# Titanium-salt Flocculation and its Sludge Resource Recovery to Photocatalyst for Advanced Water Treatment

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#### Certificate

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of a candidature for any other degree.

I also certify that the thesis has been written by me. Any help that I have received with all information sources and literature used are indicated in the thesis.



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### List of Abbreviations and Symbols

#### **Abbreviations**

APHA : American Public Health Association

AW-TN : Acid washed-titanate nanotubes

BET : Brunauer, Emmett and Teller

BTSE : Biologically treated sewage effluent

COD : Chemical oxygen demand

DCA : Dichloro acetic acid

DI : Deionised water

DOC : Dissolved organic carbon

DW : Drinking water

E1 : Estrone

E2 : 17β-estradiol

E2Ac : β-estradiol 17-acetate

E3 : Estriol

EC50 : Effective concentration of a 50% loss of bioluminescence obtained

after 15 min exposure

EDCs : Endocrine distrusting chemicals

EE2 :  $17\alpha$ -ethinylestradiol

GC/FID : Gas chromatograph with a flame ionisation detector

HA: Humic acids

HPSEC : High pressure size exclusion chromatography

HRTEM : High-resolution transmission electron microscopy

log K<sub>ow</sub> : Octanol-water partition coefficient

LC : Median lethal concentration

M&M : Metsulfurn methyl

MQ : Milli-Q

MW : Molecular weight

NOM : Natural organic matter

PCBs : Dioxin-like polychlorinated biphenyls

PCDDs : Polychlorinated dibenzo-p-dioxins

PCDFs : Polychlorinated dibenzo-furans

pH<sub>ZPC</sub> : pH at zero point charge

Pka : Acidity

POPs : Persistent organic pollutants

PPCPs : Pharmaceutical and personal care products

RhB : Rhodamine B

rpm : Round per minute

SBR : Sequencing batch reactor

SEM/EDX : Scanning electron microscopy and energy dispersive X-ray

SUVA : Specific ultraviolet absorbance

SW : Sea water

SWW : Synthetic wastewater

TD-TN : Thiourea doped-titanate nanotubes

TEM : Transmission electron microscopy

TN : Titanate nanotubes

USEPA : United States Environmental Protection Agency

UV : Ultraviolet

UV-254 : Ultra-violet at 254 nanometre absorption

v/v : Volume ratio

w/v : Weight to volume ratio

WW : Wastewater

WW-TN : Water washed-titanate nanotubes

XPS : X-ray photoelectron spectroscopy

XRD : X-ray diffraction

#### **Symbols**

A : Accepter

B : Full width at half max in radians

c : Concentration of substrate (mg/L)

c<sub>0</sub> : Initial concentration of substrate (mg/L)

d : Donor

e : Electron

h : Hour

h<sup>+</sup> : Positively charged hole

hv : Photonic energy

I : Irradiation intensity (mW cm<sup>-2</sup>)

k : Apparent reaction rate constant (min<sup>-1</sup>)

K : Langmuir adsorption coefficient (L mg<sup>-1</sup>)

min : Minute

O<sub>2</sub>\*- : Superoxide anions

OH : Hydroxide radical

R<sup>2</sup> : Correlation coefficient

t : Thickness of an crystallite (nm)

V : Volume (mL or L)

 $\theta_B$  : Bragg angle of the  $2\theta$  peak

λ : X-ray wavelength (nm)

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#### **Abstract**

This research embraces several objectives targeting different aspects of environmental concern in terms of wastewater flocculation, sludge disposal and removing of persistent organic pollutants from water and wastewater. The production of a large amount of sludge using coagulants of iron (Fe) and aluminium (Al) salts that needs disposal is considered as the most costly and environmentally problematic challenge in wastewater treatment. Titanium (Ti) salt used as an alternative coagulant reduces the cost of sludge disposal and protects the environment by producing titania photocatalyst from the incinerated sludge. However, titania photocatalyst is only a UV light responsive and its pollutant-specific photocatalytic degradation for various organic pollutants has not being examined. Thus, the main objectives of this study are:

- 1. Increase the efficiency of Ti-salt flocculation in terms of organic matter removal and sludge reduction by using a natural polymer of chitosan as a coagulant-aid.
- Trace the seasonal variation in the characteristics of Ti-salt flocculation and as prepared-titania photocatalyst.
- 3. Produce pollutant-specific titania photocatalyst by synthesising titanate nanotubes (TN) and thiourea (CSN<sub>2</sub>H<sub>4</sub>) doped-titanate nanotubes (TD-TN) photocatalysts through the hydrothermal treatment of as prepared-titania.
- 4. Investigate the pollutant-specific photocatalytic activity of as prepared-titania and the synthesised titania photocatalysts in photodegrading of organic pollutant of gaseous acetaldehyde, humic acid (HA), dichloroacetic acid (DCA), rhodamine B (RhB), metsulfuron methyl (M&M) and phenol under UV, visible and solar light irradiation.

5. Then, select the best pollutant-specific titania for removing of 16 micropollutants of pharmaceutical and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) in water.

Our findings indicated that Ti-salt flocculation exhibited more reduction in turbidity, and colour of wastewater compared with Fe- and Al-salt flocculation. In addition, the use of chitosan was very efficient for enhancing the performance of Ti-salt flocculation. Ti-salt and chitosan flocculation improved significantly the turbidity and organic removal of wastewater up to 85%, considerably reduced the optimum dose of Ti-salt from 25 mg/L to less than 5 mg/L, solved the low pH of Ti-salt flocculation, and achieved in 40% reduction of Ti-salt flocculation sludge. The change in wastewater characteristics in different seasons has a negligible influence in the characteristics of Tisalt flocculation and as prepared-titania. During the whole seasons, the turbidity and orthophosphate removal of Ti-salt flocculation were varied from 70 to 90% and 96 to 99%, respectively. As prepared-titania photocatalyst exhibited predominant anatase structure, high BET surface area and insignificant change in its photocatalytic activity. The photocatalytic degradation of HA and RhB was varied from 85 to 90% and 91 to 98%, respectively. The modified TD-TN photocatalyst exhibited superior photocatalytic activity than as prepared-titania and TN photocatalysts for photocatalytic degradation of the tested organic pollutants under visible and solar light. TD-TN photocatalyst was selected to photodegrade a set of 16 micropollutants of PPCPS and EDCs in water, exhibited a complete photocatalytic degradation of 7 micropollutants at TD-NT concentration of 50 mg/L. The photocatalytic degradation significantly increased with increasing in TD-NT concentration and complete photocatalytic degradation was achieved at TD-NT concentration of 500 mg/L after 90 minutes. The high photocatalysis activity of TD-NT in decomposing persistent organic pollutants and

micropollutants would increase the attention to use of Ti-salt coagulant and titania photocatalyst as alternatives in water and wastewater treatment.