative, in the expense of lost catalyst surface area. Here, the photocatalysts were coated onto glass beads using a simple dip coating technique followed by drying, calcination and washing with water to remove any loosely bonded catalysts. The immobilised catalysts proved to be capable of photodegrading EE2. The catalysts were easily reused by removing the glass beads, washing and drying them in furnace.

Transmitting light over long distances and underwater currently restricts the application of TiO_2 photocatalysis to the surface layer of water. This study addresses this limitation with: (i) a novel modified air-clad optical fibre and (ii) a flexible waterproof LED strip, reactor systems. The silica core of the air-clad fibres were capable of transmitting UVA and white light emission whilst the higher numerical aperture of the air-clad fibres compared to the conventional fibres enabled higher transmitted powers, effectively translating into significantly lower energy consumption. Efficient side emission of light from the optical fibres was obtained by collapsing the air-holes of an air-clad optical fibre using a fusion splicer. The optical fibre utilised photocatalytic reactor system efficiently removed the pollutants under

UVA, where 4 *wt.*% Au-TiO_2 showed enhanced activity compared to P25 TiO_2. The rate of photodegradation for both the catalysts was found to follow pseudo 1st order kinetics. EE2 $t_{1/2}$ under UVA were 1.26 h and 0.78 h, in the presence of P25 TiO_2 and the gold modified catalysts, respectively. The catalysts as well as the fibres were found to be stable for multiple reaction cycles with small loss of activity at the end of each cycle (6% decrease in degradation efficiency was noted after three cycles). A white light waterproof LED strip reactor showed good removal efficiency for the pollutant E3 in the presence of Au-TiO_2 photocatalysts, following pseudo 1st order kinetics with k = 0.13 h^{-1} and $t_{1/2}$ = 4.62 h. No degradation of the pollutants was observed in the absence of the catalysts (photolysis). There was no change in the E3 concentration after the initial adsorption under darkness in the presence of P25 TiO_2, since it is inactive under visible light. Thus, air-clad optical fibres and the flexible waterproof LED strips are promising modes of light transmittance for photocatalysis.