Hybrid membrane VIS-LED photoreactor for simultaneous pharmaceuticals degradation and photocatalysts separation

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**HYBRID MEMBRANE VIS-LED
PHOTOREACTOR FOR SIMULTANEOUS
PHARMACEUTICALS DEGRADATION AND
PHOTOCATALYSTS SEPARATION**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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ABSTRACT

In recent years, TiO_2 -assisted photocatalysis has become a potentially cost-effective and environmentally-sustainable treatment technology for water reclamation and reuse. However, TiO_2 could be photoexcited only under UV irradiation due to its large band gap which hampers its commercial-scale application. In addition, the key challenge for applying the TiO_2 suspension system is that the TiO_2 particles have to be separated from the product water. This study therefore focused on (1) developing visible-light responsive TiO_2 -based photocatalysts for photocatalytic degradation (PCD) of pharmaceuticals under visible-light irradiation, and (2) developing hybrid membrane photoreactor (MPR) systems for photocatalyst recovery and reuse in the photoreactor.

The first phase of this study was the synthesis of C-sensitized and N-doped TiO_2 (C/N- TiO_2) for PCD of sulfanilamide (SNM) under visible-light-emitting diode (vis-LED) irradiation. It was found that the C/N- TiO_2 calcined at 300 °C (T300) exhibited the highest photocatalytic activity for SNM degradation, due to the presence of optimal content of carbonaceous species (serve as photosensitizer) and the nitrogen doping (lead to the remarkable red shift of absorption edge). The PCD of SNM was more efficient in acidic conditions due to the carbon photosensitizing effect. Bicarbonate, phosphate and silica could inhibit the SNM mineralization to different degrees. T300 exhibited good photochemical stability and its absorption onset could be extended to ca. 600 nm.

In order to harness visible light and solar light more efficiently, another novel C-N-S tridoped TiO_2 was synthesized for PCD of tetracycline (TC) under visible-light and simulated solar irradiations in the second phase of this study. It was suggested that the photocatalyst with thiourea : Ti molar ratio of 0.05:1 and

calcined at 450 °C (T0.05–450) exhibited the highest PCD efficiency of TC. This could be attributed to the synergistic effects of TC adsorption on T0.05–450, band-gap narrowing resulting from C–N–S tridoping, presence of carbonaceous species serving as photosensitizer, and the well-formed anatase phase. The slightly alkaline pH condition was more favorable for the PCD of TC. TC degradation was more efficient under solar irradiation. The photocatalytic activity of T0.05–450 was compared with that of T300 for the PCD of SNM and TC under visible-light irradiation. It was found that T0.05–450 exhibited higher visible-light photocatalytic activity.

The third phase of this study was the development of a hybrid MPR system combining a separate vis-LED photoreactor and a cross-flow flat sheet PVDF microfiltration (MF) (mean pore size of 0.22 μm) membrane module. It was investigated for the simultaneous separation of T300 and T0.05–450 and degradation of penicillin G (PG) in both closed-loop and continuous flow-through modes. The effective separation of TiO_2 particles by the MF membrane was realized. It is confirmed that the MPR system operated at a higher transmembrane pressure (TMP) or lower cross-flow velocity (CFV) in the closed-loop (recirculating) mode was more prone to induce TiO_2 deposition on the membrane surface without backwashing, which resulted in the membrane fouling, the loss of TiO_2 from the photoreactor and the decrease of PCD efficiency of PG. With backwashing of the membrane, the PCD efficiencies of PG could be significantly enhanced, which were almost comparable to those achieved in the batch photoreactor.

The MPR system as mentioned above requires a large footprint which might not be suitable to install in a land-scare urban setting. Therefore, a more compact MPR system, namely submerged membrane photoreactor (sMPR) system, was developed in the last phase of this study. It was fabricated with a hollow fiber PVDF MF (mean pore size of 0.1 μm) membrane module submerged into a vis-LED

photoreactor, and was operated in a continuous flow-through mode. The MF membrane realized effective separation of T0.05–450. A steady-state TMP was achieved after the deposition of a thin TiO₂ cake layer on the membrane surface. An alkaline pH condition was favorable for the PCD of carbamazepine (CBZ) using T0.05–450 as photocatalyst. The inhibitory effects of inorganic anions on the PCD of CBZ followed the order of silica > phosphate > nitrate > bicarbonate > sulfate > chloride. The net effect of humic acid (HA) on the CBZ degradation depended on the three competitive phenomena: (i) HA as an electron shuttle promoting the generation of $\bullet\text{O}_2^-$ while reducing the electron-hole recombination, (ii) HA competing with CBZ for the active sites of the photocatalyst, and (iii) HA contributing to the light attenuation in the photoreactor.

Overall, one of the major contributions arising from this study is the preparation of visible-light responsive TiO₂ for the degradation of pharmaceuticals. The findings imply that the as-prepared photocatalysts could be also applied in solar photocatalysis for water/wastewater treatment. Another major contribution is the development of vis-LED irradiated hybrid MPR systems for the simultaneous pharmaceuticals degradation and TiO₂ separation. These hybrid systems show the scientific merit and practical significance for treating real waters using visible-light photocatalysis and low-pressure membrane process.

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LIST OF ABBREVIATIONS

APIs	Active pharmaceutical ingredients
ATR–FTIR	Attenuated total reflectance–Fourier transform infrared spectroscopy/spectroscope
BET	Brunauer–Emmett–Teller
BJH	Barret–Joyner–Hallender
BQ	Benzoquinone
CB	Conduction band
CBZ	Carbamazepine
CFV	Cross–flow velocity
COD	Chemical oxygen demand
CPCs	Compound parabolic collectors
CSTR	Continuous stirrer tank reactor
CT	Carbon–doped titanium dioxide
C–TiO ₂	Carbon–doped titanium dioxide
C/N–TiO ₂	Carbon–sensitized and nitrogen–doped titanium dioxide
DAD	Diode array detector
DMSO	Dimethyl sufoxide
DOC	Dissolved organic carbon
DRS	UV–Vis diffuse reflectance spectroscopy/spectroscope
EDX	Energy dispersive X–ray
E _g	Band–gap energy
FESEM	Field emission scanning electron microscopy/microscope
HA	Humic acid
HPLC	High performance liquid chromatography
HRT	Hydraulic residence time

HRTEM	High-resolution transmission electron microscopy/microscope
IC	Ion chromatography
LDA	Local density approximation
LED	Light-emitting diode
LED-B	LED emitting blue light, $\lambda = 465$ nm
LED-G	LED emitting green light, $\lambda = 523$ nm
LED-W	LED emitting white light, $\lambda = 450$ nm
LED-Y	LED emitting yellow light, $\lambda = 589$ nm
MF	Microfiltration
MPR	Membrane photoreactor
MQ	Millipore Co. MilliQ water
MWCO	Molecular weight cut off
NF	Nanofiltration
NOM	Natural organic matter
NT	Nitrogen-doped titanium dioxide
NTU	Nephelometric turbidity unit
N-TiO ₂	Nitrogen-doped titanium dioxide
P25	Evonik P25 (TiO ₂)
PCD	Photocatalytic degradation
PG	Penicillin G
PL	Photoluminescence
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
ROSs	Reactive oxygen species
SEM	Scanning electron microscopy/microscope
sMPR	Submerged membrane photoreactor
SNM	Sulfanilamide

Solar-150W	One-sun solar intensity 150 W Xenon arc lamp (280–630 nm)
ST	Sulfur-doped titanium dioxide
S-TiO ₂	Sulfur-doped titanium dioxide
TC	Tetracycline
TEM	Transmission electron microscopy/microscope
TGA	Thermogravimetric analysis
TiO ₂	Titanium dioxide
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet
UVA	Ultraviolet A
UVC	Ultraviolet C
UV-LED	UV-light-emitting diode
VB	Valence band
Vis-LED	Visible-light-emitting diode
XPS	X-ray photoelectron spectroscopy/spectroscopy
XRD	X-ray diffraction

LIST OF PUBLICATIONS

Parts of the findings presented in this thesis have been published in the following journal papers:

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- **Wang, P.**, Yap, P.-S. and Lim, T.-T., 2011. C–N–S tridoped TiO₂ for photocatalytic degradation of tetracycline under visible-light irradiation. *Applied Catalysis A: General* 399(1–2), 252–261.
- **Wang, P.** and Lim, T.-T., 2012. Membrane vis-LED photoreactor for simultaneous penicillin G degradation and TiO₂ separation. *Water Research* 46(6), 1825–1837.
- **Wang, P.**, Fane, A. G. and Lim, T.-T., 2013. Evaluation of a submerged membrane vis-LED photoreactor (sMPR) for carbamazepine degradation and TiO₂ separation. *Chemical Engineering Journal* 215–216(0), 240–251.
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Publication as a co-author in others' work:

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- Chen, C., **Wang, P.**, Lim, T.-T., Liu, L., Liu, S. and Xu, R., 2013. A facile synthesis of monodispersed hierarchical layered double hydroxide on silica spheres for efficient removal of pharmaceuticals from water. *Journal of Materials Chemistry A* 1(12), 3877–3880.

CHAPTER 1 INTRODUCTION

1.1 Background

In recent years, the global water scarcity is continuously getting worse along with population growth, rapid urbanization and increased domestic and industrial water uses. The frequent releases of various contaminants of emerging concern including pharmaceuticals into the natural and engineered water systems have induced the increasingly critical situation for the available water resources (Daughton and Ternes 1999a, Kümmerer 2009a, Kümmerer 2009c, Klavarioti et al. 2009). The deteriorating quality of water resources has been attracting a great attention, and the water and wastewater treatment has become an increasing challenge nowadays.

Most of pharmaceuticals are resistant to biological degradation processes. Thus, the conventional water treatment processes cannot effectively remove pharmaceuticals from water. In this context, active pharmaceutical ingredients (APIs) and their metabolites have been frequently detected in sewage water, surface water, groundwater and drinking water with concentrations in the range of ng L^{-1} to $\mu\text{g L}^{-1}$ (Daughton and Ternes 1999a, Kümmerer 2009a, Kümmerer 2009c). As pseudo-persistent contaminants of emerging concern, trace concentrations of APIs and their metabolites in the aquatic environment have become one of the most concerned issues due to their potential adverse effects on human beings and the aquatic ecological environment (Daughton and Ternes 1999a, Kümmerer 2009b, Kümmerer 2009c). It is reported that they are also responsible for the emergence of antibiotic resistant bacteria and genes (Daughton and Ternes 1999b, Kümmerer 2009b, Munir et al. 2011). To address this emerging concern, exploration of more efficient and robust water treatment technologies has received increasing attention.

In recent years, heterogeneous photocatalysis for pharmaceuticals degradation has become a potentially cost-effective and environmentally-sustainable water and wastewater treatment alternative (Klavarioti et al. 2009). Titanium dioxide (TiO_2) is the most suitable photocatalyst for water treatment and reclamation due to its high photocatalytic activity, good chemical and biological stability, high energy efficiency, relatively low cost and non-toxicity (Carp et al. 2004, Fox and Dulay 1993, Kabra et al. 2004, Lim et al. 2011). The major advantages of photocatalysis are as follow:

1. Mineralization of organic pollutants by the hydroxyl radical ($\bullet\text{OH}$) with no selectivity;
2. Energy efficient, utilizing renewable and pollution-free solar energy;
3. No consumption of expensive chemicals;
4. Operation at ambient conditions;
5. Applicable to aqueous, gaseous and even solid phase treatments to some extent;
6. Little or no secondary waste disposal problems;
7. Easy operation;
8. Relatively low cost.

1.2 Knowledge gap and research motivation

As mentioned above, TiO_2 exhibits multiple advantages in its application for photocatalysis. However, due to its large band gap, TiO_2 could be photoexcited only under irradiation of ultraviolet (UV) with wavelength <387 nm which makes up only 3–5% of the solar spectrum (Anpo 2000), thereby hampering its commercial-scale application. Great efforts have been made to develop visible-light responsive TiO_2 to harness solar energy for photocatalysis. Doping TiO_2 with non-metals, such as C (Choi et al. 2004, Górska et al. 2008, Orlanducci et al. 2006), N (Asahi et al. 2001, Subagio et al. 2010), S (Nishijima et al. 2007, Rengifo-Herrera and Pulgarin 2010) and F (Li and Shang 2010, Wu and Chen 2008),

is one of the most efficient methods to shift the spectral response of TiO_2 from UV to visible–light region. In recent years, a higher visible–light photocatalytic activity of codoped TiO_2 with non–metals has been observed compared to single–doped TiO_2 (Chen et al. 2007, Huo et al. 2009). Meanwhile, tridoped TiO_2 was also paid great attention most recently (Ao et al. 2009b, Wang et al. 2009, Xiao and Ouyang 2011, Xiao et al. 2010, Zhou and Yu 2008). However, further investigation on codoped and tridoped TiO_2 should be carried out in order to understand the comprehensive mechanisms of photocatalysis. In addition, it is worth noting that inorganic anions are prevalent in water and wastewater systems. Thus, from a practical point of view, it is imperative to investigate the influences of pH and inorganic anions on the visible–light photocatalytic activity of codoped and tridoped TiO_2 for the removal of organic pollutants from water.

The key challenge for applying the TiO_2 suspension system is that the TiO_2 particles have to be separated from the product water. Sedimentation and coagulation have been applied in the separation of TiO_2 from its slurry (Kagaya et al. 1999), but the TiO_2 particles will be present in sludge. This makes the sedimentation and coagulation processes impractical to recover TiO_2 particles for reuse in the photoreactor. Coating TiO_2 onto magnetic particles has also been attempted (Ao et al. 2009a), but its limitation is that the treated water cannot be withdrawn continuously without losing TiO_2 and a batch system has to be adopted. In addition, TiO_2 can be immobilized on the glass, quartz or stainless steel to eliminate the need for TiO_2 separation (Carp et al. 2004). However, this will reduce the TiO_2 effective surface area, impede the mass transport and lead to the loss of photocatalytic activity. In this context, one of the promising solutions for separating TiO_2 from the product water is to use low–pressure membrane separation process, namely microfiltration (MF) and ultrafiltration (UF). The membrane process has low energy consumption and small facility and chemical footprints. In recent years, the hybrid membrane photoreactor (MPR) systems coupling photocatalysis and membrane

process have increasingly attracted research attention. The MPR systems exhibit high effectiveness in retaining the powdered TiO_2 while allowing the photocatalytic degradation (PCD) of the pollutants (Lim et al. 2011, Molinari et al. 2010, Mozia 2010). Nevertheless, it is rather challenging to design such MPR systems due to the inherent complexities associated with the membrane module and light distribution therein. Moreover, most of the previous researches on MPR systems were associated with Evonik P25 (TiO_2) under UV irradiation. In order to make good use of visible light and meanwhile to separate TiO_2 from the product water, further investigation on the MPR systems should be conducted using visible-light responsive TiO_2 under visible-light irradiation. This will provide practical significance of the MPR systems for the application in water and wastewater treatment.

1.3 Objectives and scopes of research

This research was aimed to synthesize highly visible-light responsive TiO_2 -based photocatalysts for PCD of pharmaceuticals under visible-light irradiation. Furthermore, this research was also aimed to develop effective separation systems for recovery and reuse of the photocatalysts in the photoreactor under continuous flow-through operating mode. The scope of the research is described below:

1. C-sensitized and N-doped TiO_2 (C/N- TiO_2)

- To synthesize and characterize C/N- TiO_2 ;
- To examine the photocatalytic activity of C/N- TiO_2 for the degradation of sulfanilamide (SNM) under visible-light-emitting diode (vis-LED) irradiation;
- To evaluate the photochemical stability and durability of the as-prepared photocatalyst;
- To illuminate the acute toxicity of SNM solution during photocatalysis.

2. C–N–S tridoped TiO₂

- To synthesize and characterize C–N–S tridoped TiO₂;
- To investigate the photocatalytic activity of C–N–S tridoped TiO₂ for the degradation of tetracycline (TC) under visible–light and solar irradiations;
- To evaluate the evolution of acute toxicity of TC solution during photocatalysis;
- To compare the visible–light photocatalytic activity of C–N–S tridoped TiO₂ with that of C/N–TiO₂.

3. Hybrid membrane photoreactor (MPR) system

- To develop a hybrid MPR system comprising a vis–LED photoreactor and a separate cross–flow MF membrane module;
- To investigate the performances of the MPR system operated in the closed–loop mode with and without backwashing;
- To evaluate the performances of the MPR system operated in the continuous flow–through mode with fractional recirculation.

4. Hybrid submerged membrane photoreactor (sMPR) system

- To develop a hybrid sMPR system with a hollow fiber MF membrane module submerged into a vis–LED photoreactor;
- To investigate the performances of the sMPR system operated in the continuous flow–through mode;
- To evaluate the long–term performances of the sMPR system.

1.4 Organization of thesis

Chapter 1 includes the introduction to the background, knowledge gap and research motivation, objectives and scopes of research, as well as the organization of this thesis. Chapter 2 provides a detailed literature review on the mechanism of TiO₂–assisted photocatalysis, fundamentals, syntheses and characterizations of

non-metal doped TiO_2 , operating parameters affecting the PCD process, applications of photocatalysis for pharmaceuticals removal in water, and hybrid MPR systems with different configurations for the photocatalyst separation. Chapter 3 describes the synthesis and characterization of C/N- TiO_2 for PCD of SNM under vis-LED irradiation. Chapter 4 presents the synthesis and characterization of C-N-S tridoped TiO_2 for PCD of TC under visible-light and solar irradiations, and provides the comparison of the photocatalytic activity of C-N-S tridoped TiO_2 with that of C/N- TiO_2 under visible-light irradiation. Chapter 5 evaluates a hybrid MPR system, operated in the closed-loop and continuous flow-through modes with and without backwashing, for its performances in penicillin G (PG) degradation, TiO_2 separation and membrane fouling propensity. Chapter 6 elucidates a hybrid sMPR system operated in the continuous flow-through mode with regard to the carbamazepine (CBZ) degradation, TiO_2 separation and membrane fouling propensity. Chapter 7 summarizes the overall research findings, presents general conclusions and provides several recommendations for the future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This literature review provides a comprehensive introduction on photocatalysis and membrane photoreactor (MPR) systems. Photocatalysis will be focused on mechanism, non-metal doped TiO_2 (i.e. fundamentals, syntheses, characterizations and photocatalytic activities), operating parameters affecting the PCD process, and applications of photocatalysis for pharmaceuticals removal in water. MPR systems will be focused on their different configurations (i.e. separated MPR systems and combined MPR systems) and performances (i.e. photocatalyst separation, permeate flux and membrane fouling, photodegradation efficiency and permeate quality). It is expected that this literature review can provide inspiration for (1) novel visible-light responsive TiO_2 synthesis for PCD of pharmaceuticals, and (2) hybrid MPR systems development for effective recovery and reuse of the photocatalysts and simultaneous PCD of pharmaceuticals in the photoreactor.

2.2 Photocatalysis

Unlike metal which has a continuum of electronic state, a semiconductor material has an energy gap between its conduction band (CB) and valence band (VB) (Table 2.1). This unique characteristic makes semiconductor materials suitable for photocatalytic reactions, during which they could promote reaction in the presence of light while not be consumed in the overall reaction.

Table 2.1 Band-gap energies of some common semiconductor materials at 0 K (Kabra et al. 2004, Thiruvengkatachari et al. 2008).

Semiconductor	Band-gap energy (eV)	Semiconductor	Band-gap energy (eV)
TiO ₂ (rutile)	3.0	Cu ₂ O	3.9
TiO ₂ (anatase)	3.2	WO ₃	3.4
ZnO	3.4	SnO ₂	0.3
CdS	2.3	ZrO ₂	3.6
ZnS	3.1	SrTiO ₃	2.4
PbS	2.2	PbSe	0.2
Fe ₂ O ₃	2.8	CdSe	1.7
α -Fe ₂ O ₃	3.5	WSe ₂	1.2

Many kinds of metal oxide/sulfide/selenide semiconductors could be used as photocatalysts, among which TiO₂, ZnO and CdS have been found to exhibit high photocatalytic activity (Hoffmann et al. 1995, Klavarioti et al. 2009, Thiruvengkatachari et al. 2008). However, ZnO is unstable for use in aqueous system due to its incongruous dissolution to yield Zn(OH)₂ on the ZnO particle surfaces and thus leading to photocatalyst inactivation over time, while CdS readily undergoes photoanodic corrosion and Cd is the second most toxic metal after mercury (Hg). By far, TiO₂ has been proven to be the most suitable and intensively investigated photocatalyst for applications in water, such as water purification, water disinfection, and wastewater treatment and reclamation, due to its high photocatalytic activity, good chemical and biological stability, high energy efficiency, relatively low cost and non-toxicity (Carp et al. 2004, Fox and Dulay 1993, Kabra et al. 2004, Lim et al. 2011).

2.2.1 Mechanism of TiO₂-assisted photocatalysis

Ever since 1972 when Fujishima and Honda discovered the photochemical splitting of water into hydrogen and oxygen with TiO₂ (Fujishima and Honda 1972), intensive studies have been carried out to gain better understanding of photocatalysis over TiO₂ (Carp et al. 2004, Gaya and Abdullah 2008, Hoffmann et al. 1995, Kabra et al. 2004, Linsebigler et al. 1995, Thiruvengkatachari et al. 2008,

Turchi and Ollis 1990). The general schematic diagram illustrating the photocatalytic process over TiO_2 is presented in Fig. 2.1. Generally, when TiO_2 is irradiated with sufficient photon energy that is equal to or greater than its intrinsic band-gap energy, the photogenerated electron (e^-) is transferred from its VB to CB, hence leaving photogenerated hole (h^+) in its VB. The reaction between h^+ and electron donors (such as adsorbed water or hydroxide (OH^-)) produces $\bullet\text{OH}$, while the reaction between e^- and electron acceptors (such as dissolved oxygen) produces superoxide radical ($\bullet\text{O}_2^-$) followed by the formation of $\text{HO}_2\bullet$, H_2O_2 , $\bullet\text{OH}$ and singlet oxygen ($^1\text{O}_2$). In addition, the charge carriers may recombine either in the bulk of TiO_2 if they are not properly scavenged or trapped. This could compromise the production of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$, and thus limit the efficiency of the photocatalytic process. The main processes involving the charge carriers and their associated characteristic timescales are given in Table 2.2. In the general mechanism, it is assumed that organic pollutant does not undergo oxidation via direct h^+ transfer, but takes place through a surface-bound $\bullet\text{OH}$. However, there was another group of researchers argued in favor of a direct oxidation via h^+ (Turchi and Ollis 1990).

Fig. 2.1 General schematic diagram of photocatalytic process over TiO_2 ((a) reduction involving photogenerated electrons, (b) oxidation involving photogenerated holes, recombination of charge carriers (c) in the bulk of TiO_2 and (d) on the surface of TiO_2) (modified from (Carp et al. 2004)).

Table 2.2 Primary steps in TiO₂–assisted PCD of organic pollutants and the corresponding characteristic time (Hoffmann et al. 1995).

Major processes*	Characteristic time
Charge–carrier generation $\text{TiO}_2 + h\nu \rightarrow h^+ + e^-$	fs (very fast)
Charge–carrier trapping $h^+ + >\text{Ti}^{\text{IV}}\text{OH} \rightarrow \{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\}$ $e^- + >\text{Ti}^{\text{IV}}\text{OH} \leftrightarrow \{>\text{Ti}^{\text{III}}\text{OH}\}$ $e^- + >\text{Ti}^{\text{IV}} \rightarrow >\text{Ti}^{\text{III}}$	10 ns (fast) 100 ps 10 ns (deep trap)
Charge–carrier recombination $e^- + \{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$ $h^+ + >\text{Ti}^{\text{III}}\text{OH} \rightarrow >\text{Ti}^{\text{IV}}\text{OH}$	100 ns (slow) 10 ns (fast)
Interfacial charge transfer $\{>\text{Ti}^{\text{IV}}\text{OH}^{*+}\} + \text{organic pollutant} \rightarrow \text{Ti}^{\text{IV}}\text{OH} + \text{oxidized pollutant}$ $\{>\text{Ti}^{\text{III}}\text{OH}\} + \text{O}_2 \rightarrow >\text{Ti}^{\text{IV}}\text{OH} + \bullet\text{O}_2^-$	100 ns (slow) ms (very slow)

*>TiOH represents the primary hydrated surface functional group of TiO₂;

{>Ti^{IV}OH^{*+}} is the surface–trapped valence band hole (or surface–bound •OH);

{>Ti^{III}OH} is the surface–trapped conduction band electron.

2.2.2 Non–metal doped TiO₂

With a large band gap, TiO₂ could be photoexcited only under UV irradiation ($\lambda < 387$ nm). Only 3–5% of the solar spectrum is for UV, while 45% for visible light (Anpo 2000). Therefore, the inefficient usage of solar light is one of the practical issues inhibiting the wide applications of TiO₂ powders in photocatalysis. Various strategies have been explored to modify TiO₂ in order to make good use of the solar energy and indoor lights for photocatalysis, such as doping with metals and non–metals, coupling with narrow band–gap semiconductors, surface sensitization with organic dyes, and doping with upconversion luminescence agent, etc (Carp et al. 2004, Chen and Mao 2007, Zaleska 2008). Among them, metal and non–metal doped TiO₂ have attracted great attentions.

TiO₂ doping with metals (e.g. Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt,

Zn, Sn, Ce, Zr, Ho, Li, La, Pd) is one of the typical approaches to extend the absorption edge of TiO_2 to visible-light region (Zaleska 2008). This could be attributed to the dispersion of metal nanoparticles in the TiO_2 matrix followed by the generation of a new energy level in the band gap of TiO_2 . However, metal ions likely behave as recombination centers of the charge carriers (Dholam et al. 2009), which could lower the quantum efficiency and lead to poor photocatalytic activity and photostability. In addition, metal doped TiO_2 have several other disadvantages such as thermal instability, exorbitant material costs, and possible secondary water contamination (if the metals are toxic) (Liu et al. 2008).

Great efforts have also been made for TiO_2 modification through non-metal doping (e.g. C, N, S, F) to extend the spectral response of TiO_2 to visible light and thus enhance its photocatalytic activity (Zaleska 2008). It has been reported that the role of non-metal as a recombination center in the non-metal doped TiO_2 might be minimized by the introducing of impurity states near the VB edge of TiO_2 as compared to that of the metal doped TiO_2 (Wang and Lewis 2006). There are arguments on the origin of the photocatalytic activity of the non-metal doped TiO_2 under visible-light irradiation. It might be related to the different methods used by different research groups for the incorporation of non-metals in TiO_2 . Different synthesis methods could result in materials with different physicochemical properties. The various scenarios for the possible changes that might occur to the band gap structure of TiO_2 are illustrated in Fig. 2.2 (Serpone 2006b).

Fig. 2.2 Various schemes illustrating the possible changes that might occur to the band gap electronic structure of anatase TiO_2 on doping with various non-metals: (a) band gap of pristine TiO_2 ; (b) doped TiO_2 with localized dopant levels near the VB and the CB; (c) band gap narrowing resulting from broadening of the VB; (d) localized dopant levels and electronic transitions to the CB; and (e) electronic transitions from localized levels near the VB to their corresponding excited states for Ti^{3+} and F^+ centers (Serpone 2006a).

Liquid and gas phase methods have been used for the preparation of non-metal doped TiO_2 (Carp et al. 2004, Chen and Mao 2007, Zaleska 2008). The most commonly used liquid phase routes include sol-gel method, hydrothermal method, solvothermal method, precipitation method, microemulsion method, combustion synthesis, and electrochemical synthesis. The main gas phase methods include chemical vapor deposition (CVD), physical vapor deposition (PVD), spray pyrolysis deposition (SPD), sputtering (either using direct current (DC) or radio frequency (RF)), molecular beam epitaxy, ion implantation, and dynamic ion beam mixing.

Various characterization techniques have been used to examine the physicochemical, mineralogical, photochemical and crystallochemical properties of non-metal doped TiO_2 . The most commonly used techniques include X-ray diffraction (XRD), porosimetry analysis, (field emission) scanning electron microscopy ((FE)SEM), (high-resolution) transmission electron microscopy ((HR)TEM), energy dispersive

X-ray (EDX) spectroscopy, thermogravimetric analysis (TGA), UV–Vis diffuse reflectance spectroscopy (DRS), fourier–transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL).

XRD could provide structural and mineralogical information for TiO₂ by examination of its crystal phases (i.e. anatase, rutile, or brookite). The characteristic peaks for TiO₂ anatase phase are generally located at 25.3° (101), 37.8° (004), 48.0° (200), 53.8° (105), 54.9° (211) and 62.5° (204), rutile at 27.4° (110), 36.1° (101), 41.2° (111) and 54.3° (211), while brookite at 31.1° (Ao et al. 2008, Zhang et al. 2005). Rietveld analysis could be carried out to determine the polycrystalline compositions of TiO₂. TiO₂ crystallite size is often estimated using the Scherrer–Debye’s equation (Debye and Scherrer 1917):

$$d = \frac{k \lambda}{\beta \cos \theta} \quad (2.1)$$

where d is crystallite size (nm), k is Scherrer’s constant (0.9), λ is wavelength of X-ray radiation (0.15418 nm), β is full width half maxima (FWHM) (radian), and θ is X-ray diffraction angle (°). It has been reported that the doping of TiO₂ does not induce any noticeable changes in the XRD pattern (Li et al. 2006a, Peng et al. 2008, Sathish et al. 2005). Specific surface area of TiO₂ could be determined using the Brunauer–Emmett–Teller (BET) method by nitrogen adsorption/desorption isotherms. Average pore size and total pore volume could be determined using the Brunauer–Emmett–Teller (BJH) method at 77 K in the relative pressure (P/P_0) range of 0.05–0.30. Some non–metal doping could inhibit the growth of particle size and thus increase the specific surface area. SEM and TEM could be employed to gain insights into the surface morphology of TiO₂. TEM could also be used to observe the particle sizes of TiO₂. EDX could be used for the elemental composition analysis of TiO₂ through EDX spectra and elemental mapping images. DRS is one of the most reported techniques used to investigate optical property of non–metal

doped TiO_2 . Based on the optical absorption edge obtained from the DRS, the respective band-gap energy could be calculated using the transformed Kubelka–Munk function (Serpone et al. 1995). FTIR spectra could provide specific information about the functional groups in TiO_2 . For example, FTIR absorption peaks at ca. 3400, 3000 and 1630 cm^{-1} are often ascribed to the associated hydroxyls from either water molecules or surface hydroxyl groups (Kuroda et al. 2005). The peak at $400\text{--}800\text{ cm}^{-1}$ could be attributed to Ti–O stretching and Ti–O–Ti bridging stretching modes (Kumar et al. 2000). XPS could measure the elemental composition and chemical state of TiO_2 within the depth of 1–10 nm. XPS spectra peaks for Ti and O could be influenced by the non-metal doping and synthesis condition. Therefore, the reported core level binding energies for the Ti and O peaks are quite questionable, and the assignments are not always consistent with one another.

2.2.2.1 N-doped TiO_2

2.2.2.1.1 Fundamental

Based on the spin-restricted local density approximation (LDA) calculations, Asahi et al. (2001) proposed that N-doped TiO_2 (N- TiO_2) was the TiO_2 -based photocatalyst with the most efficient visible-light photocatalytic activity due to its band-gap narrowing through the mixing of N 2p states with O 2p states in the valence band. Di Valentin et al. (2004, 2005) investigated the origins for the photocatalytic activities of anatase and rutile N- TiO_2 . The supercell models for anatase and rutile N- TiO_2 are depicted in Fig. 2.3, and the model structures for substitutional and interstitial N- TiO_2 in anatase phase in Fig. 2.4. In the substitutional model, the nitrogen atom in a negative oxidation state replaced one lattice oxygen atom and bound to three titanium atoms in TiO_2 . In the interstitial model, the nitrogen atom bound to one lattice oxygen atom and was thus in a positive oxidation state. Based on the theoretical model for the density of states

within the conduction band of N-TiO₂, they concluded that the photocatalytic activity of N-TiO₂ was originated from the substitutional N-doping. Zhao and Liu (2008) and Chen et al. (2004) also suggested that the substitutional N-doping was accountable for the photocatalytic activity. However, it is also reported that interstitial N-doping is responsible for the visible-light photocatalytic activity of TiO₂. Diwald et al. (2004) found that the interstitial N-doping was effective in reducing the threshold photon energy from 3.0 to 2.4 eV. In addition, Fang et al. (2008) reported that the doped nitrogen species located at the interstitial sites in TiO₂ could lead to the band-gap narrowing of TiO₂. It is found that the formation of oxygen vacancies and color centers (Ti³⁺) in the lattice could lead to the visible-light photocatalytic activity (Lee et al. 1999, Nakamura et al. 2000, Yin et al. 2006). In addition, isolated impurity energy levels formed above the valence band could also contribute to the visible-light photocatalytic activity of N-TiO₂ (Irie et al. 2003b). In summary, the proposed mechanisms for the visible-light photocatalytic activity over N-TiO₂ include: (1) band-gap narrowing, (2) creating oxygen vacancies, and (3) introducing impurity energy levels.

Fig. 2.3 Supercell models for N-TiO₂: (a) anatase and (b) rutile (Di Valentin et al. 2004).

Fig. 2.4 Model structures for substitutional and interstitial N-TiO₂ in anatase phase (Di Valentin et al. 2005).

2.2.2.1.2 Synthesis

Sol-gel method is one of the most commonly used chemical methods to synthesize N-TiO₂ using titanium alkoxides (e.g. titanium tetraisopropoxide and titanium butoxide) or inorganic titanium precursors (e.g. TiCl₄, TiCl₃ or Ti(SO₄)₂). Urea (Ananpattarachai et al. 2009, Sreethawong et al. 2008), thiourea (Wei et al. 2008), tetramethylammonium hydroxide (TMAH) (Wang and Lim 2010), diethanolamine (Ananpattarachai et al. 2009), triethylamine (Ananpattarachai et al. 2009), ethylenediamine (Wang et al. 2006), hexamethylenetetramine (Wang et al. 2006), hydrazine hydrate (Sun et al. 2009), guanidine (Nosaka et al. 2005), ammonium fluoride (Li et al. 2005a), ammonium carbonate (Yin et al. 2005), and ammonium hydroxide (Subagio et al. 2010, Xu et al. 2008) have been widely used as nitrogen precursor. Various calcination atmospheres have been used to incorporate nitrogen in the TiO₂ lattice, such as air, N₂, mixture of N₂/NH₃ (Horikawa et al. 2008), mixture of NH₃/Ar (Irie et al. 2003b, Zhang et al. 2009), and so on. As low temperature synthesis, hydrothermal (Hu et al. 2010, Huang et al. 2008a, Kometani et al. 2008) and solvothermal methods (Chi et al. 2007, Jiang et al. 2008, Wang and Lim 2010) have been employed for the N-TiO₂ synthesis. Recently, combinations of hydrothermal or solvothermal methods with other treatments have been attempted (Chen et al. 2008, Cong et al. 2007).

2.2.2.1.3 Characterization

The band-gap narrowing and visible-light absorption due to nitrogen doping could be characterized by DRS. Zhang et al. (2009) reported that the band gap of N-TiO₂ shifted to lower energy and the absorption increased in the visible-light region by increasing the annealing temperature from 400 to 700 °C. Wang et al. (2007b) indicated that the band gap of TiO_{2-x}N_x calcinated at 350 °C became narrowed compared to pure TiO₂, along with the visible-light absorption extended to 600 nm.

The occurrence of Ti-N bonds and other nitrogen species could be confirmed by FTIR analysis. The peaks around 1450, 1220 and 1160 cm⁻¹ could be attributed to the vibrations of Ti-N bond, the peak at 1390 cm⁻¹ to the vibration of surface-adsorbed NH₃, while the peak at 1385 cm⁻¹ to the vibrational mode of hyponitrite (Gao et al. 2006, Huo et al. 2009).

The chemical state of N, Ti and O in N-TiO₂ could be studied using XPS. The N 1s peaks located at 395.8–397.8 eV could be associated to Ti-N bonding (Yang et al. 2008a). The N 1s peaks located at 398.8–403.3 eV might be caused by N₂ chemisorption, nitrogen contaminant or oxynitride doping, such as Ti-O-N, Ti-O-N, N_x-Ti-O_y, and O-Ti-N (Asahi et al. 2001, Wang and Lim 2010, Wei et al. 2008, Yang et al. 2008a). The N 1s peaks around 403.9–404.3 eV could be attributed to an additional N-doping state of -(NO₂) in the TiO₂ lattice (Jirsak et al. 1999). The core level binding energies of Ti 2p around 455.0–459.5 eV for Ti 2p_{3/2} and 461.0–465.0 eV for Ti 2p_{1/2} could be significantly lowered by introducing more negatively charged N into the matrix (Yang et al. 2008a). The binding energy of O 1s with peaks at 528.1–531.1 eV could be assigned to the Ti-O bonds, while peaks at 531.4–533.7 eV could be resulted from Ti-N, Ti-C and/or Ti-H bonds (Xu et al. 2010).

2.2.2.2 C-doped/sensitized TiO₂

2.2.2.2.1 Fundamental

In C-doped TiO₂ (C-TiO₂), carbon is incorporated into the TiO₂ lattice and mainly present in the form of Ti-C bonds (Irie et al. 2003a) which could lead to the red shift of absorption edge followed by the enhancement of visible-light photocatalytic activity. Carbon could also stabilize anatase structure and increase adsorption of organic molecules on the TiO₂ surface (Górska et al. 2008). According to the theoretical predictions (FIREBALL, which is a first-principles tight-binding molecular dynamics simulation technique based on a self-consistent version of the Harris-Foulkes functional) and experimental results, Wang and Lewis (2006) reported that C-TiO₂ possessed the best photoresponse in the visible-light region compared to the other anion-doped TiO₂ due to a significant overlap between the O 2p state and the carbon states near the valence band edge. Their results disagree with the conclusion of Asahi et al. (2001), who reported that N-TiO₂ was the most preferable candidate for the TiO₂-based photocatalyst with efficient visible-light activity based on the spin-restricted LDA calculations.

Visible-light photocatalytic activity of TiO₂ could also be enhanced by carbon photosensitization, for which the carbon dopants mainly exist as the C-C bonds (carbonaceous species), and C-O and O=C-O bonds (carbonate species). Carbonaceous species could create the interface states which narrow the band gap (Treschev et al. 2008), and meanwhile, as photosensitizer, they could extend the absorption band tailing to the visible-light region (Chou et al. 2006, Górska et al. 2008, Lettmann et al. 2001, Tseng et al. 2006). In addition, the carbonaceous species could play a role of electron scavenger to inhibit the electron-hole recombination (Dong et al. 2008, Lettmann et al. 2001). Another possible mechanism is the promotion of production of $\bullet\text{O}_2^-$ which is capable of degrading organic pollutants. However, excessive carbonaceous species could reduce the

visible–light photons available to the photocatalysts, and consequently lowered their photocatalytic activity.

2.2.2.2.2 Synthesis

Sol–gel method is one of the mostly used methods for the synthesis of C–TiO₂. During sol–gel process, hydrolysis of titanium alkoxide (e.g. titanium tetraisopropoxide and titanium butoxide) or inorganic titanium precursors (e.g. TiCl₄, TiCl₃ or Ti(SO₄)₂) occurs in a mixed aqueous solution containing different carbon precursors, such as urea (Li et al. 2006b), glucose (Ren et al. 2007), sucrose (Lin et al. 2005), carbonic ink (Xie et al. 2007), carbon blacks (Rincón et al. 2005), cyclohexane (Treschev et al. 2008), diethanolamine (Huang et al. 2008b), tetrabutylammonium hydroxide (Sakthivel and Kisch 2003, Xu et al. 2006), poly(vinyl alcohol), hydroxyl propyl cellulose and poly(ethylene terephthalate) (Inagaki et al. 2005), and so on, followed by calcination to obtain C–TiO₂. Hydrothermal (Ren et al. 2007, Wang et al. 2007a) and solvothermal methods (Wang and Lim 2010) are alternatives to prepare C–TiO₂ under low calcination temperature. C–TiO₂ could also be prepared by temperature programmed carbonization of TiO₂ in a flow of vapors of ethanol (Janus et al. 2006), cyclohexane (Li et al. 2005b), n–hexane (Janus et al. 2004, Morawski et al. 2006), etc. In addition, C–TiO₂ could be synthesized by oxidative annealing of titanium carbide (TiC) (Irie et al. 2003a, Shen et al. 2006).

For the C–sensitized TiO₂, it is generally synthesized using sol–gel method. It is indicated that the incorporation of carbonaceous species in TiO₂ could be realized using titanium alkoxide but without external carbon source under controlled calcination temperature (Park et al. 2009). Lettmann et al. (2001) prepared coke–containing TiO₂ by a modified sol–gel process using different alkoxide precursors in the absence of other dopant. Tseng et al. (2006) synthesized visible–light responsive TiO₂ (a mixed crystal lattice of anatase, brookite and rutile

phases) using a sol–gel method with tetrabutyl orthotitanate and ethanol under acid catalyzed condition and low calcination. Another carbon–containing mixed–phase TiO_2 was prepared by Treschev et al. (2008) using a modified sol–gel method. Chou et al. (2006) and Górska et al. (2008) using a sol–gel method prepared visible–light responsive carbon–containing TiO_2 with carbonaceous species incorporation in highly condensed and coke–like structure, respectively.

2.2.2.2.3 Characterization

The absorption of C–doped/sensitized TiO_2 in the visible–light region has been found to be related to the carbon content. However, the relationship between the visible–light absorption and carbon content is not constant due to the varying synthesis processes and calculation methods that influence the resulting carbon content. Sakthivel and Kisch (2003) reported that the band–gap energies for their C–doped TiO_2 were 3.02 and 3.11 eV with 2.98% and 0.42% of carbon contents, respectively. Chou et al. (2006) prepared TiO_2 calcinated at 150 °C (C150) and 200 °C (C200C), respectively. C150 had a sharp edge extended to 446 nm corresponding to a band gap of 2.8 eV, while it extended to near 486 nm corresponding to a band gap of 2.7 eV in C200.

FTIR spectra could be used to detect the carbon presence in the photocatalyst. The peaks in the range of 1000–1300 cm^{-1} correspond to the C–OH stretching and OH bending vibrations (Sun and Li 2004, Yang et al. 2006). Two major peaks centered at 1590 and 1390 cm^{-1} could be assigned to asymmetric and symmetric stretching vibrations of COO^- groups, respectively. The peaks at ca. 1710 and 1620 cm^{-1} could be attributed to C=O and C=C vibrations, respectively. The peak at 1741 cm^{-1} could be assigned to the –COOH. The peaks around 2350 cm^{-1} could be associated to the structure of CO_2 , 2800–3000 cm^{-1} to CH_2 and CH_3 vibrations, and 1300–1500 cm^{-1} to CH_2 and CH_3 stretching.

The chemical state of C, Ti and O in C-doped/sensitized TiO₂ could be investigated with XPS. Peaks for C 1s XPS spectra are generally located at around 284.8, 281–283, and 286–289 eV (Górska et al. 2008, Park et al. 2009, Yang et al. 2008a). The C1s peak at 284.8 eV is ascribed to the adventitious elemental carbon or carbon residues from the organic precursor (mainly C–C bonds), and it is usually used for the calibration of other spectra. The C 1s peaks at 281–282 eV are attributed to Ti–C bonds, indicating carbon substitutional doping, while the C 1s peaks at 286–289 eV are assigned to the C–O, C=O and O=C–O bonds (carbonate species). For the Ti⁴⁺ oxidation state, peaks at 458 and 464 eV are for Ti 2p_{3/2} and Ti 2p_{1/2}, respectively (Yang et al. 2008a). These peaks might shift due to the presence of Ti–C. In the O 1s XPS spectra, O 1s peaks at around 529–530 eV are for Ti–O bonds and 530–533 eV for the oxygen atoms in the surface hydroxyl groups (H–O bonds) and/or in the carboxyl groups (C–O bonds) (Xu et al. 2010).

2.2.2.3 S-doped TiO₂

2.2.2.3.1 Fundamental

The enhanced visible-light photocatalytic activity of S-doped TiO₂ (S–TiO₂) could be attributed to the band-gap narrowing through the mixing of the S 3p states with the valence band of TiO₂ (Ao et al. 2009b, Ohno et al. 2004, Rengifo-Herrera et al. 2008, Rengifo-Herrera et al. 2009b, Umebayashi et al. 2002). There are two kinds of sulfur doping in TiO₂. For the anionic S–TiO₂, the lattice O^{2–} is substituted by S^{2–} to form Ti–S bonds. While the substitution of Ti⁴⁺ by S⁶⁺ occurs in cationic S–TiO₂, which is more favorable than replacing O^{2–} with S^{2–} if thiourea is used (Ohno 2004, Ohno et al. 2004). Moreover, it is postulated that SO₄^{2–} could be incorporated into the network of Ti–O–Ti during the doping process (Liu et al. 2009), which could also enhance the visible-light photocatalytic activity of the resulting S–TiO₂.

2.2.2.3.2 Synthesis

S-TiO₂ could be synthesized by modified sol-gel method with sulfur source, such as thiourea (Crisan et al. 2008, Hamadani et al. 2009, Liu and Chen 2008, Ohno 2004, Ohno et al. 2004, Yu et al. 2005), sulfuric acid (Periyat et al. 2008), sulfate (Liu et al. 2009, Parida et al. 2008), ammonium thiocyanate (Katoh et al. 2006) and so on. Oxidation annealing of titanium disulfide (TiS₂) has also been used to synthesize S-TiO₂ (Umebayashi et al. 2002, Umebayashi et al. 2003). In addition, there are several studies focused on the hydrothermal (Ho et al. 2006, Tian et al. 2009) and solvothermal (Yu et al. 2009a) methods to prepare S-TiO₂.

2.2.2.3.3 Characterization

The optical properties of S-TiO₂ are usually evaluated by DRS analysis. Noticeable shifts of the absorbance shoulder from a wavelength below 400 nm to the visible-light region have been observed for the S-TiO₂ (Wang et al. 2009, Yu et al. 2005). Moreover, the absorbance edge shifts to the longer wavelength and the visible light absorbance increases with the increase of S-doping content (Ho et al. 2006, Liu and Chen 2008).

FTIR spectroscopy has been used to identify the bonding characteristic of functional groups in the S-TiO₂ photocatalysts. S-doping is found to have no effect on the properties of surface -OH compared to naked TiO₂ (Liu and Chen 2008). The FTIR peak at 1030 cm⁻¹ could be related to Ti-O-S, suggesting a conjugation effect between the S and Ti-O bonds (Liu et al. 2009). The peaks at 1050 and 1131 cm⁻¹ could be associated to the characteristic frequencies of SO₄²⁻ with bidentate bond (Liu and Chen 2008).

The peak at around 168 eV in the XPS spectra is the standard binding energy of S⁶⁺ (such as SO₄²⁻) (Ohno et al. 2004, Rengifo-Herrera et al. 2008). Due to the presence of the Ti-O-S bond, the peak for S⁶⁺ will shift in the range of 167–169 eV

(Rengifo-Herrera et al. 2009b, Umebayashi et al. 2002). The peaks at around 160–163 eV for Ti–S bonds indicates anionic sulfur doping that S^{2-} substitutes for the lattice O^{2-} (Ao et al. 2009b).

2.2.2.4 Photocatalytic activity of non–metal doped TiO_2

Due to the enhancement of visible–light responsiveness, non–metal doped TiO_2 has been reported to exhibit greater visible–light photocatalytic activity as compared to the undoped TiO_2 . In recent years, a further enhanced visible–light photocatalytic activity of non–metal codoped/tridoped TiO_2 compared to the undoped and non–metal single doped TiO_2 has been observed due to the synergistic effects of the dopants. Table 2.3 summarizes the photocatalytic activity of various non–metal doped TiO_2 .

Table 2.3 Photocatalytic activity of various non-metal doped TiO₂.

References	TiO ₂	Synthesis technique	PCD experimental conditions	Summary of findings
Ananpattara chai et al. (2009)	N-TiO ₂	Sol-gel	<ul style="list-style-type: none"> 2-chlorophenol: 25 mg L⁻¹ TiO₂ dosage: 1.0 g L⁻¹ A 150 W halogen lamp: $\lambda > 420$ nm 	<ul style="list-style-type: none"> The photocatalytic activity of all N-TiO₂ can be arranged in the following order: TiO₂/diethanolamine (dopant) > TiO₂/triethylamine > TiO₂/urea > undoped TiO₂. The initial rate of 2-chlorophenol degradation using the interstitial N-TiO₂ with diethanolamine was 0.59 mg L⁻¹min⁻¹, and the kinetic constant was 2.34×10^{-2} min⁻¹ with a half-life of 98 min.
Ao et al. (2009b)	C-N-S tridoped TiO ₂	Sol-gel	<ul style="list-style-type: none"> Reactive Brilliant Red dye X-3B: 100 mg L⁻¹ TiO₂ dosage: 1.5 g L⁻¹ A 250 W halogen lamp with a filter: $\lambda > 400$ nm 	<ul style="list-style-type: none"> C-N-S tridoped TiO₂ showed a high photocatalytic activity for the removal of Reactive Brilliant Red dye X-3B under visible-light irradiation compared to P25.
Chen et al. (2007)	C-N codoped TiO ₂	Sol-gel	<ul style="list-style-type: none"> Methylene blue: 1.8×10^{-5} mol L⁻¹ TiO₂ dosage: 0.5 g L⁻¹ A 150 W xenon arc lamp with a 420 nm cutoff filter: $\lambda > 420$ nm 	<ul style="list-style-type: none"> Compared to C-TiO₂ and N-TiO₂, C-N codoped TiO₂ exhibited the highest photocatalytic activity, which could be assigned to the synergistic effect of doped C and N atoms.
Du et al. (2009)	N-F codoped	Solvothermal	<ul style="list-style-type: none"> Methylene blue: 1–10 mg L⁻¹ TiO₂ dosage: 1.0 g L⁻¹ 	<ul style="list-style-type: none"> 77.6% of methylene blue degradation was achieved after 5 h light irradiation using N-F

References	TiO ₂	Synthesis technique	PCD experimental conditions	Summary of findings
	TiO ₂		<ul style="list-style-type: none"> • A 500 W high pressure mercury lamp with a filter: $\lambda > 400$ nm 	codoped TiO ₂ , which was much higher than that using P25.
Górska et al. (2008)	C–TiO ₂	Sol–gel	<ul style="list-style-type: none"> • Phenol: 2.1×10^{-4} mol L⁻¹ • TiO₂ dosage: 5.0 g L⁻¹ • A 1000 W Xenon lamp with filters to control its light spectrum 	<ul style="list-style-type: none"> • TiO₂ powder calcinated at 350 °C was most active in phenol degradation under visible–light irradiation ($\lambda > 400$ nm), while the photocatalyst treated at 450 °C had the best activity under UV irradiation ($250 < \lambda < 400$ nm, $\lambda_{\text{max}} = 330$ nm).
Hu et al. (2010)	N–TiO ₂ , C–TiO ₂	Hydrothermal	<ul style="list-style-type: none"> • Brilliant Blue KN–R: 50 mg L⁻¹ • TiO₂ dosage: 0.4 g L⁻¹ • UV source: a 125 W high pressure mercury lamp • Visible light source: a 110 W high pressure sodium lamp 	<ul style="list-style-type: none"> • N–TiO₂ showed much higher photocatalytic activity than commercial P25 under both UV and visible light irradiations, which was over 10–fold the activity of P25. • N–TiO₂ showed one order of magnitude lower activity under visible–light irradiation than under UV irradiation. • C–TiO₂ showed two times higher activity than P25 under visible–light irradiation, while its activity is less than half that of P25 under UV irradiation. • N–TiO₂ exhibited much higher photocatalytic activity than C–TiO₂.
Lin et al. (2007)	N–P codoped	Sol–gel	<ul style="list-style-type: none"> • 4–chlorophenol: 2.5×10^{-4} mol L⁻¹ • TiO₂ dosage: 1.0 g L⁻¹ 	<ul style="list-style-type: none"> • The photocatalytic activity of TiO₂ modified by only nitrogen was much lower than that

References	TiO ₂	Synthesis technique	PCD experimental conditions	Summary of findings
	TiO ₂		<ul style="list-style-type: none"> UV source: a 8 W medium pressure mercury lamp ($\lambda_{\max} = 365$ nm) Visible light source: a 150 W halogen–tungsten lamp with a UV cut–off filter ($\lambda < 400$ nm) 	modified by phosphor. However, when TiO ₂ was co–doped with both phosphor and nitrogen, the photocatalytic activity was further enhanced efficiently.
Ren et al. (2007)	C–TiO ₂	Hydrothermal	<ul style="list-style-type: none"> Rhodamine B: 5 mg L^{−1} TiO₂ dosage: 1.0 g L^{−1} A 500 W tungsten halogen lamp: $\lambda > 420$ nm 	<ul style="list-style-type: none"> C–TiO₂ exhibited significantly higher photocatalytic activity than the undoped counterpart and P25 on the degradation of rhodamine B.
Subagio et al. (2010)	N–TiO ₂ hollow sphere	Sol–gel	<ul style="list-style-type: none"> Bisphenol A: 5 mg L^{−1} TiO₂ dosage: 0.5 g L^{−1} 2 m flexible LED strip (SMD 5050, 30 pcs m^{−1}, 7.5W m^{−1}), emitting white light ($\lambda = 450$ nm), blue light ($\lambda = 465$ nm), green light ($\lambda = 523$ nm) and yellow light ($\lambda = 589$ nm) 	<ul style="list-style-type: none"> N–TiO₂ hollow sphere exhibited significant increase of bisphenol A degradation and mineralization under blue, green and yellow lights as compared to the undoped TiO₂ hollow sphere, powder TiO₂, and Hombikat UV100. At circumneutral pH, 90% of bisphenol A was degraded in 2 h under irradiation of blue light with N–TiO₂ hollow sphere, while TOC removal was 66% after 6 h of irradiation.
Sun et al. (2006)	C–S codoped TiO ₂	Sol–gel	<ul style="list-style-type: none"> 4–chlorophenol: 1.5×10^{-4} mol L^{−1} TiO₂ dosage: 1.0 g L^{−1} UV source: a 250 W high pressure mercury lamp Visible light source: a 250 W Xe lamp 	<ul style="list-style-type: none"> C–S codoped TiO₂ exhibited the highest photocatalytic activity compared to the as–prepared pure TiO₂ and P25.

References	TiO ₂	Synthesis technique	PCD experimental conditions	Summary of findings
Sun et al. (2009)	N-TiO ₂	Sol-gel	$(\lambda_{\max} = 470 \text{ nm})$ <ul style="list-style-type: none"> 4-chlorophenol: $1.5 \times 10^{-4} \text{ mol L}^{-1}$ TiO₂ dosage: 1.0 g L^{-1} UV source: a 250 W high pressure mercury lamp Visible light source: a 250 W Xe lamp with a 400 nm cutoff filter 	<ul style="list-style-type: none"> N-TiO₂ showed higher photocatalytic activity under both UV and visible-light irradiations. Under 6 h of sunlight irradiation, the degradation efficiency of 4-chlorophenol over N-TiO₂ using a mixture of ammonia and hydrazine hydrate as nitrogen precursor was 82.0%, which was higher than 66.2% of the pure TiO₂, 60.1% or 65.2% of the N-TiO₂ using single ammonia or hydrazine hydrate as precursor.
Tian et al. (2009)	S-TiO ₂	Hydrothermal	<ul style="list-style-type: none"> Methyl orange: 20 mg L^{-1} TiO₂ dosage: 1.0 g L^{-1} A 400 W high pressure Hg lamp: $\lambda_{\max} = 365 \text{ nm}$ 	<ul style="list-style-type: none"> The anatase/rutile ratio and the photocatalytic activity of the as-prepared S-TiO₂ powders increased with the increase of the S-dopant amount.
Wang and Lim (2010)	C-N codoped TiO ₂	Solvothermal	<ul style="list-style-type: none"> Bisphenol A: 5 mg L^{-1} TiO₂ dosage: 0.5 g L^{-1} 2 m flexible LED strip (SMD 5050, 30 pcs m^{-1}, 7.5 W m^{-1}), emitting white light ($\lambda = 450 \text{ nm}$), blue light ($\lambda = 465 \text{ nm}$), green light ($\lambda = 523 \text{ nm}$) and yellow light ($\lambda = 589 \text{ nm}$) 	<ul style="list-style-type: none"> Bisphenol A degradation efficiencies were >99%, >99%, 84% and 24% under 5 h of irradiation with white, blue, green and yellow LED lights, respectively, while the corresponding percentages of mineralization were 70%, 60%, 45% and 9%. Presence of sulfate, chloride and nitrate at 5.0 mM only slightly retarded bisphenol A

References	TiO ₂	Synthesis technique	PCD experimental conditions	Summary of findings
Wei et al. (2008)	N–S codoped TiO ₂	Hydrothermal	<ul style="list-style-type: none"> • Methyl orange: 10 mg L⁻¹ • TiO₂ dosage: 0.125 g L⁻¹ • UV source: an 18 W low pressure mercury lamp • Visible light source: real sunlight 	<p>degradation, while bicarbonate and silica inhibited the process to a much larger extent.</p> <ul style="list-style-type: none"> • N–S codoped TiO₂ exhibited a high activity for decompositions of methyl orange both under UV and visible–light irradiation comparing to S–TiO₂ and undoped TiO₂.
Xie et al. (2007)	C–TiO ₂	Sol–gel	<ul style="list-style-type: none"> • Methyl orange: 10 mg L⁻¹ • TiO₂ dosage: 1.0 g L⁻¹ • A 125 W high pressure Hg lamp: $\lambda > 420$ nm 	<ul style="list-style-type: none"> • C–TiO₂ films exhibited much higher photocatalytic activities for visible–light induced degradation of methyl orange than that of pure TiO₂ film prepared at the same conditions.
Yu et al. (2009a)	S–TiO ₂	Solvothermal	<ul style="list-style-type: none"> • Nitrobenzene • A 60 W fluorescent lamp 	<ul style="list-style-type: none"> • 85% of nitrobenzene was removed under visible–light irradiation for 3 h.
Zhang et al. (2009)	N–TiO ₂	Hydrothermal	<ul style="list-style-type: none"> • Methylene blue: 6.01×10^{-5} mol L⁻¹ • TiO₂ dosage: 0.2 g L⁻¹ • A 400 W high pressure Hg lamp 	<ul style="list-style-type: none"> • The photocatalytic activity of N–TiO₂ was higher than that of TiO₂.

2.2.3 Operating parameters affecting photocatalytic degradation process

The PCD efficiencies of pollutants are highly dependent on a number of operating parameters which also govern the kinetics of photomineralization.

2.2.3.1 Initial pollutant concentration

Langmuir–Hinshelwood model has been widely applied for analysis of heterogeneous PCD kinetics of pollutants in the aqueous phase (Herrmann 2005). Generally, the degradation rate of a pollutant increases with the increase of its initial concentration to a certain level and a further increase in the concentration leads to a decrease of the degradation rate (Konstantinou and Albanis 2004). The main steps in the photocatalytic process occur on the surface of the solid photocatalyst. Therefore, a high adsorption capacity is associated with a higher reaction rate. However, at a high initial pollutant concentration whereby all the catalytic sites are occupied, a further increase of the pollutant concentration does not affect the actual catalyst surface concentration and thus the rate constant. On the other hand, the generation and migration of photogenerated electron–hole pairs and their reaction with organic compounds occur in series. At low concentrations, the latter governs the overall process and thus the degradation rate increases linearly with concentration. However, at high concentrations, the former will become the governing step, and the degradation rate increases slowly with concentration. Furthermore, intermediates generated during the photocatalytic process also affect the rate constant of their parent compounds. A higher initial concentration will yield a higher concentration of adsorbed intermediates, which will affect the overall rate.

2.2.3.2 Photocatalyst dosage

In general, with the increase of photocatalyst dosage, the photocatalyst surface area available for adsorption and degradation increases, while the solution opacity (light scattering and attenuation) also increases, leading to a decrease in the penetration of

the photon flux in the reactor and a consequent rate decrease (Kamble et al. 2003). Moreover, the loss in the surface area by agglomeration (particle–particle interactions) at a high solid concentration has also been observed (Kaneco et al. 2004). As a result, at a low photocatalyst dosage, the initial reaction rate is directly proportional to the photocatalyst dosage. However, above a certain dosage, the reaction rate becomes independent of photocatalyst dosage and remains constant or even decreases with further increase of the photocatalyst dosage. In order to avoid excessive photocatalyst dosage in photoreactor and to ensure a total absorption of incident photons, it is very important to select an optimum photocatalyst dosage for a particular photoreactor system.

2.2.3.3 Light intensity

The effect of light intensity on the kinetics of photocatalytic reaction has been systematically investigated (Konstantinou and Albanis 2004, Ollis et al. 1991). It has been demonstrated that, at low light intensities ($<20 \text{ mW cm}^{-2}$), the reaction rate increases linearly with increasing light intensity (first order), because reactions involving electron–hole formation are predominant and electron–hole recombination is negligible. At intermediate light intensities (approximately 25 mW cm^{-2}), the rate depends on the square root of the light intensity (half order) because of the competition between electron–hole pair separation and recombination, thereby causing lower effect on the reaction rate. At high light intensities, the rate is independent of light intensity. In summary, increased light intensity results in an increase in the reaction rate until the mass transfer limitation is the determining factor.

2.2.3.4 Solution pH

As an amphoteric material in aqueous solution, the TiO_2 surface is positively charged at a pH lower than its point of zero charge while negatively charged at a pH

higher than its point of zero charge. In addition, pH may affect the states of ionization of the target organic compounds, hence strongly influencing the adsorption of organic compounds on the TiO_2 surface. Specifically, the adsorption of positively and negatively charged pollutants is favored respectively at $\text{pH} > \text{point of zero charge}$ and $\text{pH} < \text{point of zero charge of } \text{TiO}_2$. In addition, TiO_2 particles tend to agglomerate under acidic conditions and the surface area available for adsorption of pollutants and photon would be reduced which finally affects the photodegradation rate (Paz 2006). On the other hand, $\bullet\text{OH}$ could be formed by the reaction between OH^- ions and h^+ , and the reaction is favorable in the alkaline solutions which lead to an improvement of the process efficiency. On the contrary, at low pH, the positive h^+ are considered as the major oxidation species, and the direct oxidation of pollutants by h^+ dominates (Konstantinou and Albanis 2004). The optimal solution pH for a specific application should be selected based on the preliminary investigations, since the effect of pH is multitudinous and complex.

2.2.3.5 Inorganic anions

The inorganic anions, such as Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and HCO_3^- , are prevalent in surface water, groundwater and wastewater. These species directly compete for adsorptive sites, absorb UV, and act as h^+ and $\bullet\text{OH}$ scavengers (Konstantinou and Albanis 2004), leading to the formation of inorganic anion radicals (e.g. $\text{NO}_3\bullet$, $\text{CO}_3\bullet^-$, etc.) which are not as reactive as h^+ and $\bullet\text{OH}$. Therefore, varying degrees of inhibitory effects of inorganic ions on the PCD efficiency are usually observed. In addition, the inorganic anions could have effect on TiO_2 deactivation. Therefore, the investigation of the influence of inorganic anions is necessary to evaluate the durability of TiO_2 in the treatment of natural waters and wastewaters.

2.2.3.6 Humic acid

Humic acids (HAs), one of the most significant fractions of natural organic matters

(NOMs), is ubiquitous in nearly all the natural waters. HA comprises a variety of functional groups such as carboxylic, phenolic and alcoholic hydroxyls, ketone and quinone groups. It possesses a typical molecular weight ranging from a few thousand to a few hundred thousand Daltons. As an electron shuttle (Lovley et al. 1996), HA could transfer electrons to oxygen to promote the generation of $\bullet\text{O}_2^-$ as well as reduce the recombination of electron-hole pairs, thus enhance the degradation of pollutants. However, the PCD of pollutants could be retarded by the combination effects of light attenuation, competition of HA with pollutants for active sites, and TiO_2 surface deactivation because of HA adsorption. Therefore, the overall effect of HA on the pollutants degradation would depend on the net effect of the aforementioned competitive phenomena.

2.2.3.7 Other operating parameters

In most cases, photocatalytic systems are operated at room temperature without heating. An increase of the photodecomposition rate has been observed with the reaction temperature increasing from 20 to 80 °C (Herrmann 2005). At very low temperatures (below 0 °C), the photocatalytic activity decreases as desorption of final product from the photocatalyst surface becomes the rate limiting step. When the temperature increases above 80 °C and approaches the boiling point of water, the exothermic adsorption of pollutant is disfavored and becomes the rate limiting step, leading to the decrease of photocatalytic activity.

Dissolved oxygen plays an important role in the PCD process. It was found that dissolved oxygen might hinder or improve the photodegradation efficiency depending on the PCD mechanism of the pollutants (Shirayama et al. 2001, Wang and Hong 2000).

2.2.4 Application of photocatalysis for pharmaceuticals removal

Pharmaceuticals are designed to have biological activity against organisms, thus, it

is expected that they will be effectively persistent against bacteria, fungi and possibly non target higher organisms. Moreover, it is inferred that APIs and their metabolites are extremely resistant to biological degradation processes. Therefore, due to the ineffective removal of pharmaceuticals by the conventional water treatment processes, they have been frequently detected in sewage water, surface water, groundwater, drinking water and sludge (Daughton and Ternes 1999a, Kümmerer 2009a, Kümmerer 2009c, Klavarioti et al. 2009). APIs and their metabolites in the aquatic environment have become one of the most concerned issues with regard to public health. They exhibit potential toxicity to human beings and aquatic organisms, and are responsible for the emergence of antibiotic resistant bacteria and genes (Daughton and Ternes 1999a, Kümmerer 2009b, Kümmerer 2009c). Therefore, it is imperative to develop more effective and robust non-biological water treatment technologies for the removal of APIs and their metabolites.

Recently, heterogeneous photocatalysis for pharmaceuticals degradation has become a potentially cost-effective and environmentally-sustainable water and wastewater treatment alternative (Klavarioti et al. 2009). A comprehensive summary of the various applications of batch photocatalysis using suspended TiO_2 for the removal of pharmaceuticals from water systems is provided in Table 2.4. It can be concluded that UV-excited TiO_2 has been mostly used in heterogeneous photocatalysis for the removal of pharmaceuticals. Most of the reported investigations on photocatalysis are based on batch- and lab-scale studies. With the recent development of various visible-light responsive TiO_2 , great attentions have been paid on the photocatalytic removal of pharmaceuticals under visible-light and solar irradiation (Table 2.3).

Table 2.4 The application of batch photocatalysis using suspended TiO_2 for the removal of pharmaceuticals from aqueous systems.

References	PCD experimental conditions	Summary of findings
Abellán et al. (2007)	<ul style="list-style-type: none"> Sulfamethoxazole: $25\text{--}200\text{ mg L}^{-1}$ P25: $0.1\text{--}2.0\text{ g L}^{-1}$ Solar simulator with a 1000 W Xenon lamp: $\lambda > 290\text{ nm}$ 	<ul style="list-style-type: none"> Sulfamethoxazole degradation and total organic carbon (TOC) reduction were improved when TiO_2 concentration was increased, until an optimum located between $0.5\text{--}1.0\text{ g TiO}_2\text{ L}^{-1}$. 82% of sulfamethoxazole degradation and 23% of TOC reduction was achieved when working with $0.5\text{ g TiO}_2\text{ L}^{-1}$. The initial pH seemed to influence the process in some extent, although the antibiotic degradation was not affected by this variable, TOC reduction was dramatically decreased when the initial pH was 2, probably due to interferences caused by the sulfate anion.
Abellán et al. (2009)	<ul style="list-style-type: none"> Sulfamethoxazole and trimethoprim: 100 mg L^{-1} P25: $0.1\text{--}2.0\text{ g L}^{-1}$ Solar simulator with a 1500 W Xenon lamp: $\lambda > 280\text{ nm}$ 	<ul style="list-style-type: none"> The degradation and TOC reduction were improved when TiO_2 concentration was increased up to 0.5 and $0.2\text{--}0.5\text{ g TiO}_2\text{ L}^{-1}$ in the case of sulfamethoxazole and trimethoprim, respectively.
Bernabeu et al. (2011)	<ul style="list-style-type: none"> Trimethoprim, ofloxacin, enrofloxacin, diclofenac, clarithromycin, caffeine, acetaminophen, thiabendazole, carbamazepine, acetamiprid and erythromycin: 5 g L^{-1} P25: $0.2\text{--}0.5\text{ g L}^{-1}$ Compound parabolic collectors (CPCs), with a concentration factor (R_c) of 1 	<ul style="list-style-type: none"> A significant removal of all the emerging pollutants was realized.
Doll and	<ul style="list-style-type: none"> Clofibric acid, iomeprol and 	<ul style="list-style-type: none"> P25 had a better photocatalytic activity for the degradation of clofibric

References	PCD experimental conditions	Summary of findings
Frimmel (2004)	carbamazepine: 0.5–10 mg L ⁻¹ <ul style="list-style-type: none"> • P25 and Hombikat UV100: 0.1–1000 mg L⁻¹ • Solar UV simulator with a 1000 W Xe short-arc lamp: $\lambda > 400$ nm 	acid and carbamazepine than Hombikat UV100. <ul style="list-style-type: none"> • Hombikat UV100 was more suitable than P25 for the PCD of iomeprol.
Elmolla and Chaudhuri (2010)	<ul style="list-style-type: none"> • Amoxicillin, ampicillin and cloxacillin: 103–105 mg L⁻¹ • P25: 0.5–2.0 g L⁻¹ • UVA irradiation with a 6 W EA-160/FE lamp: $\lambda_{\max} = 365$ nm 	<ul style="list-style-type: none"> • pH had a great effect on antibiotic degradation. • Photocatalytic reactions approximately followed pseudo-first order kinetics and the rate constants (<i>k</i>) were 0.007, 0.003 and 0.029 min⁻¹ for amoxicillin, ampicillin and cloxacillin, respectively. • Addition of H₂O₂ at ambient pH 5 and TiO₂ 1.0 g L⁻¹ resulted in complete degradation of amoxicillin, ampicillin and cloxacillin in 30 min.
Giraldo et al. (2010)	<ul style="list-style-type: none"> • Oxolinic acid: 20 mg L⁻¹ • P25: 0.2–1.5 g L⁻¹, pH = 7.5–11 • UVA irradiation with a luxtech cylindrical black light lamp: $\lambda_{\max} = 365$ nm 	<ul style="list-style-type: none"> • Low pH values and 1.0 g L⁻¹ of TiO₂ favored the degradation efficiency of oxolinic acid. • Under optimal conditions, after 30 min, the TiO₂ photocatalytic system was able to reduce the toxicity of the solution by 60%, with 53% of both initial DOC and COD remained in solution.
Hapeshi et al. (2010)	<ul style="list-style-type: none"> • Ofloxacin and atenolol: 5–20 mg L⁻¹ • Six commercially TiO₂ samples: (a) P25, (b) Hombikat UV100, (c) Tronox A-K-1, (d) Tronox TR, (e) Tronox TR-HP-2, and (f) Aldrich (A), 0.05–1.5 g L⁻¹ • UVA irradiation with a 9 W UVA 	<ul style="list-style-type: none"> • P25 was found to be more active than other TiO₂. • Conversion generally increased with increasing catalyst loading, decreasing initial substrate concentration and adding H₂O₂, while the effect of solution pH was substrate-specific. • High concentrations of H₂O₂ had an adverse effect on reaction, presumably due to excessive oxidant scavenging radicals and other reactive species.

References	PCD experimental conditions	Summary of findings
	lamp: $\lambda = 350\text{--}400\text{ nm}$	
Haque and Muneer (2007)	<ul style="list-style-type: none"> Norfloxacin: 0.15–0.5 mM P25, Hombikat UV100 and PC500: 0.5–3.0 g L⁻¹, pH = 4–11 UV irradiation with a 125 W medium–pressure mercury lamp 	<ul style="list-style-type: none"> Both the decomposition and mineralization fitted reasonably well with the first order kinetic model. The degradation of norfloxacin was slightly faster in the presence of P25. The degradation of norfloxacin increased with pH from 4 to 11, substrate concentration from 0.15 to 0.5 mM, and P25 dosage from 0.5 to 3 g L⁻¹.
Hu et al. (2007)	<ul style="list-style-type: none"> Sulfamethoxazole and related sulfonamide antimicrobial agents (sulfisoxazole, sulfathiazole and sulfamethizole): 5–480 μM P25, Hombikat UV100 and TiOxide: 0.01–1.0 g L⁻¹ Light irradiation with a 450 W ozone–free xenon arc lamp: (1) visible light only ($\lambda \geq 400\text{ nm}$), (2) visible light and UVA ($\lambda = 324\text{--}400\text{ nm}$) 	<ul style="list-style-type: none"> Sulfamethoxazole degradation rates using UVA–TiO₂ were dependent upon initial sulfamethoxazole/catalyst/electron acceptor concentrations, and the presence of non–target water constituents, while not sensitive to changes in sulfonamide structure. pH had little direct effect on reaction rates, the presence of NOM inhibited PCD of sulfamethoxazole to a much greater extent at pH 5 than pH 9. The presence of bicarbonate led to enhanced sulfamethoxazole photocatalysis at pH 9.
Kaniou et al. (2005)	<ul style="list-style-type: none"> Sulfamethazine: 50 mg L⁻¹ P25 and ZnO: 0.1–4.0 g L⁻¹ UVA irradiation with a 9 W Osram Dulux S 9 W/7 lamp: $\lambda_{\text{max}} = 366\text{ nm}$ 	<ul style="list-style-type: none"> The disappearance of the organic molecule followed approximately a pseudo–first–order kinetics according to the Langmuir–Hinshelwood model. After 4 h, the desulfurization of the substrate was complete, while only 30% of the nitrogen was recovered in the form of nitrate and ammonium ions.

References	PCD experimental conditions	Summary of findings
Klauson et al. (2010)	<ul style="list-style-type: none"> Amoxicillin: 5–100 mg L⁻¹ P25 and C–Fe codoped TiO₂: 1.0 g L⁻¹ An artificial UVA light source: a 15 W Phillips low–pressure luminescent mercury lamp, $\lambda_{\max}$ = 365 nm An artificial daylight: a Phillips TL–D 15 W/33–640 fluorescent lamp 	<ul style="list-style-type: none"> The addition of H₂O₂ led, in the case of P25, to a twofold increase on the reaction rate, while a negative effect was observed in the presence of ZnO. The degradation of amoxicillin proceeded with maximum efficiency in neutral solutions. The degradation efficiency increased with growing concentration of amoxicillin until 50 mg L⁻¹, and remained constant with further concentration increase.
Laera et al. (2011)	<ul style="list-style-type: none"> Carbamazepine: 10 mg L⁻¹ P25 and hydrogen titanate nanofibers (H–T–NF): 0.1–1.0 g L⁻¹ UVA irradiation with a 8 W lamp: $\lambda_{\max}$ = 360 nm 	<ul style="list-style-type: none"> The degradation selectivity strongly depended on the initial adsorption step. A weak influence of different anions, but a strong influence of the divalent calcium was found in the photocatalytic system using H–T–NF catalyst. The influence of the organic substances in the real effluent was negative.
Li et al. (2008b)	<ul style="list-style-type: none"> Penicillin: initial COD of 300 mg L⁻¹ P25 and S–N codoped TiO₂: 0.5 g L⁻¹ Visible–light source: a 40 W fluorescent lamp, λ = 465 nm (mainly) 	<ul style="list-style-type: none"> The photocatalytic activities of S–N codoped TiO₂ for penicillin degradation in visible–light region were about three times higher than that of P25.
Martínez et al. (2011)	<ul style="list-style-type: none"> Carbamazepine: 8 mg L⁻¹ P25, synthesized TiO₂, ZnO and multi–walled carbon nanotubes–anatase 	<ul style="list-style-type: none"> Optimal conditions for degradation of carbamazepine were obtained using P25 (0.5 g L⁻¹), 5 mM of H₂O₂ or 50% O₂ (v/v), with rate constants ca. 0.3144 and 0.2005 min⁻¹, respectively.

References	PCD experimental conditions	Summary of findings
	composites: 0.1–2.0 g L ⁻¹	
	<ul style="list-style-type: none"> • Near UV–Vis irradiation with a Heraeus TQ 150 medium–pressure mercury–vapor lamp: $\lambda > 366$ nm • UV irradiation with a Heraeus TNN 15/32 low–pressure mercury–vapor lamp: $\lambda_{\max} = 254$ nm 	
Méndez–Arriaga et al. (2008)	<ul style="list-style-type: none"> • Diclofenac, naproxen and ibuprofen: 25–200 mg L⁻¹ • P25: 0.07–1.0 g L⁻¹ • UV irradiation with a Xe–OP lamp: $\lambda = 290$–400 nm 	<ul style="list-style-type: none"> • The optimum amount of TiO₂ for the degradation of ibuprofen was 1 g L⁻¹, while it was 0.1 g L⁻¹ for both diclofenac and naproxen. • Temperature had a significant effect only for naproxen degradation. • Dissolved oxygen concentration was an important parameter to increase the degradation for naproxen and ibuprofen. However, its rate of mineralization did not increase.
Nasuhoglu et al. (2011)	<ul style="list-style-type: none"> • Sulfamethoxazole: 3–12 mg L⁻¹ • P25: 0.01–0.5 g L⁻¹ • UVC irradiation with a mercury–Argon lamp: $\lambda_{\max} = 254$ nm 	<ul style="list-style-type: none"> • Higher COD removal was found for photocatalysis compared to photolysis. • After 6 h of reaction with photolysis and photocatalysis, 24% and 87% removal of COD was observed, respectively.
Palominos et al. (2009)	<ul style="list-style-type: none"> • Tetracycline: 20 mg L⁻¹ • TiO₂ and ZnO: 0.2–1.5 g L⁻¹ • Simulated solar light: SUNTEST XLS⁺ with a Xe lamp, $\lambda = 300$–800 nm 	<ul style="list-style-type: none"> • The optimal oxidation conditions were 1.5 g L⁻¹ and pH 8.7 for TiO₂, and 1.0 g L⁻¹ and pH 11 for ZnO. • ZnO presented a slightly higher oxidation rates than TiO₂ under optimized conditions. • Using radical scavengers, it was found that tetracycline oxidation on TiO₂ occurred principally by direct hole oxidation with participation of •OH, while the oxidation on ZnO was driven mainly by •OH.

References	PCD experimental conditions	Summary of findings
Reyes et al. (2006)	<ul style="list-style-type: none"> • Tetracycline: 40 mg L⁻¹ • P25: 0.5–1.0 g L⁻¹ • UVC irradiation: a 125 W Philip HPLN lamp, $\lambda > 254$ nm • Six 20 W Philips HB31 solarium lamps, $\lambda = 300$–400 nm • UVA irradiation: a 160 W Philips black light MLW lamp, $\lambda_{\text{max}} = 365$ nm 	<ul style="list-style-type: none"> • Rapid tetracycline degradation was observed in the presence of 0.5 g L⁻¹ of TiO₂. • Close to 50% of its initial concentration was eliminated after 10, 20 and 120 min when the irradiation source used was a UVC, solarium and UVA lamp, respectively. • Significant mineralization was obtained using the UVC and solarium lamp.
Rizzo et al. (2009a)	<ul style="list-style-type: none"> • Amoxicillin: 10 mg L⁻¹, carbamazepine: 5 mg L⁻¹, and diclofenac: 2.5 mg L⁻¹ • P25: 0.2–0.8 g L⁻¹ • UVA irradiation with a 125 W black light fluorescent lamp: $\lambda_{\text{max}} = 350$ nm 	<ul style="list-style-type: none"> • A pseudo–first order kinetic model was found to fit well the experimental data. • The mineralization rate of the wastewater contaminated with the pharmaceuticals was found to be really slow ($t_{1/2} = 86.6$ min) compared to that of the same pharmaceuticals spiked in deionized water ($t_{1/2} = 46.5$ min).
Rizzo et al. (2009b)	<ul style="list-style-type: none"> • Diclofenac: 5–80 mg L⁻¹ • P25: 0.2–1.6 g L⁻¹ • UVA irradiation with a 125 W black light fluorescent lamp: $\lambda_{\text{max}} = 350$ nm 	<ul style="list-style-type: none"> • A pseudo–first–order kinetic model was found to fit well most of the experimental data, while at high initial diclofenac concentrations (40 and 80 mg L⁻¹) and at 1.6 g TiO₂ L⁻¹ photocatalyst loading a second–order kinetic model was found to fit the data better.
Wang et al. (2011)	<ul style="list-style-type: none"> • Bisphenol A and clofibric acid: 5 mg L⁻¹ • Anatase Fe–C codoped TiO₂: 0.5 g L⁻¹ • Vis–LED: $\lambda_{\text{max}} = 450$ nm • UVA irradiation with a mercury lamp: $\lambda_{\text{max}} = 365$ nm 	<ul style="list-style-type: none"> • The synergistic effects of Fe and C codoping into TiO₂ resulted in improved photocatalytic activities as compared to C–TiO₂, Fe–TiO₂ and P25. • After 4 h of irradiation with visible light, bisphenol A and clofibric acid were completely removed by the Fe–C codoped TiO₂, concomitantly 61% and 71% of TOC were mineralized, respectively.

References	PCD experimental conditions	Summary of findings
Yang et al. (2010)	<ul style="list-style-type: none"> Solar simulator with a 150 W xenon arc lamp: $\lambda > 400$ nm Atenolol, metoprolol and propranolol: 100 μM P25: 2.0 g L^{-1} UVA irradiation with a high-pressure mercury lamp: $\lambda_{\text{max}} = 365$ nm 	<ul style="list-style-type: none"> The disappearance of the compounds followed pseudo-first-order kinetics according to the Langmuir-Hinshelwood model and the rate constants were 0.075, 0.072 and 0.182 min^{-1} for atenolol, metoprolol and propranolol, respectively. After 240 min irradiation, the reaction intermediates were completely mineralized to CO_2 and the nitrogen was predominantly as NH_4^+.
Zhang et al. (2008b)	<ul style="list-style-type: none"> Acetaminophen: 20–200 μM TiO_2: 0.25–1.0 g L^{-1} UVA irradiation with a 250 W metal halide lamp: $\lambda \geq 365$ nm 	<ul style="list-style-type: none"> After 100 min irradiation, ca. 95% of acetaminophen was decomposed in the 1.0 g L^{-1} TiO_2 aqueous solution with an initial concentration of 100 μM. At pH 3.5, acetaminophen was readily adsorbed and degraded at a faster rate. Reaction rate at pH 6.9 and pH 9.5 was 2.84 and 2.96 $\mu\text{M min}^{-1}$, respectively.
Zhao et al. (2010)	<ul style="list-style-type: none"> Oxytetracycline: 20–80 mg L^{-1} TiO_2 loaded 5A and 13X zeolite: 0.1 g L^{-1}, pH = 5–11 UVC irradiation with two 16 W UV sterilization lamps: $\lambda_{\text{max}} = 254$ nm 	<ul style="list-style-type: none"> The 15wt% TiO_2 loaded 5A zeolite and 10wt% TiO_2 loaded 13X zeolite were found optimum for oxytetracycline removal and degradation in aqueous phase.

2.3 Membrane photoreactors

The difficulty in separation of the dispersed TiO_2 particles from the product water is one challenge for the practical application of TiO_2 particles in water and wastewater treatment. In recent years, photocatalytic membranes with photocatalyst immobilized in/on them have attracted attentions (Albu et al. 2007, Alem et al. 2009a, Alem et al. 2009b, Athanasekou et al. 2012, Choi et al. 2006, Damodar et al. 2009, Ding et al. 2006, Essawy et al. 2008, Hamid et al. 2011, Ke et al. 2011, Lin et al. 2012, Liu and Li 2003, Ma et al. 2010, Molinari et al. 2000, Oh et al. 2009, Rahimpour et al. 2008, Shang et al. 2010, Song et al. 2012, Sun et al. 2012, Zhang et al. 2008a, Zhou et al. 2008). These photocatalytic membranes could avoid the separation of TiO_2 . Obviously, the photocatalytic membrane will be irradiated under light, thus the oxidation of pollutants occurs on the external surface and within the pores of the membrane which potentially mitigates membrane fouling. However, there are several disadvantages. First, the effectiveness of pollutants degradation is lower than that in the case of photocatalyst in suspension. Second, there is a risk of damage of polymer membranes by the UV or $\bullet\text{OH}$. Although ceramic membrane can be a favorable choice over the polymeric membrane, it is remarkably more costly. Third, it is necessary for the membrane replacement when the photocatalyst activity is lost.

The hybrid MPR systems with photocatalyst in suspension have increasingly attracted research attentions recently (Lim et al. 2011, Molinari et al. 2010, Mozia 2010). Flat sheet (Jiang et al. 2010, Molinari et al. 2002b, Molinari et al. 2004), hollow fiber (Chin et al. 2007a, Chin et al. 2007b, Choo et al. 2008b, Xi and Geissen 2001) and ceramic (Benotti et al. 2009, Doll and Frimmel 2005) membrane modules have been used in different membrane processes, such as MF (Benotti et al. 2009, Choo et al. 2008b, Doll and Frimmel 2005, Xi and Geissen 2001), UF (Chin et al. 2007a, Chin et al. 2007b, Jiang et al. 2010) and NF (Molinari et al. 2002b,

Molinari et al. 2004). Generally, reverse osmosis (RO) should not be used for separation of suspended solids. Therefore, the application of RO in the MPR systems for separation of photocatalyst in suspension seems to be rather limited. Due to their low energy consumption, both MF and UF (low-pressure membrane processes) are widely used for colloids removal during water treatment and wastewater reclamation, with the former being more cost-effective due to its higher membrane permeability.

In the MPR systems, photocatalysis could act as the pre-treatment process to mitigate membrane fouling to some degree. Compared to other separation systems, MPR systems seem to be the most promising application that can take the advantages of both the classical photoreactors and the membrane processes. However, there is still a common problem which is the deposition of TiO_2 particles on the membrane surface and inside its pores. This would induce membrane fouling along with the loss of TiO_2 particles for photoactivation. Therefore, effort should be carried out to prevent membrane fouling caused by TiO_2 deposition.

2.3.1 MPR configurations

In general, there are two distinctive configurations for the MPR systems with photocatalyst in suspension, namely separated MPR systems and combined MPR systems (Lim et al. 2011, Molinari et al. 2010, Mozia 2010). Both of them exhibit the effectiveness in retaining the powdered TiO_2 while allowing PCD of pollutants.

2.3.1.1 Separated MPR systems

In the separated MPR systems, pollutant degradation and filtration process occur in two separate chambers, respectively. This configuration could realize the optimization for design and operation of both the photoreactor and the membrane module. However, it requires a large footprint which might not be suitable in land scarce setting.

Molinari et al. investigated a laboratory-scale separated MPR system for the removal of dyes (Molinari et al. 2004) and pharmaceuticals (Molinari et al. 2006) from water, respectively (Fig. 2.5). A 125 W medium-pressure mercury lamp was located axially inside the annular photoreactor, which was enclosed by a cooling jacket. The feed was pumped using a diaphragm pump to the NF membrane module. This MPR system could be operated in both batch and continuous flow modes. In addition, they illustrated another similar configuration of a continuous flow MPR system but with a 500 W medium-pressure mercury lamp positioned above the photoreactor (Molinari et al. 2001, Molinari et al. 2002b).

Fig. 2.5 Schematic diagram of a laboratory-scale separated MPR system with photocatalyst in suspension ((a) oxygen cylinder, (b) photoreactor, (c) thermostatic bath with cooling water, (d) power supply, (e) medium-pressure mercury lamp with cooling jacket, (f) manometer, (g) rotameter, (h) pressurized cell containing the membrane, (i) magnetic stirrer, (l) pump, (m) graduated cylinder for permeate sampling, (n) feed tank (continuous regime), (o) waste tank (continuous regime)) (Molinari et al. 2004).

Fig. 2.6 shows a laboratory-scale separated MPR system for the degradation of acid red B wastewater (Jiang et al. 2010). A 100 W low pressure UVA lamp ($\lambda_{\max} = 365$ nm) equipped with a quartz tube was immersed in the center of a double layer cylindrical photoreactor. The photocatalytic treated wastewater containing fine TiO_2

particles was transported continuously to a plate frame UF membrane separation unit. Lee et al. (2001) developed a similar laboratory-scale separated MPR system for organic removal and TiO_2 separation in drinking water treatment, which consisted of a photoreactor (with a 450 W mercury UV lamp) and a cross-flow plate frame UF membrane module. Fu et al. (2006b) and Fang et al. (2005) investigated a laboratory-scale separated MPR system consisting of an annular photocatalytic oxidation unit ($\lambda_{\text{max}} = 253.7 \text{ nm}$) and a hollow fiber UF membrane unit for the removal of fulvic acids and humic acids, respectively.

Fig. 2.6 Schematic diagram of a laboratory-scale separated MPR system with a 100 W low pressure UVA lamp and a plate frame UF membrane module (Jiang et al. 2010).

Similar laboratory-scale separated MPR systems were also investigated using MF membrane module. Choo et al. (2008b) fabricated a system for the removal of trichloroethylene from water, in which a UVA lamp and a hollow fiber MF membrane module were incorporated. Another similar laboratory-scale separated MPR system combining a photoreactor (with four 25 W UVC lamps) and a hollow fiber MF membrane module was studied for grey water treatment (Rivero et al. 2006). In addition, Fig. 2.7 shows another laboratory-scale separated MPR system for treatment of synthetic wastewater (Shon et al. 2008). Three 15 W UVA lamps

encased within transparent glass were immersed in the photoreactor, while one 15 W UVA lamp enclosed in a box was placed above the cross-flow flat sheet MF membrane unit. The experiments were performed with either UV lamps in the photoreactor or UV lamp above the membrane module in use.

Fig. 2.7 Schematic diagram of a laboratory-scale separated MPR system with UV lamps both immersed in the photoreactor and placed above the membrane module (Shon et al. 2008).

Recently, pilot-scale separated MPRs have attracted great attentions based on the investigation of the laboratory-scale separated MPRs. Fig. 2.8 shows pilot-scale MPRs operated either in batch or continuous flow mode for the removal of lincomycin from water (Augugliaro et al. 2005). The photodegradation was carried out in a plug flow photoreactor (PFP1) which consisted of UV-transparent glass tubes. The installation was provided with compound parabolic collectors (CPCs) modules in series placed on fixed supports to ensure a maximum daily absorption of solar radiation. The aqueous suspension was continuously fed to the PFP1 from the not-reacting tank by means of a centrifugal pump. The reaction solution from the reactor (PFP1) was pumped to the NF membrane module for separation of TiO_2 from the flow stream.

Fig. 2.8 Schematic diagram of (a) batch and (b) continuous flow pilot-scale separated MPRs with photocatalyst in suspension ((A) switch valve, (B) thermocouple, (C) not-reacting tank, (D) pump, (E) regulation valve, (F) manometer, (G) membrane vessel, (H) line under pressure, (I) rotameter, (L) feed tank, (PFP) plug flow photoreactor) (Augugliaro et al. 2005).

In order to prevent TiO_2 cake layer formation, backwashing and back-pulsing have been investigated in the pilot-scale separated MPR systems. A combination of photocatalysis with cross-flow MF membrane module equipped with a computer-controlled periodical backwashing system was applied for PCD of pharmaceutical and diagnostic residues (Doll and Frimmel 2005) (Fig. 2.9). The photochemical reactor consisted of three co-axial tubes, of which the inner quartz tube contained a 14 W low-pressure mercury lamp ($\lambda_{\text{max}} = 254 \text{ nm}$) and the outer tube was used as a cooling jacket. A self-made tubular module with a ceramic single channel membrane of α -aluminium oxide was used due to its resistance to abrasion and backwashing. The retentate from the filter and the filter bypass streams were mixed and recycled to the photochemical reactor, while 97.5% of permeate was recycled. Another installation of a patented pilot unit (Photo-CatTM, Purifics ES Inc.) combining UV/ TiO_2 photocatalysis with filtration and recycling of the photocatalyst by a ceramic cross-flow MF membrane followed by interval back-pulsed was applied for the removal of pharmaceuticals, endocrine disrupting compounds and estrogenic activity from Colorado River water (Benotti et al. 2009) (Fig. 2.10). 32 UV lamps ($\lambda_{\text{max}} = 254$ and 185 nm) were aligned in series, and could be individually turned on or off to control the irradiation intensity. The treated water

was channeled to the unit (9) and the rejected TiO_2 was mixed with influent (5) prior to the UV reactor.

Fig. 2.9 Schematic diagram of a pilot-scale separated MPR system in a partial continuous flow mode (P1 and P2: pumps 1 and 2, rot 1, 2, 3 and 4: rotameters 1, 2, 3 and 4, p: manometer, mv 1, 2 and 3: computer controlled magnetic valves 1, 2 and 3, online data from the sensors of pH, temperature (T), and dissolved oxygen (O_2)) (Doll and Frimmel 2005).

Fig. 2.10 Schematic diagram of a pilot-scale separated MPR system (Photo-CatTM) (1: Raw water feed, 2: bag filter, 3: cartridge filter, 4: influent sampling location, 5: TiO_2 slurry addition, 6: UV reactor, 7: sampling location, 8: TiO_2 recovery unit, 9: effluent sampling location) (Benotti et al. 2009).

2.3.1.2 Combined MPR systems

The combined MPR systems, namely submerged membrane photoreactor (sMPR) systems, are depressurized systems with the membrane submerged in the photoreactor. PCD of pollutants and separation of photocatalysts could be realized simultaneously and thus membrane fouling could be mitigated. However, the membrane packing density can be inevitably reduced. In addition, this system has an inherent problem associated with membrane deterioration. Except PVDF, most of the polymeric membrane materials are not resistant to UV or $\bullet\text{OH}$ attacks (Chin et al. 2006, Molinari et al. 2002b). While ceramic membrane can be a favorable choice over the polymeric membranes for the combined system (Horng et al. 2009), it is remarkably more costly.

The removal of NOM in surface water treatment was investigated in a laboratory-scale sMPR system (Yao et al. 2009) (Fig. 2.11), in which an 8 W black light blue UV lamp and a hollow fiber MF membrane module were submerged in a photoreactor. Similar laboratory-scale sMPRs were investigated by Kim et al. (2010) as a pretreatment process of RO and by Choo et al. (2008a) for the removal of NOM in water, respectively. Damodar et al. (2012, 2010) studied another similar laboratory-scale sMPR system for advanced dye wastewater treatment. Their sMPR system comprised a cylindrical photoreactor (with two 15 W low-pressure mercury UVC lamps) and a submerged flat sheet MF membrane module. The purification of water containing bisphenol A was also investigated in a laboratory-scale sMPR system (Chin et al. 2007a, Chin et al. 2007b) (Fig. 2.12), which combined a borosilicate glass photoreactor and a submerged hollow fiber MF membrane module. Four 8 W black light fluorescent UVA lamps were located on the four sides of the photoreactor, which was used as external UV source.

Fig. 2.11 Schematic diagram of a laboratory-scale sMPR system with an internal UV lamp and a submerged hollow fiber MF membrane module (Yao et al. 2009).

Fig. 2.12 Schematic diagram of a laboratory-scale sMPR system with external UV lamps and a submerged hollow fiber MF membrane module (Chin et al. 2007a, Chin et al. 2007b).

In the aforementioned sMPR systems, the membrane module was not separated from the UV irradiation. Thus, the selection of the membrane material is critical. In order to prevent the membrane from deterioration by UV irradiation and make more membrane materials applicable in the sMPR systems, the membrane module could be shielded from the UV irradiation. Fig. 2.13 presents a laboratory-scale sMPR

system for the degradation of 4-chlorophenol (Horng et al. 2009). The sMPR system was divided into two sections (a photocatalytic reaction chamber and a membrane separation chamber) by a UV blocking baffle. Four 4 W or 8 W black lamps ($\lambda_{\max} = 365$ nm) were immersed in the photocatalytic reaction chamber, while a non-woven fabric membrane module was submerged in the membrane separation chamber. Similar laboratory-scale sMPR system with an 11 W low pressure UV lamp and a submerged membranes for the removal of fulvic acids from water was investigated by Fu et al. (2006a).

Fig. 2.13 Schematic diagram of a laboratory-scale sMPR system with the submerged membrane module separated from the UV irradiation (1: photocatalytic reaction region, 2: membrane separation zone, 3: influent pump, 4: effluent pump, 5 and 6: blower, 7 and 8: air distributor, 9: membrane module, 10: UVA lamp, 11: photocatalyst suspension) (Horng et al. 2009).

Pilot-scale sMPR systems have also been studied recently based on the investigation of the laboratory-scale sMPR systems. Fig. 2.14 shows a pilot-scale sMPR system for the removal of organic pollutants (Ryu et al. 2005). A submerged hollow fiber MF membrane module was surrounded by ten 30 W black light blue lamps ($\lambda_{\max} = 365$ nm) in the sMPR system. The reactor was operated either in continuous or in intermittent suction mode. Pilot-scale sMPR system divided into two compartments by one baffle plate has also been investigated. Fig. 2.15 presents a pilot-scale sMPR system for the degradation of 4-chlorobenzoate in the artificial

wastewater (Huang et al. 2007), in which one compartment was for housing UV lamps and the other for membrane modules. Sixteen 29 W low-pressure mercury lamps with each enveloped by a quartz tube were located in the lamp compartment, while two hollow fiber membrane modules were positioned in the membrane compartment. The same pilot-scale sMPR system was also used for the treatment of polluted river water (Meng et al. 2005).

Fig. 2.14 Schematic diagram of a pilot-scale sMPR system with internal UV lamps and a submerged hollow fiber MF membrane module (Ryu et al. 2005).

Fig. 2.15 Schematic diagram of a pilot-scale sMPR system with two compartments divided by one baffle plate (Huang et al. 2007).

2.3.2 Photocatalyst separation

The TiO_2 separation from the product water is one of the factors to evaluate the performance of the MPR systems. Generally, the primary particles of TiO_2 are in nano-sizes particles. However, they tend to form aggregations of several micron sizes in the liquid phase. It is noteworthy that there is a portion of TiO_2 with aggregated particle sizes which are still smaller than the membrane pore size and might have a chance to pass through the membrane. Nevertheless, the big TiO_2 particles could form a porous cake layer (secondary dynamic membrane) on top of the membrane during filtration, which would help further retain the smaller particles. The effectiveness of TiO_2 separation strongly depends on the membrane properties and operating conditions.

MF membranes have been evaluated for the separation of TiO_2 by many researchers. Horng et al. (2009) investigated the TiO_2 separation by a non-woven membrane with pore size of 2.0 μm in a laboratory-scale sMPR system. They reported that, although the primary particle sizes of P25 were in the range of 20–30 nm, the average secondary particle sizes after aggregation in the liquid phase were in the range of 3–8 μm . The residual turbidity of permeate was 0.5–1.5 NTU (Nephelometric turbidity unit), and there was non-detectable concentration of TiO_2 . Membrane with smaller pore size was investigated by Meng et al. (2005). In their study, the mean particle size of TiO_2 was 1.35 μm , which was readily rejected by the membrane with pore size of 0.4 μm . Damodar et al. (2010) evaluated the TiO_2 separation by a flat sheet polytetrafluoroethylene (PTFE) hydrophobic membrane with pore size of 0.22 μm . They found that the TiO_2 particles in aqueous media were distributed in 100–5000 nm range which was measured using a fine particle size analyzer (10–5000 nm range), and the distribution was slowly shifted towards higher size range (>500 nm) as time proceeded. With a medium particle sized analyzer (1–100 μm range), the TiO_2 particle size was varied from 1 to 5 μm range

when they were fresh, and then increased slowly with operating time (2–20 μm). The turbidity of permeate was higher at the start (1.62–1.85 NTU), and then decreased gradually to 0.87–1.16 NTU in 100–120 min and 0.32–0.56 NTU in 200–240 min, and finally maintained below 0.3 NTU. Hollow fiber polyvinylidene fluoride (PVDF) membrane with pore size of 0.2 μm was evaluated for TiO_2 separation by Chin et al. (2007b). The mean sizes of TiO_2 particles increased to 0.75 and 0.31 μm after 1.5 h of aeration with rate of 0.2 and 4 L min^{-1} , respectively. Higher aeration rates produced greater shear rates to prevent agglomeration of particles. The turbidity of permeate was similar to that of deionized water, indicating no leakage of TiO_2 from the sMPR system. In the investigation of Choo et al. (2008b), they found that the majority of TiO_2 particles was $>0.4 \mu\text{m}$ which was larger than the membrane pore size of 0.1 μm , and meanwhile the TiO_2 concentration and turbidity in permeate were $<0.5 \mu\text{g L}^{-1}$ and <0.1 NTU, respectively. Huang et al. (2007) also investigated the membrane with pore size of 0.1 μm for the TiO_2 separation. It was found that TiO_2 particles had a size distribution within 10.5–23.5 μm . $<5\%$ of TiO_2 particles passed through the membrane in the beginning 48 h, but the particles could hardly penetrate the membrane afterwards. All the aforementioned examples verified the successful separation of TiO_2 particles by MF membranes from treated water.

Similarly, UF has also been attested for the effective TiO_2 separation in the MPR systems. Mozia et al. (2006) successfully used membrane with molecular weight cut off (MWCO) of 500 kDa to separate TiO_2 particles. It was found that the turbidity of the feed was equal to ca. 2100 NTU while the turbidity of permeate amounted to ca. 0.08 NTU after 5 h of UF. Sopajaree et al. (1999) applied membrane with MWCO of 100 kDa for TiO_2 separation. The initial particle size distribution in the TiO_2 slurry was larger than the membrane pore size, and it shifted to a larger-size range after ten repeat cycles of use. The permeate turbidity was down to the 0.26–0.45 NTU level from the initial turbidity in the 5000–6500 NTU range of the

suspension. In the study of laboratory-scale MPR system conducted by Jiang et al. (2010), the average volume diameter of TiO_2 particles in the solution was $9.5 \mu\text{m}$, which was easily rejected by UF membranes with MWCO of 70 kDa, as confirmed by the reduced turbidity of the permeate ($<0.3 \text{ NTU}$).

Molinari et al. (2002a, 2008, 2001, 2004, 2006) have systematically investigated the TiO_2 separation by NF membranes in various MPR systems. They reported almost completely separation of TiO_2 from the product water.

2.3.3 Permeate flux and membrane fouling

A common problem in the MPR systems with photocatalyst in suspension is the deposition of TiO_2 particles on the membrane surface and/or inside its pores, thus inducing membrane fouling along with the loss of TiO_2 particles for photoactivation. The main factors influencing membrane fouling in the MPR systems are summarized below.

Generally, an increase of particle concentration in feed would enhance the particle transfer rate to the cake layer, namely the thickness of TiO_2 cake layer on the membrane surface was proportional to the TiO_2 concentration. In addition, the cake resistance increases while the permeate flux decreases more severely at a higher TiO_2 concentration. Sopajaree et al. (1999) studied the influence of TiO_2 concentration on UF permeate flux. They found that the permeate flux linearly decreased when the photocatalyst concentration was increased from 0.5 to 3.0 g L^{-1} . Similar phenomenon was reported by Shon et al. (2008). They observed a negligible decline of MF permeate flux with $0.001 \text{ g TiO}_2 \text{ L}^{-1}$. However, with 0.01 , 0.10 and $1.00 \text{ g TiO}_2 \text{ L}^{-1}$, the flux decline increased to 15% , 64% and 94% respectively after 2 h of operation.

The effect of TiO_2 concentration on the membrane fouling is significantly different at different pH. Xi and Geissen (2001) found that the permeate flux increased by 60%

at pH 6.9 (which was close to the isoelectric point of TiO_2) with the TiO_2 concentration increasing from 0.08 to 0.13 vol%, while only 16% of permeate flux increase was found at pH 5.0. This most sensitive behavior of the TiO_2 concentration at its isoelectric point was attributed to the largest degree of polydispersity of TiO_2 particles. Permeate flux applied would also influence the effect of TiO_2 concentration on the membrane fouling. A lower permeate flux usually induces a lower filtration resistance. Horng et al. (2009) reported nearly no filtration resistance for TiO_2 concentration in the range of 0.25–3.0 g L⁻¹ at flux of 3.0 m³ m² d⁻¹, while the filtration resistance increased at above 4.0 m³ m² d⁻¹ with the increase of TiO_2 concentration.

The membrane fouling at different pH was closely linked with the surface charge (zeta potential) and hydrophilicity of both TiO_2 particles and membranes. Damodar et al. (2012) found that the deposition of TiO_2 on the membrane surface was accelerated at pH 5.0 due to the electrostatic attraction effect between the membranes and TiO_2 particles, as the membranes were negatively charged and the TiO_2 particles were positively charged at pH 5.0. While at pH ≥ 7.0 , both the membranes and TiO_2 particles were negatively charged, thus an insignificant deposition of TiO_2 on the membrane surface was observed due to the net electrostatic repulsion. Correspondingly, the TiO_2 cake layer accumulated on the membrane surface was much denser at pH 5.0 than that at pH ≥ 7.0 . In addition, the TiO_2 slurry concentration dropped rapidly at pH 5.0 when the permeate flux was increased from 32 to 64 L m⁻² h⁻¹, indicating a severe membrane fouling. At pH ≥ 7.0 , an increase in the permeate flux did not show much difference in the fouling characteristics. Furthermore, the TiO_2 cake layer on the membrane surface might alter the hydrophilicity of membrane surface, and then slightly change the filtration resistance of the fouled membrane.

The presence of NOM in feed solution is another factor contributing to the

membrane fouling in the MPR systems. It was found that the cake layer consisting of HAs and TiO₂ particles was much denser than the TiO₂-only cake layer (Fang et al. 2005, Lee et al. 2001). As a result, an increase of cake resistance was observed with the presence of HAs, leading to a decrease of permeate flux. However, the humic substances would be decomposed in the presence of TiO₂ under UV irradiation, and thus the permeate flux could be recovered to some degree (Lee et al. 2001). Choo et al. (2008a) indicated that the transmembrane pressure (TMP) of the sMPR system appeared to be very stable under UV irradiation, but it started to increase sharply when the UV irradiation stopped. Similar observation was also found by Shon et al. (2008). Although TiO₂ would deposit on the membrane surface to induce membrane fouling, the combination of TiO₂ with UV irradiation might mitigate membrane fouling during treatment of NOM polluted waters.

The hydraulic parameters, such as TMP and cross-flow velocity (CFV), could also influence the permeate flux in the MPR systems. Xi and Geissen (2001) reported that high TMP enhanced the deposition of TiO₂ on the membrane surface, followed by an increase of cake resistance. The building up of the polarization/gel layer is generally hindered at high shear rates, thus increasing CFV would induce a significant increase in permeate flux. Choo et al. (2008b) found the significant reduction of permeability with the CFV decreasing from 1.45 to 0.19 m s⁻¹.

In order to mitigate membrane fouling, different operating conditions could be applied. Chin et al. (2007a, 2007b) reported that aeration could provide a mechanical agitation, thus maintaining the TiO₂ in suspension and reducing the membrane fouling. Damodar et al. (2010) found that intermittent aeration could reduce the chances of TiO₂ accumulation on the membrane surface. The advantages of aeration were also investigated by Huang et al. (2007). They demonstrated that fine bubble aeration could control the sedimentation of the suspended TiO₂, while an intermittent coarse bubbling under the membrane module was able to return the

entrapped TiO_2 back into suspension. However, Chin et al. (2007a, 2007b) found that increasing aeration would result in higher energy consumption and could also attenuate UV transmission in the photoreactor. In this context, intermittent permeation was an alternative in order to reduce membrane fouling, thus maintaining the high flux operation at lower energy input for aeration. Intermittent permeation operation would reduce the operating cost of the sMPR system. Nevertheless, this operation mode would lead to a decrease in water production. Similar intermittent operations were also applied for the mitigation of membrane fouling by Choi (2006) and Ryu et al. (2005). Backwash was another feasible operation to prevent TiO_2 deposition on the membrane surface. Meng et al. (2005) indicated that intermittent backwash was effective to retard the membrane fouling and enable stable membrane operation for more than 1 month. Yao et al. (2009) suggested that backwash could remove the reversible membrane fouling to maintain a lower hydraulic filtration resistance. Doll and Frimmel (2005) also verified the successful application of backwash for the membrane fouling control in a pilot-scale MPR system.

2.3.4 Photodegradation efficiency and permeate quality

MF, UF and NF membranes are widely used in the MPR systems. All of them are not able to reject low molecular weight compounds, resulting in the transportation of products and by-products of photodegradation to the permeate side. Therefore, the pollutant removal efficiency and the permeate quality mainly depend on the photocatalysis. Except from the factors introduced in Section 2.2.3, some additional parameters associated with the membrane process should be taken into consideration for the removal of pollutant in the MPR systems.

The position of light source in the MPR systems is very important for the degradation of pollutants. Molinari et al. (2004) compared the photodegradation rate of Congo Red with two different UV irradiation modes. They found that Congo Red

was photodegraded much more rapidly (ca. 50 times) when the immersed lamp was used, although its power was ca. 4 times lower than that of the external lamp.

Generally, a higher hydraulic retention time (HRT) (corresponding to lower permeate flux) would enhance the degradation efficiency of organic pollutants, and then induce an improved permeate quality. Chin et al. (2007a) found that the mineralization efficiency of bisphenol A increased with HRT (TOC values were 6 and 1.5 mg L⁻¹ with HRT of 1.95 and 4.87 h respectively after 3 h of photocatalytic reaction). Higher degree of pollutant mineralization at lower permeate flux was also reported by Rivero et al. (2006). They found that the reduction of chemical oxygen demand (COD) was 78–83% and 70–73% for 15 and 55 L m⁻² h⁻¹, respectively. Similarly, Molinari et al. (2000) reported that the degradation efficiency of 4-nitrophenol was slightly higher for less permeable membranes due to its longer contact time in the TiO₂ suspension.

The batch and continuous operating modes have great effect on the photodegradation effectiveness and permeate quality. Molinari et al. (2002b) investigated the removal effectiveness of 4-nitrophenol in the MPR systems in both batch and continuous modes. The concentration of 4-nitrophenol in retentate and permeate for the continuous operating mode was decreasing less rapidly than that for the recycle mode. With the similar MPR systems, Molinari et al. (2002a) also investigated the removal of Patent Blue in alternate batch–continuous operating modes. During the continuous mode, the concentration of Patent Blue increased with time. After 240 min of reaction, the operating mode was switched to the batch mode. This change of the process operation resulted in a decrease of dye concentration. When the continuous mode was reestablished, the concentration of Patent Blue increased sharply. Despite lower removal efficiency of model compounds in the continuous mode, they suggested that the continuous system is more promising than the batch one due to its potential industrial application

(Molinari et al. 2002a, Molinari et al. 2002b).

The intermittent and continuous operating modes also have effect on the photodegradation effectiveness and permeate quality. Ryu et al. (2005) found that the degradation efficiency of 4-chlorophenol was slightly reduced with intermittent operation. However, Chin et al. (2007b) reported that the mineralization rate of bisphenol A during intermittent permeation operation was similar to that in the case of a continuous operation. The contradictory findings reported by the different research groups might be attributed to their different operating conditions.

2.4 Conclusions

TiO₂ could be photoexcited only under UV irradiation ($\lambda < 387$ nm) due to its large band gap. This inhibits the wide applications of TiO₂ powders using solar light in photocatalysis. In order to harness solar energy for photocatalysis, visible-light responsive TiO₂ has been developed. Doping TiO₂ with non-metals is one of the most efficient methods to shift the spectral response of TiO₂ from UV to visible-light region. In recent years, a higher visible-light photocatalytic activity of codoped or tridoped TiO₂ with non-metals has been observed compared to single-doped TiO₂. However, comprehensive mechanisms of photocatalysis with codoped and tridoped TiO₂ will need to be further investigated. Due to the ineffective removal of pharmaceuticals by the conventional water treatment processes, they have been frequently detected in water systems. Therefore, the investigation of pharmaceuticals removals over visible-light responsive TiO₂ will be necessary as a water and wastewater treatment alternative.

In recent years, the hybrid MPR systems coupling photocatalysis and membrane process have increasingly attracted research attention in order to separate TiO₂ particles from the product water. However, it is rather challenging to design such MPR systems due to the inherent complexities associated with the membrane

module and light distribution therein. Moreover, most of the previous researches on MPR systems were associated with Evonik P25 (TiO_2) under UV irradiation. Further investigation on the MPR systems should be necessary using visible–light responsive TiO_2 under visible–light irradiation. This will provide practical significance for the MPR systems to treat real waters using visible–light photocatalysis and low–pressure membrane process.

CHAPTER 3 DEVELOPMENT OF C-SENSITIZED AND N-DOPED TiO₂ FOR PHOTOCATALYTIC DEGRADATION OF SULFANILAMIDE UNDER VISIBLE-LIGHT IRRADIATION

3.1 Introduction

TiO₂ doping with non-metals (e.g. C, N, S, F) has been proven as one of the most efficient methods to shift the spectral response of TiO₂ from UV to visible-light region (Asahi et al. 2001, Górska et al. 2008, Li and Shang 2010, Rengifo-Herrera and Pulgarin 2010, Subagio et al. 2010, Zaleska et al. 2008). Visible-light photocatalytic activity of TiO₂ could also be enhanced by carbon sensitization (Chou et al. 2006, Górska et al. 2008, Lettmann et al. 2001). To the best knowledge of the author, there is no report thus far about the synthesis of TiO₂ with synergistic effects of both carbon-sensitizing and nitrogen-doping for application in water treatment.

This chapter describes a novel carbon-sensitized and nitrogen-doped TiO₂ (C/N-TiO₂) prepared via a facile sol-gel method under controlled calcination temperature. The physicochemical properties of C/N-TiO₂ were investigated by various characterization techniques. The visible-light photocatalytic activities of C/N-TiO₂ were evaluated under vis-LED irradiation using SNM as the target pollutant. SNM is one of sulfonamides antibiotics frequently used for human and veterinary medicine as antibacterial drugs and growth promoters (Kümmerer 2009a). The ubiquitous appearances of SNM and its metabolites in the sewage water, surface water, groundwater, drinking water and sludge have been reported

(Kümmerer 2009a, Kümmerer 2009b, Le-Minh et al. 2010). As persistent pollutants, SNM and its metabolites in the aquatic environment have become one of the most concerned issues with regard to public health. They exhibit potential toxicity to human beings and aquatic organisms, and are responsible for the emergence of antibiotic resistant bacteria and genes (Daughton and Ternes 1999b, Kümmerer 2009b, Munir et al. 2011). The chemical structure of SNM is shown as follows.

LEDs, known for their varying monochromatic wavelengths with high spectral purity, reliability, long lifetime, energy efficiency, flexibility and small footprint, provide potential for optimized optical solution such as uniform illumination, inherent compactness and higher photon efficiency in photoreactor systems. Vis-LEDs have increasingly attracted research attention as visible-light source in recent years (Ghosh et al. 2008, Ghosh et al. 2009, Liu et al. 2009, Subagio et al. 2010, Wang and Lim 2010, Yin et al. 2008). In this phase of study, vis-LEDs that emit white, blue, green and yellow lights were used as visible-light sources to investigate the photoresponse of C/N-TiO₂ in the visible-light region.

The effects of calcination temperature on the resulting C/N-TiO₂ and their effectiveness in SNM degradation and mineralization were investigated. Since inorganic anions are prevalent in aqueous phase in different pH conditions, the effects of pH and inorganic anions on SNM degradation and mineralization were also investigated. The organic intermediates and end-products formed during photocatalysis were monitored. Deactivation test was conducted to investigate the photochemical stability and durability of the photocatalyst. Microtox assay was carried out to evaluate the evolution of acute toxicity of SNM solution during photocatalysis.

3.2 Experimental

3.2.1 Synthesis of C/N–TiO₂

All chemicals were used as received without further purification and Millipore Co. MilliQ (MQ) water with resistivity of 18.2 MΩ cm was used throughout the thesis unless otherwise stated. Titanium butoxide (Ti(OC₄H₉)₄, 97%, Sigma–Aldrich) was used as both titanium precursor and carbon source. Nitric acid (70%, Labscan) was used to catalyze the hydrolysis and condensation reactions and as nitrogen source. In a typical synthesis, 10 mL titanium butoxide was added dropwise into 50 mL absolute ethanol (99.9%, Merck) under magnetic stirring for 30 min at ambient temperature (26 ± 1 °C). Then a mixture of 3 mL MQ water, 3 mL absolute ethanol and 1 mL nitric acid was added dropwise into the above solution, followed by stirring for 6 h and aging overnight to obtain the gel. The gel was dried at 80 °C for ca. 10 h in an oven, ground into fine powder, and calcinated at 200, 250, 300, 350 and 400 °C for 2 h in a muffle furnace under air atmosphere to obtain the final products, which are denoted as T200, T250, T300, T350 and T400, respectively. Under these controlled calcination temperatures, different contents of carbonaceous species would be incorporated in the as-synthesized C/N–TiO₂.

3.2.2 Characterization of C/N–TiO₂

X-ray diffraction (XRD) patterns were obtained from a Bruker D8 ADVANCE X-ray Diffractometer with Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$) in a 2θ range of 5–80°. The crystallite size and phase content were obtained from TOPAS 2.0 software. The specific surface area was calculated using the BET equation with a Quantachrome Autosorb–1 instrument at 77 K. The particle morphology was observed with a JEOL–2100F transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. The surface element content was collected using JEOL JSM6360 scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy

(EDX). The surface chemical compositions and bonding states of the photocatalysts were probed by X-ray photoelectron spectroscopy (XPS) analysis on a KratosAxis Ultra spectrometer using a monochromatized Al K α (1486.71 eV) X-ray source. All the spectra were calibrated with the adventitious carbon at 284.8 eV. The UV–vis diffuse reflectance spectroscopy (DRS) were obtained using a Perkin Elmer Lambda 35 UV–vis spectrophotometer equipped with an integrating sphere assembly with BaSO₄ as the reflectance standard. Photoluminescence (PL) emission spectra of the samples were recorded at room temperature using SPEX Fluorolog–3 spectrometer (Horiba Scientific, New Jersey, USA) with excitation wavelength at 320 nm.

3.2.3 Vis–LED photoreactor and evaluation of photocatalytic activity

The PCD of SNM was carried out in a vis–LED photoreactor (Fig. 3.1). Typically, 500 mL borosilicate glass reactor was wrapped with a 2 m long vis–LED flexible strip (SMD 5050, 30 unit m⁻¹, 7.5 W m⁻¹) comprising 60 LED units (vis–LED unit size was 4 mm $\times$ 4 mm). The beam angle of the light source from vis–LED was 120° and the LED array was not contagious but they spaced out at average 3.3 cm. Four different LED strips were used, emitting white light (LED–W, main emission wavelength λ = 450 nm), blue light (LED–B, λ = 465 nm), green light (LED–G, λ = 523 nm) and yellow light (LED–Y, λ = 589 nm), respectively. The spectrum of LED–W clearly showed blue light emitted at ca. 450 nm and more broadband Stokes–shift light emitted at roughly 500–600 nm. The visible–light and UV intensities of the LEDs were ca. 5 W m⁻² and < 0.5 W m⁻², respectively, as measured by a digital power meter SP 1065 (Janco Impex) and an Accumax XRP–3000 radiometer when the power meter was placed in the middle of the spiral LED strips. The changes of reactor temperature are insignificant throughout the experiment. A mirror cover was used to minimize light penetration from surrounding and water loss due to evaporation.

Fig. 3.1 Schematic diagram of the vis-LED photoreactor.

The PCD of SNM (>99.0%, Sigma-Aldrich) was systematically evaluated with the C/N-TiO₂ compared with the commercial P25 (BET area = $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ and average primary particle size = 21 nm, Jebsen & Jessen Chemicals) at ambient temperature. Before turning on the LED-W, 400 mL suspension with photocatalyst dosage of 1.0 g L^{-1} and initial SNM concentration of 5.0 mg L^{-1} in MQ water was stirred in dark to reach adsorption equilibrium within 1 h. During photocatalysis, sample aliquots were collected at appropriate time intervals and filtered using $0.45 \mu\text{m}$ cellulose acetate syringe membrane filters for high performance liquid chromatography (HPLC) analysis. TOC were measured with a Shimadzu ASI-V TOC Analyzer. The effect of solution pH was investigated through pH adjustment using 1 M HCl and 1 M NaOH solutions. To investigate the influence of inorganic anions, NaCl, NaNO₃, Na₂SO₄, NaHCO₃, NaH₂PO₄ • 2H₂O and Na₂SiO₃ • 9H₂O were introduced into the SNM solution to obtain a concentration of 1 mM, respectively. The adsorption of SNM on T300 in the presence of these inorganic anions was also carried out.

3.2.4 Analytical method

The HPLC analysis was performed with a Spherisorb ODS-2 column (150 mm × 4.6 mm I.D., 5 μm) and a SPD-M20A diode array detector (DAD) using a Shimadzu LC system (LC-20AD). Methanol (HPLC-grade, Merck) and MQ water was used as mobile phase A and B ($v_A/v_B = 40/60$), respectively, at a flow rate of

0.5 mL min⁻¹. The oven temperature was maintained at 30 °C. The detector wavelength was set at 260 nm and injection volume was 20 µL.

Carboxylates (acetate, oxalate, formate and propionate) and inorganic anions (sulfate, nitrate and nitrite) were monitored by a Dionex ICS-1000 ion chromatography (IC) system equipped with a conductivity detector. An IonPac AS15 anion-exchange column (4 × 250 mm) was employed with an elution containing 36 mM KOH at a flow rate of 1.2 mL min⁻¹. Ammonium was determined using the colorimetric nesslerization method (HACH Method 8038) with a HACH DR/2400 spectrophotometer.

Zeta potential data were obtained using a Malvern Nano-ZS Zetasizer with T300 concentration of 0.3 g L⁻¹ in suspension. The pH value of the suspension was adjusted using 1 M HCl and 1 M NaOH solutions.

3.2.5 Photocatalytic degradation kinetics

Langmuir-Hinshelwood model as defined by Eq. (3.1) has been widely applied for analysis of heterogeneous PCD kinetics of pollutants in the aqueous phase (Herrmann 2005):

$$r_0 = - \frac{dC}{dt} = - \frac{kKC}{1 + KC} \quad (3.1)$$

where r_0 is the initial reaction rate (mg L⁻¹ min⁻¹), C is the concentration of pollutants (mg L⁻¹), t is the reaction time (min), k is the Langmuir-Hinshelwood reaction rate constant (mg L⁻¹ min⁻¹), and K is the Langmuir adsorption equilibrium constant (L mg⁻¹). At a dilute concentration of pollutants (i.e. $KC \ll 1$), pseudo-first-order kinetics model can be assumed as shown in Eqs. (3.2) and (3.3):

$$r_0 = - \frac{dC}{dt} = -kKC \quad (3.2)$$

$$\ln\left(\frac{C}{C_0}\right) = -kKt = -k_{app}t \quad (3.3)$$

where k_{app} is the apparent rate constant (min^{-1}), and C_0 is the initial concentration of pollutants (mg L^{-1}).

3.2.6 Initial quantum yield

Quantum yield is defined as the ratio of the reaction rate in molecules transformed to the rate of photons absorption (Herrmann 1995). However, since the reaction rate is a function of the substrate concentration which may vary with light irradiation time, quantum yield appears to be a kinetic parameter which is time-dependent. The best estimation of quantum yield is given by the initial value as expressed in Eq. (3.4) (Chatzitakis et al. 2008):

$$\varphi_0 (\%) = \frac{r_0}{1000 M_w I_A} \times 100 \quad (3.4)$$

where φ_0 is initial quantum yield, r_0 can be calculated from k_{app} and C_0 ($r_0 = k_{app}C_0$, $\text{mg L}^{-1} \text{ min}^{-1}$), M_w is the molecular weight of SNM ($172.20 \text{ g mol}^{-1}$), I_A is the irradiation intensity absorbed by the photocatalyst which is assumed equal to the incident photon flux intensity ($\text{mol photons L}^{-1} \text{ min}^{-1}$).

According to the quantum theory, I_A can be calculated by Eqs. (3.5)–(3.7):

$$I_A = \frac{M Q}{V t} \quad (3.5)$$

$$M = \frac{\lambda}{h c \times N_A} \quad (3.6)$$

$$Q = 60 \times I S t \quad (3.7)$$

where M is the mole photons needed to derive one Joule of energy ($\text{mol photons J}^{-1}$), Q is the energy produced by light during reaction (J), V is the volume of the treated water in the reactor (L), t is the reaction time (min), λ is the wavelength of the incident light (m), h is Plank's constant ($6.626 \times 10^{-34} \text{ J s}$), c is the light velocity ($3.0 \times 10^8 \text{ m s}^{-1}$), N_A is Avagadro's number (6.02×10^{23}), I is the light intensity (W m^{-2}), and S is the irradiation area (m^2).

3.2.7 Acute toxicity test

The acute toxicity of SNM solution during photocatalysis was examined with *Vibrio fischeri* (NRRL number B-11177) using a Microtox Model 500 Analyzer (Azur Environment, Workingham, England) within 24 h after irradiation. *V. fischeri* was obtained as a freeze-dried reagent and stored at $-20\text{ }^{\circ}\text{C}$. Prior to the test, the freeze-dried *V. fischeri* was activated by hydration with a sterilized solution of sodium chloride. The sample was filtered using $0.45\text{ }\mu\text{m}$ cellulose acetate syringe membrane filter. The sample pH was adjusted to between 6 and 8 using NaOH or HCl and the sample osmolality was adjusted to 2% by adding high purity sodium chloride. *V. fischeri* emits light as a by-product of their cellular respiration and metabolic processes. Decrease in the respiration rate, corresponding to the inhibition of bioluminescence, will be caused by the presence of toxic compounds. The bioluminescence of *V. fischeri* was recorded after 5, 15 and 30 min-incubation time at $15\text{ }^{\circ}\text{C}$. The EC₅₀ values (% v/v, the percentage of sample dilution that causes a 50% reduction in bioluminescence of *V. fischeri*) were calculated with MicrotoxOmni software.

3.3 Results and discussion

3.3.1 Characteristics of C/N-TiO₂

3.3.1.1 Structure and textural properties

For all the C/N-TiO₂, obvious XRD diffraction peaks associated with the anatase phase appeared as shown in Fig. 3.2. Although there were no obvious XRD diffraction peaks for both brookite and rutile phase, the brookite phase was present in the C/N-TiO₂ according to the phase content analysis with TOPAS 2.0 software, while the rutile phase did not exist. According to Carp et al. (2004), the calcination temperature in this study was not high enough for the transformation of TiO₂ from the anatase to rutile phase. The diffraction peaks became sharper with the

calcination temperature increased from 200 to 400 °C, indicating the TiO₂ crystal growth which resulted in the crystallite size increased from ca. 8.3 to 13.5 nm and the specific surface area decreased from 188 to 109 m² g⁻¹ (Table 3.1). Also the anatase phase content increased with the calcination temperature, suggesting the crystallinity enhancement.

Fig. 3.2 XRD patterns of the C/N-TiO₂ and P25.

Table 3.1 Physicochemical properties of the C/N-TiO₂.

TiO ₂	Crystallite size ^a (nm)	Anatase content ^a (%)	SSA ^b (m ² g ⁻¹)	Surface element content ^c (wt%)			
				N	C	Ti	O
T200	8.3	75	188	BLQ ^d	9.76	40.36	49.88
T250	8.4	77	183	BLQ	7.33	41.84	50.83
T300	10.1	79	160	BLQ	5.42	51.95	42.63
T350	11.0	90	138	BLQ	4.72	46.03	49.25
T400	13.5	95	109	BLQ	3.19	54.99	41.82

^a Derived from XRD patterns.

^b Specific surface area, calculated using the BET equation.

^c Determined via EDX analysis.

^d BLQ, below the limit of quantification.

Fig. 3.3a shows that the T300 particle sizes were ca. 10 nm which is in agreement with the XRD results. The indices of the spotted rings shown in the selected area electron diffraction (SAED) pattern of T300 validated the anatase tetragonal phase of TiO₂. Fig. 3.3b presents the HRTEM image of T300 to further confirm the anatase-crystal nature. The lattice spacing (d) was ca. 0.35 nm between adjacent

lattice planes, matching well with the distance between the (1 0 1) crystal planes of anatase TiO_2 .

Fig. 3.3 (a) TEM and (b) HRTEM images of T300. Inset shows SAED pattern of T300.

3.3.1.2 EDX analysis

Table 3.1 shows the result of EDX elemental microanalysis as obtained from the EDX spectra and elemental mappings. According to the EDX spectra, the C/N- TiO_2 was mainly composed of C, Ti and O, while the characteristic peak for nitrogen was not evidenced. However, nitrogen was detected to be present rather uniformly in the EDX elemental mappings of the C/N- TiO_2 . It is noted that the carbon content on the surface of the C/N- TiO_2 decreased from 10 to 3% when the calcination temperature increased from 200 to 400 °C, due to the increasing decomposition of carbon from the organic precursor. Correspondingly, the color of the C/N- TiO_2 appeared to change from yellow to brown when the calcination temperature increased from 200 to 300 °C, and changed to grayish and white when calcinated at 350 °C and 400 °C, respectively.

3.3.1.3 XPS analysis

XPS spectra reveal the presence of C, N, O and Ti on the T300 surface (Fig. 3.4). Fig. 3.4a shows that the C 1s peaks were observed at 284.8, 286.1 and 288.9 eV

with atomic percentages (at%, estimated from the relative area intensities of peaks) of 20.26, 5.68 and 2.05, respectively. The C1s peak at 284.8 eV is usually ascribed to the adventitious elemental carbon or carbon residues from the organic precursor (mainly C–C bonds) (Gu et al. 2008, Yang et al. 2008a). The C 1s peaks at 286.1 and 288.9 eV are assigned to the carbonate species, such as C–O, C=O, O=C–O and C–N bonds (Yang et al. 2008a). No peak was found around 282 eV, thus the possibility of carbon substitutional doping in the form of Ti–C bonds cannot be confirmed (Gu et al. 2008, Yang et al. 2008a). These carbonaceous species could act as photosensitizer to induce the visible–light absorption and response (Chou et al. 2006, Górska et al. 2008, Lettmann et al. 2001), which is responsible for the enhancement of visible–light photocatalytic activity. In addition, they could narrow the band gap by creating interface states (Treschev et al. 2008).

Three peaks were observed from the N1s XPS spectra (Fig. 3.4b). The peak at 396.5 (0.05 at%) is ascribed to the Ti–N bonds resulted from the nitrogen substitutional incorporation into the TiO₂ lattice (Popa et al. 2010, Yang et al. 2008a). The peak at 399.5 (0.53 at%) is assigned to the molecularly chemisorbed γ -N₂ (N–H, N–N, N–O, N–C bonds), such as Ti–N–O and Ti–O–N sites (Wang and Lim 2010, Wei et al. 2008, Yang et al. 2008a). The peak at 402.1 eV (0.03 at%) is attributed to the molecularly adsorbed nitrogen species (i.e. NO_x or NH_x) (Yang et al. 2008a). These three peaks indicated that nitrogen was interstitially and substitutionally doped into the TiO₂ lattices. Nitrogen doping is related to the band–gap narrowing with red shift of absorption edge to the visible–light region (Asahi et al. 2001, Wang and Lim 2010), leading to the enhanced visible–light photocatalytic activity.

Fig. 3.4 XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s and (d) Ti 2p region for T300.

Fig. 3.4c shows one peak at 529.2 eV (41.34 at%) for Ti–O bonds and another at 530.9 eV (10.00 at%) for the oxygen atoms in the surface hydroxyl groups (H–O bonds) and/or in the carboxyl groups (C–O bonds) (Górska et al. 2008, Xu et al. 2010). Ti^{4+} oxidation state was confirmed by peaks at 458.2 (13.67 at%) and 463.9 eV (6.39 at%) for Ti 2p_{3/2} and Ti 2p_{1/2}, respectively (Yang et al. 2008a) (Fig. 3.4d). No peak for Ti^{3+} was observed which is in agreement with the study by Górska et al (2008) who found that TiO_2 mainly contained Ti^{4+} at low calcination temperature. Ti 2p peak at around 455 eV was not observed to further indicate the absence of the Ti–C bonds (Gu et al. 2008).

3.3.1.4 Optical properties

Fig. 3.5 indicates that the C/N– TiO_2 exhibited remarkable red shift of absorption edge with long band tailings to the visible–light region. The red shift phenomenon could be attributed to the interface states created by the carbonaceous species

(Treschev et al. 2008), and/or the nitrogen incorporated into the TiO_2 lattice through the mixing of N 2p states with O 2p states (Asahi et al. 2001, Wang and Lim 2010). The extended band tailing in the visible–light region could originate from the carbonaceous species working as photosensitizer (Chou et al. 2006, Górska et al. 2008, Lettmann et al. 2001).

Fig. 3.5 DRS of the C/N– TiO_2 and P25.

3.3.2 Photocatalytic degradation

3.3.2.1 Effect of calcination temperature for C/N– TiO_2 synthesis

In dark without photocatalyst added, SNM concentration remained unchanged (5.0 mg L^{-1}) over 5 h, indicating that hydrolysis of SNM could be negligible. The k_{app} and φ_0 values under various experimental conditions are summarized in Table 3.2. Fig. 3.6a shows that $< 1\%$ of SNM was photodegraded via photolysis (without photocatalyst) after 5 h of LED–W irradiation. The adsorption of SNM on the C/N– TiO_2 could be negligible. The photocatalysts exhibited PCD efficiencies of SNM in the order of T300 (95%) $>$ T350 (65%) $>$ T250 (46%) $>$ T200 (29%) $>$ T400 (14%) $>$ P25 (5%) with the φ_0 decreased from 2.70 to 0.050%. P25 exhibited lower photocatalytic activity which can be validated by the result of Fig. 3.5 that the absorbance intensity of P25 in the visible–light region was lower than that of T300.

In addition, compared to P25 (the pure TiO_2), T300 was a carbon-sensitized and nitrogen-doped TiO_2 as shown in Fig. 3.4. It is postulated that T300 will possess more visible-light photocatalytic activity than that of P25. The TOC removal (maximum at 70% for T300) was less than the PCD efficiency under the same experimental condition, indicating the incomplete mineralization of SNM along with the formation of organic intermediates.

Fig. 3.6 PCD and mineralization of SNM using the C/N- TiO_2 and P25 (a) without and (b) with BQ in solution (C_0 : 5.0 mg L^{-1} ; photocatalyst dosage: 1.0 g L^{-1} ; irradiation light: LED-W; pH: neutral).

Table 3.2 k_{app} , r_0 and ϕ_0 for PCD of SNM under various experimental conditions.

TiO ₂	C ₀ (mg L ⁻¹)	TiO ₂ dosage (g L ⁻¹)	Visible light	pH	Anion	k_{app} (min ⁻¹), ×10 ⁻³	r_0 (mg L ⁻¹ min ⁻¹), ×10 ⁻³	ϕ_0 (%)
Photolysis						0.012 (0.821 ^a)	0.06	0.003
P25						0.202 (0.984)	1.01	0.050
T200	5.0	1.0	LED-W	Neutral	–	2.27 (0.989)	11.4	0.564
T250						1.34 (0.970)	6.68	0.332
T300						10.9 (0.997)	54.3	2.70
T350						4.15 (0.963)	20.7	1.03
T400						0.614 (0.957)	3.07	0.152
	5.0					10.9 (0.997)	54.3	2.70
	10					6.70 (0.997)	67.0	3.33
T300	20	1.0	LED-W	Neutral	–	4.10 (0.999)	81.9	4.07
	30					2.86 (0.997)	85.8	4.27
	50					2.06 (0.992)	103	5.13
		0.10				1.02 (0.998)	5.08	0.252
		0.25				2.41 (0.998)	12.0	0.598
T300	5.0	0.50	LED-W	Neutral	–	5.68 (0.999)	28.4	1.41
		1.0				10.9 (0.997)	54.3	2.70
		1.5				13.3 (0.999)	66.4	3.30
		2.0				14.7 (0.998)	73.4	3.64
T300	5.0	1.0	LED-W	Neutral	–	10.9 (0.997)	54.3	2.70
			LED-B			6.80 (0.984)	34.0	1.63

TiO ₂	C ₀ (mg L ⁻¹)	TiO ₂ dosage (g L ⁻¹)	Visible light	pH	Anion	k _{app} (min ⁻¹), ×10 ⁻³	r ₀ (mg L ⁻¹ min ⁻¹), ×10 ⁻³	φ ₀ (%)	
			LED-G			2.18 (0.951)	10.9	0.466	
			LED-Y			0.677 (0.825)	3.38	0.128	
				3.0±0.1		14.2 (0.995)	71.2	3.54	
				5.0±0.1		11.7 (0.995)	58.6	2.91	
T300	5.0	1.0	LED-W	7.0±0.1	—	7.36 (0.982)	36.8	1.83	
				9.0±0.1		6.73 (0.980)	33.6	1.67	
				11.0±0.1		6.19 (0.978)	31.0	1.54	
					Cl ⁻ (1mM)	9.94 (0.994)	49.7	2.47	
					NO ₃ ⁻ (1mM)	9.31 (0.989)	46.5	2.31	
					SO ₄ ²⁻ (1mM)	10.3 (0.989)	51.3	2.55	
T300	5.0	1.0	LED-W	6.9 ±0.1		HCO ₃ ⁻ (1mM)	5.78 (0.970)	28.9	1.44
						H ₂ PO ₄ ⁻ (1mM)	7.13 (0.981)	35.7	1.77
						Silica (1mM)	4.40 (0.962)	22.0	1.09

^a R², correlation of determination.

The calcination temperature has a great effect on the crystal phase structure, incorporation of nitrogen into the TiO_2 lattice and content of carbonaceous species, which is related to the visible–light photocatalytic activity. In this study, the optimal calcination temperature for PCD of SNM was 300 °C (T300). T300 mainly contained anatase phase which is photocatalytically more active than rutile and brookite phase. In addition, a fraction of amorphous phases were present in T300. In the study by Lettmann et al. (2001), they found that the amorphous phase may also carry photocatalytic activity. The nitrogen incorporated into the TiO_2 lattice could result in the band–gap narrowing and red shift of absorption edge to the visible–light region due to the mixing of N 2p states with O 2p states (Asahi et al. 2001, Wang and Lim 2010), as illustrated in Fig. 3.7. There are three possible mechanisms for the enhancement of photocatalytic activity by the carbonaceous species incorporated in T300.

Fig. 3.7 Schematic illustration of the synergistic effects of carbon–sensitizing and nitrogen–doping of T300 for the degradation of SNM (“S” represents the photosensitizer on the T300 surface).

Mechanism 1. They could serve as photosensitizer to extend the absorption band tailing to the visible–light region (Chou et al. 2006, Górska et al. 2008, Lettmann et al. 2001). Moreover, the excited photosensitizer could inject an electron into the conduction band of T300, then the electron is transferred to the molecular oxygen adsorbed on the T300 surface, producing $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ (Fig. 3.7). Both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are capable of degrading SNM (Dong et al. 2008). In order to investigate the

role of carbonaceous species, benzoquinone (BQ) was used as an effective quencher of $\bullet\text{O}_2^-$ (Raja et al. 2005) during the PCD of SNM. As shown in Fig. 3.6b, the SNM removal efficiencies decreased with the increase of BQ concentrations in solution, reflecting that BQ prevented the degradation of SNM through consuming $\bullet\text{O}_2^-$. This result confirmed the carbon photosensitizing effect that the carbonaceous species could promote the production of $\bullet\text{O}_2^-$.

Mechanism 2. They could act as the lattice defect of TiO_2 to form interface states between the anatase and brookite phases (Chou et al. 2006, Treschev et al. 2008), which could narrow the band gap effectively. According to Fig. 3.5, the band-gap energies of T300 and P25 were 2.9 eV and 3.1 eV, respectively, calculated using the transformed Kubelka–Munk function (Serpone et al. 1995).

Mechanism 3. They could also play a role of electron scavenger to inhibit the electron–hole recombination (Dong et al. 2008, Lettmann et al. 2001). PL is often used to investigate the recombination of charge carriers. If neglecting the photothermal effect, the lower PL intensity might indicate a lower electron–hole recombination rate. Fig. 3.8 shows that the PL intensity of T300 was lower than that of P25, which indicated the lower electron–hole recombination rate with T300.

Fig. 3.8 PL spectra of P25 and T300.

The photocatalysts contained carbonaceous species in the order of $\text{T200} > \text{T250} > \text{T300} > \text{T350} > \text{T400}$. T300 possessed the highest photocatalytic activity. This

indicated that there is an optimal content of carbonaceous species for highest visible–light photocatalytic activity. The excessive carbonaceous species on the T200 and T250 surface could absorb the visible light, thus reduced the visible–light photons available to generate electron–hole pairs, and consequently lowered their photocatalytic activity. For T350 and T400 with less carbonaceous species on their surfaces, the carbon photosensitizing effect was insignificant. T300 possessed the optimal content of carbonaceous species in this study. Therefore, further evaluations of photocatalytic activity as discussed in the following sections were focused on T300.

3.3.2.2 Effect of initial SNM concentration

Fig. 3.9(a1) illustrates the effect of initial SNM concentration on the PCD of SNM kinetic. The k_{app} values decreased from 10.9 to $2.06 \times 10^{-3} \text{ min}^{-1}$ and φ_0 values increased from 2.70 to 5.13% as the initial SNM concentration increased from 5.0 to 50 mg L^{-1} (Table 3.2). It is presumed that a fraction of light might be absorbed by the SNM molecules rather than T300 for solution with high SNM concentration. Another possible reason is that the organic intermediates and end products formed during photocatalysis might compete with the SNM molecules for the limited adsorption and photocatalytic sites on the T300 surface, causing inhibition of the PCD of SNM to a certain degree. Additionally, Langmuir–Hinshelwood model was used for the degradation kinetics analysis. The linear plot of Langmuir–Hinshelwood model is shown in the inset of Fig. 3.9(a1). The Langmuir–Hinshelwood reaction rate constant and Langmuir adsorption equilibrium constant are $0.103 \text{ mg L}^{-1} \text{ min}^{-1}$ and 0.215 L mg^{-1} ($R^2=0.981$), respectively. Fig. 3.9(a2) shows that the time–dependent TOC removal agreed with that of the SNM degradation. TOC removal decreased from 70 to 30% after 5 h of LED–W irradiation when the initial SNM concentration increased from 5.0 to 50 mg L^{-1} .

Fig. 3.9 Effect of (a) initial SNM concentration (Inset shows linear plot fitting of Langmuir-Hinshelwood model), (b) T300 dosage, (c) vis-LEDs, (d) solution pH and (e) inorganic anions on (1) PCD of SNM and (2) TOC removal.

3.3.2.3 Effect of T300 dosage

It can be seen from Fig. 3.9(b1) that the PCD efficiencies increased with the T300 dosage up to 1.0 g L^{-1} with k_{app} values of $10.9 \times 10^{-3} \text{ min}^{-1}$ (Table 3.2). Increase of the T300 dosage from 0.10 to 1.0 g L^{-1} led to a tenfold increase of φ_0 values from 0.252 to 2.70% , while a higher dosage resulted in slight increase of φ_0 values. With the increase of T300 dosage, the photocatalyst surface area available for adsorption and PCD was increased, while the solution opacity was also increased leading to a decrease in the penetration of the photon flux through the reactor. Moreover, the loss in the surface area by the photocatalyst agglomeration at higher T300 dosage was also observed. As a result, the optimum T300 dosage in this study was 1.0 g L^{-1} . Fig.3.9(b2) also shows that the TOC removal only increased marginally as the T300 dosage increased from 1.0 to 2.0 g L^{-1} .

3.3.2.4 Effect of type of vis-LED

It was found that $< 1\%$ of SNM was photodegraded after 5 h of LED-W, B, G and Y irradiations via photolysis. As shown in Fig. 3.9(c1), the degradation efficiency of SNM was enhanced by T300, namely, 95%, 84%, 42% and 13% of SNM was degraded after 5 h of LED-W, B, G and Y irradiations with k_{app} values of 10.9 , 6.80 , 2.18 and $0.677 \times 10^{-3} \text{ min}^{-1}$, respectively. The corresponding TOC removal agreed with that of the SNM degradation and was 70%, 61%, 34% and 9% (Fig. 3.9(c2)), respectively. Apparently, the SNM degradation and mineralization efficiencies were higher under LED-W and B irradiations than those under LED-G and Y irradiations. Meanwhile, the carbon photosensitizing effect for SNM degradation and mineralization was more significant under LED-W and -B irradiations. However, a fraction of SNM was still removed under LED-Y irradiation, showing that T300 could be photoexcited by visible light even with wavelength at around 600 nm. This confirmed the remarkable red shift of absorption edge of T300 as shown in Fig. 3.5.

3.3.2.5 Effect of solution pH

Fig. 3.9(d1) demonstrates that the PCD of SNM was more favorable in acidic conditions. After 5 h of LED–W irradiation at pH 3 and 5, > 99% and 97% of SNM was photocatalytic degraded, respectively, while the corresponding TOC removal was 76% and 74% (Fig. 3.9(d2)). With the pH increasing from 3 to 11, the k_{app} values decreased from 14.2 to $6.19 \times 10^{-3} \text{ min}^{-1}$ (Table 3.2) and the φ_0 values decreased from 3.54 to 1.54%.

As an amphoteric material, the TiO_2 surface is positively charged at a pH lower than its point of zero charge and negatively charged at a pH higher than its point of zero charge. The point of zero charge of T300 was determined to be at pH 5.5. Therefore, T300 was positively charged at $\text{pH} \leq 5$, while negatively charged at $\text{pH} \geq 7$. Additionally, SNM molecule possesses pK_a values of 2.40 and 10.43 (Baran et al. 2009). Thus, SNM is mainly neutral at pH 3, 5, 7 and 9, while negatively charged at pH 11 (García-Galán et al. 2009). The adsorption experiment confirmed that SNM adsorption decreased with increasing pH, resulting from the net electrostatic repulsion between T300 and SNM. However, it can be postulated that the adsorption effect only played a minor role in the enhancement of photocatalytic activity, as the adsorption of SNM on T300 within the pH range investigated was insignificant.

The incorporation of carbonaceous species in T300 contributed significantly to the visible–light photocatalytic activity. Generally, $\bullet\text{OH}$ can be produced according to Eq. (3.8) in both acidic and alkaline conditions. In the case of low pH, the mechanism for $\bullet\text{OH}$ formation in the presence of molecular oxygen is shown in the Eqs. (3.9)–(3.12), while in the case of high pH, direct generation of $\bullet\text{OH}$ radicals (Eq. 3.13) is possible (Malato et al. 2009).

As photosensitizer, the carbonaceous species could promote the formation of $\bullet\text{O}_2^-$ (Eq. 3.9) in acidic conditions through the injection of an electron into the conduction band followed by the reaction between the electron and molecular oxygen adsorbed on the T300 surface. Subsequently, both the formed $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ could be responsible for the PCD of SNM. The PCD of SNM still occurred at $\text{pH} > \text{p}K_{a2}$ due to the $\bullet\text{OH}$ originated from the reaction between $\text{OH}^-/\text{H}_2\text{O}$ and photogenerated holes as shown in the Eq. (3.13). Apparently, due to the carbon photosensitizing effect during which both $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ were formed as shown in Eqs. (3.9)–(3.12), the PCD efficiency of SNM was higher in acidic conditions than that in alkaline conditions.

3.3.2.6 Effect of inorganic anions

The influence of the inorganic anions on the adsorption of SNM on T300 was negligible. As shown in Table 3.2 and Fig. 3.9(e1), the inorganic anions generally did not significantly inhibit the PCD of SNM. The order of inhibitory effects induced by the anions follows silica > bicarbonate > phosphate > chloride, nitrate and sulfate. The TOC removal trend agreed with that of the SNM degradation (Fig. 3.9(e2)). It has been reported that anions, such as chloride, nitrate, sulfate, bicarbonate and phosphate could act as h^+ and $\bullet\text{OH}$ scavenger to form ionic radicals (Eqs. (3.14) and (3.15)) (Rincón and Pulgarin 2004), which are less reactive than h^+ and $\bullet\text{OH}$. Therefore, the presence of anions would inevitably inhibit the SNM mineralization to a certain extent.

Silica showed a slightly more pronounced inhibitory effect for the PCD of SNM. It is reported that silica can undergo polymerization at relatively low concentration, and polymeric or colloidal silica may be present through the condensation of monomers (Kohn et al. 2003, Yang et al. 2008b). As a result, the active sites of photocatalysts might be occupied by polymeric and/or colloidal silica surrounding the photocatalysts. In addition, the light could be intercepted by polymeric and/or colloidal silica, leading to the light screening effect. Therefore, the PCD of SNM could be inhibited to some degree.

3.3.3 Evolution of carboxylates and inorganic anions

High degree of mineralization of a variety of organic pollutants can be achieved with photocatalysis due to the non-selectivity of $\bullet OH$. However, the complete mineralization for most antibiotics are difficult due to their structural stability (Westerhoff et al. 2005). In this study, a new chromatographic peak appeared during the HPLC analysis of the SNM solution after irradiation. The peak area for the organic intermediate increased first and then decreased during the 5 h of LED-W irradiation (Fig. 3.10). On the other hand, a slow increase of acetate concentration with irradiation time was observed. Nitrate was detected but its concentration was below the limit of quantification, while nitrite was not detected in the solution. About 86% of nitrogen was released as ammonium and about 52% of sulfur was released as sulfate after 5 h of LED-W irradiation. In addition, the concentration of both ammonium and sulfate remained almost constant after a rapid release within 1 h.

Fig. 3.10 Evolution of acetate, ammonium, sulfate and organic intermediate during photocatalysis of SNM using T300 (C_0 : 5.0 mg L⁻¹; T300 dosage: 1.0 g L⁻¹; irradiation light: LED-W; pH: neutral).

3.3.4 Deactivation test

To investigate the possibility of the leaching of carbonaceous species and nitrogen dopant from T300 and the poisoning of T300 by the organic intermediates and end-products, especially sulfate, deactivation test was carried out as follows. After 5 h of LED-W irradiation, the T300 solution was centrifuged, washed with MQ water for 3 times and collected for reuse. The result shows that 88% of SNM degradation and 57% of TOC removal were still achieved after five recycles (Fig. 3.11), indicating that the activity of T300 only decreased by less than 10%. This suggested that both the leaching of carbonaceous species and nitrogen dopant and the poisoning of T300 could be negligible during its 5 times of reuse for the PCD of SNM. Apparently, T300 exhibited good photochemical stability during the PCD of SNM under vis-LED irradiation.

Fig. 3.11 Deactivation of T300 during the PCD of SNM (C_0 : 5.0 mg L⁻¹; T300 dosage: 1.0 g L⁻¹; irradiation light: LED-W; pH: neutral). Inset shows the corresponding TOC removal after 5 h of irradiation.

3.3.5 Acute toxicity evaluation

The acute toxicity evaluation of antibiotics is essential due to the possible formation of more toxic organic intermediates and end-products during treatment. Fig. 3.12 demonstrates the acute toxicity (expressed as EC50, lower EC50 value indicates higher acute toxicity to *V. fischeri*) of SNM solution as a function of irradiation time during visible-light photocatalysis using T300. The acute toxicity trends of SNM solution were similar for the cases of 5, 15 and 30 min-incubation time. The original SNM solution before visible-light irradiation showed acute toxicity to *V. fischeri* with EC50 value of ~ 23% v/v. The acute toxicity reached the maximum after 1 h of irradiation, and then it began to decrease slowly due to the further mineralization. Since the concentrations of ammonium and sulfate remained almost constant during the 5 h of irradiation, and the concentration of organic intermediates continued to decrease with time, it is concluded that ammonium and sulfate might be not toxic to *V. fischeri* while the acute toxicity might be induced by the organic intermediates. For the acetate, it could be used as the nutrient for *V. fischeri*. In addition, the synergistic effects among the species in the solution on the acute toxicity should also be considered. However, with further irradiation for more than

5 h, the acute toxicity of SNM solution continued to decrease. After 12 h of irradiation, the SNM solution exhibited much lower acute toxicity than that of the original SNM solution before irradiation. It indicated that photocatalysis using T300 is favorable for the detoxification of SNM solution.

Fig. 3.12 Acute toxicity of SNM solution during photocatalysis using T300 (C_0 : 5.0 mg L⁻¹; T300 dosage: 1.0 g L⁻¹; irradiation light: LED-W; pH: neutral).

3.4 Conclusions

A novel visible-light responsive C-sensitized and N-doped TiO₂ was synthesized by a facile sol-gel method for PCD of SNM. Under controlled calcination temperature, different contents of carbonaceous species originated from titanium butoxide could be incorporated in the resulting C/N-TiO₂. Due to the synergistic effects of carbon-sensitizing and nitrogen-doping, T300 showed the highest photocatalytic activity for SNM degradation under LED-W irradiation. The acidic conditions were favorable for the PCD of SNM due to the carbon photosensitizing effect. The presence of chloride, nitrate, and sulfate appeared to inhibit the SNM degradation insignificantly, while different degrees of inhibitory effects were observed in the presence of bicarbonate, phosphate and silica. T300 exhibited good photochemical stability and its absorption onset could be extended to ca. 600 nm. Acetate, ammonium and sulfate were produced during SNM photocatalysis.

Extending the irradiation time exhibited the decreasing trend of the acute toxicity of SNM solution to *V. fischeri*. The C-sensitized and N-doped TiO₂ under vis-LED irradiation has the potential application for the mineralization and detoxification of pollutants during visible-light photocatalysis in the water and/or wastewater treatment process.

CHAPTER 4 DEVELOPMENT OF C–N–S TRIDOPED TiO₂ FOR PHOTOCATALYTIC DEGRADATION OF TETRACYCLINE UNDER VISIBLE–LIGHT IRRADIATION

4.1 Introduction

Chapter 3 describes a novel visible–light responsive C–sensitized and N–doped TiO₂, which exhibited high photocatalytic activity for SNM degradation under visible–light irradiation due to the synergistic effects of both carbon–sensitizing and nitrogen–doping. In recent years, it is of great interest to investigate the codoped TiO₂ with non–metals (Chen et al. 2007, Rengifo-Herrera et al. 2009a, Sun et al. 2006). A higher visible–light photocatalytic activity of codoped TiO₂ compared with single–doped TiO₂ has been observed. More recently, non–metal tridoped TiO₂ have also been paid great attentions, which have been demonstrated to possess high photocatalytic activity for degradation of different kinds of organic pollutants under visible–light irradiation (Ao et al. 2009b, Wang et al. 2009, Zhou and Yu 2008). However, further investigation of non–metal tridoped TiO₂ should be conducted in order to get a more comprehensive understanding.

In order to make effort to utilize solar energy efficiently, this chapter presents a facile, cost–effective and easily scaled–up sol–gel method for the synthesis of C–N–S tridoped TiO₂ with titanium butoxide as titanium precursor and thiourea as the dopant source. Photocatalytic activity of various C–N–S tridoped TiO₂ prepared with different thiourea contents and calcination temperatures was investigated under visible–light irradiation with TC as the model pollutant. TC is another antibiotics

frequently detected in sewage water, surface water, groundwater, drinking water and sludge (Brown et al. 2006, Kümmerer 2009a, Lillenberg et al. 2009, Pailler et al. 2009) due to its ineffective removal by the conventional water treatment processes (Kümmerer 2009a). The chemical structure of TC is shown as follows.

The effects of initial TC concentration and solution pH on the PCD and mineralization of TC were evaluated. The PCD efficiencies of TC were also compared under visible-light and simulated solar irradiations. Microtox assay was employed to evaluate the evolution of acute toxicity of TC solution during photocatalysis. In addition, the visible-light photocatalytic activity of T300 and T0.05–450 was compared.

4.2 Experimental

4.2.1 Synthesis of C–N–S tridoped TiO₂

In general, C–N–S tridoped TiO₂ was synthesized using a sol–gel method which was a modification of the technique as described in Section 3.2.1. The modifications were as follows: (1) certain amount of thiourea (99%, Sigma–Aldrich) was dissolved into 50 mL absolute ethanol before the addition of 10 mL titanium butoxide; (2) ground fine powder was calcined at 350, 450, 550 and 650 °C for 2 h in a muffle furnace under air atmosphere to obtain the final products. The thiourea : Ti molar ratios were 0.03:1, 0.05:1, 0.10:1 and 0.15:1, and the as-synthesized TiO₂ were labeled as Tx–y, where x and y indicated the thiourea : Ti molar ratio and the calcination temperature, respectively. For comparison, carbon-doped TiO₂ (CT) was synthesized with the same procedure without adding thiourea. In addition,

nitrogen-doped TiO₂ (NT) and sulfur-doped TiO₂ (ST) were synthesized with the comparable contents of N and S using urea (99%, Merck) and sodium sulfate (99%, Sigma–Aldrich) as dopant sources, respectively. CT, NT and ST were finally calcined at 450 °C for 2 h in a muffle furnace under air atmosphere.

4.2.2 Characterization of C–N–S tridoped TiO₂

The characterization of C–N–S tridoped TiO₂, including XRD, porosimetry, TEM, SEM/EDX, XPS, and DRS, were carried out using the similar methods described in Section 3.2.2.

4.2.3 Photocatalytic activity test

A tubular borosilicate glass reactor with diameter of 7 cm and height of 30 cm was used in this study. A F6T5/D cold white visible lamp (6 W, Japan), which was wrapped with two layers of polycarbonate filter sheet to cut off UV (wavelength < 420 nm) emitted from the lamp, encapsulated in a quartz jacket and positioned in the middle of the reactor, was used as the visible–light source (denoted as visible–1). The visible–light and UV intensities were ca. 32 and 0.4 W m^{–2} as measured on the surface of quartz jacket with a digital power meter SP 1065 (Janco Impex) and an Accumax XRP–3000 radiometer, respectively. All the photocatalytic experiments were performed at ambient temperature.

In a typical experiment, 400 mg photocatalyst was dispersed into 800 mL TC (>99.0%, Sigma–Aldrich) solution with an initial TC concentration of 5.0 mg L^{–1} under magnetic stirring to obtain the photocatalyst dosage of 0.5 g L^{–1}. Before turning on the lamp, the solution was stirred in dark for 1 h to reach adsorption equilibrium. During photocatalytic experiment, sample aliquots were collected at appropriate time intervals and filtered using 0.45 µm cellulose acetate syringe membrane filters for HPLC analysis which was similar to that described in Section 3.2.4. The differences included: (1) an Inertsil ODS–3 column (150 mm × 4.6 mm

I.D., 5 μm) was used; (2) methanol and 0.01 M oxalic acid buffer solution was used as mobile phase A and B ($v_A/v_B = 40/60$), respectively; and (3) the detector wavelength was set at 269 nm. TOC was measured with a Shimadzu ASI-V TOC Analyzer. The influences of initial TC concentration and solution pH on the PCD of TC were also studied.

To investigate the effect of light intensity and light source, a solar simulator (Newport, USA) equipped with a 150 W Xenon arc lamp was used. Typically, the photocatalytic experiment was carried out in a 250 mL TC solution without aeration (initial TC concentration of 5.0 mg L^{-1} and photocatalyst dosage of 0.5 g L^{-1}). A quartz cover was placed on top of the glass reactor to minimize the loss of water due to evaporation. The simulated solar irradiation (280–630 nm, denoted as solar) possessed the light intensity of ca. 1000 W m^{-2} (one sun power) as measured by a digital power meter SP 1065 (Janco Impex) on the surface of the solution, and its UV intensity was ca. 25 W m^{-2} as measured by Accumax XRP-3000 radiometer. Dichroic mirrors were used to control light wavelengths in specific ranges of UV (280–400 nm, denoted as UV) and visible-light (420–630 nm, denoted as visible-2) irradiation. The UV intensity was ca. 30 W m^{-2} for the case of UV irradiation. In the case of visible-2 irradiation, the light intensity was ca. 325 W m^{-2} , and an additional polycarbonate filter was used to cut off UV spectrum (wavelength < 420 nm) and reduce the UV intensity to less than ca. 0.1 W m^{-2} .

4.2.4 Acute toxicity test

The acute toxicity of TC solution during photocatalysis was examined with *Vibrio fischeri* using a Microtox Model 500 Analyzer. The detailed procedure could be found in Section 3.2.6.

4.3 Results and discussion

4.3.1 Characteristics of C–N–S tridoped TiO₂

4.3.1.1 Structure and textural properties

As shown in Fig. 4.1, obvious diffraction peaks attributed to the anatase phase appeared while there was no rutile phase for all the C–N–S tridoped TiO₂, CT, NT and ST. The diffraction peaks became wider with the increase of the thiourea content (Fig. 4.1a), indicating that thiourea could suppress the crystal growth of the anatase TiO₂ which was also observed by Wang et al. (Wang et al. 2010). Meanwhile, the crystallite size increased with the calcination temperature. The crystallite sizes and anatase contents of the as-synthesized TiO₂ were shown in Table 4.1. No rutile phase was formed in T0.05–550 and T0.05–650, while rutile phase was present in T0–550 and T0–650 (Fig. 4.1b). It implies that thiourea could inhibit the transformation of TiO₂ from anatase to rutile phase which is in agreement with the result reported by Hamadanian et al. (Hamadanian et al. 2009).

Fig. 4.1 XRD patterns of the as-synthesized TiO₂.

Table 4.1 Physicochemical properties of the as-synthesized TiO₂.

TiO ₂	Crystallite size ^a (nm)	Anatase content ^a (%)	SSA ^b (m ² g ⁻¹)	Pore volume ^c (cm ³ g ⁻¹)	Pore diameter ^c (nm)	E _g ^d (eV)	Surface elemental content ^e (wt%)				
							C	N	S	Ti	O
T0.03–450	12.5	96	69.0	0.063	21.9	2.95	4.51	BLQ ^f	1.16	57.45	36.88
T0.05–450	10.7	94	89.6	0.067	16.9	2.67	5.55	BLQ	1.67	50.55	42.23
T0.10–450	9.3	86	118.1	0.069	14.5	2.49	5.73	BLQ	1.82	46.59	45.85
T0.15–450	8.1	77	157.9	0.074	14.2	2.28	7.21	BLQ	1.98	51.77	39.04
T0.05–350	9.7	85	183.9	0.076	14.2	1.88	5.79	BLQ	1.72	55.88	36.61
T0.05–550	13.7	91	8.0	0.016	21.8	2.86	4.82	BLQ	1.61	46.93	46.64
T0.05–650	30.3	95	6.3	0.016	38.2	2.89	4.63	BLQ	1.38	60.36	33.63
CT	19.1	97	27.7	0.041	34.1	3.00	2.97	0	0	49.23	47.80
NT	12.6	99	20.11	0.033	33.9	2.90	3.19	BLQ	0	57.48	39.33
ST	12.4	90	82.86	0.042	24.2	2.96	1.89	0	1.98	56.48	39.65

^a Derived from XRD patterns.^b Specific surface area, calculated using the BET equation.^c Obtained from the desorption branch of nitrogen isotherm by the BJH method.^d Band-gap energy, calculated using the transformed Kubelka–Munk function.^e Determined via EDX analysis.^f BLQ, below the limit of quantification.

The specific surface area, pore volume and pore diameter of various C–N–S tridoped TiO_2 , CT, NT and ST are shown in Table 4.1. The specific surface area increased with the thiourea content due to the suppression of the TiO_2 crystal growth by thiourea. But the specific surface area decreased with the calcination temperature due to the sintering and crystal growth of TiO_2 particles. The high specific surface area could be feasible for the adsorption of TC on the C–N–S tridoped TiO_2 , followed by the enhanced photocatalytic activity.

Figs. 4.2a and 2c show that the T0.05–450 and CT particle sizes were at ca. 10 nm and 20 nm, respectively, which is in agreement with the XRD results. It is noted from the selected area electron diffraction (SAED) patterns of TiO_2 that both T0.05–450 and CT were mainly anatase which could be further validated by the HRTEM image in Figs. 4.2b and 2d.

Fig. 4.2 TEM and HRTEM images of (a, b) T0.05–450 and (c, d) CT. Insets show SAED patterns of TiO_2 .

4.3.1.2 EDX analysis

The result of EDX elemental microanalysis of the as-synthesized TiO_2 is shown in Table 4.1. Nitrogen was not detected in CT and ST, while sulfur was not detected in CT and NT. The typical EDX spectra of the C–N–S tridoped TiO_2 showed the appearance of peaks of C, S, O, Ti, indicating that they were mainly composed of these elements. Although the characteristic peak for nitrogen was not evidenced in the C–N–S tridoped TiO_2 , it was indeed detected and present rather uniformly from the EDX elemental mapping, implying that the nitrogen content was lower than the limit of quantification. It is noted that the carbon and sulfur contents on the surface of the C–N–S tridoped TiO_2 increased with the increase of thiourea content, while decreased with the calcination temperature.

4.3.1.3 XPS analysis

Fig. 4.3 illustrates the XPS spectra of C 1s, N 1s, S 2p, O 1s and Ti 2p for the as-synthesized T0.05–450, CT, NT and ST. Fig. 4.3a shows that all the samples share a common peak located at 284.8 eV, which is usually ascribed to the adventitious carbon or carbon residues from the organic precursor (mainly C–C bonds) (Gu et al. 2008, Yang et al. 2008a). In addition, weak peaks positioned at ca. 286 and 288 eV were present in almost all the samples. These peaks around 288 and 286 eV are assigned to C=O, O=C–O and C–N bonds, suggesting the formation of carbonate species (Park et al. 2009, Yang et al. 2008a). These carbonaceous species incorporated could act as photosensitizer to induce the visible–light absorption and response (Górska et al. 2008, Tseng et al. 2006), which was possibly responsible for the enhanced visible–light photocatalytic activity. As for T0.05–450, CT and ST, additional weaker peaks around 282 eV were observed, which are associated with Ti–C bonds indicating that carbon substituted some of oxygen into the TiO_2 lattice (Gu et al. 2008, Yang et al. 2008a) which could contribute to the red shift of absorption edge.

Fig. 4.3 XPS spectra of (a) C 1s, (b) N 1s, (c) S 2p, (d) O 1s and (e) Ti 2p for (A) T0.05-450, (B) CT, (C) NT and (D) ST.

As shown in Fig. 4.3b, there were no detectable N1s peaks for CT and ST, while two peaks and one peak were observed for T0.05-450 and NT, respectively. The peaks around 399 are assigned to the molecularly chemisorbed γ -N₂ (N-H, N-N, N-O bonds), such as Ti-N-O and Ti-O-N sites (Wang and Lim 2010, Wei et al. 2008), while the peak around 401 eV is attributed to the O-Ti-N sites substitutionally incorporated into the TiO₂ lattice (Wei et al. 2008). These peaks

indicated that nitrogen was doped into both T0.05–450 and NT. Nitrogen doping is related to the band–gap narrowing which can enhance the photocatalytic activity.

Sulfur was not detected for CT and NT, while two peaks at ca. 166–167 and 168 eV were observed for both T0.05–450 and ST (Fig. 4.3c). It was reported that 169 eV was the standard binding energy of S^{6+} (such as SO_4^{2-}) (Ao et al. 2009b, Rengifo-Herrera et al. 2009b). In this study, the peak at ca. 168 eV might be related to the Ti–O–S bonds. The peak at ca. 166–167 eV could be attributed to the cationic sulfur doping, namely, S^{6+} substituted for the lattice Ti^{4+} (Ohno et al. 2004, Rengifo-Herrera et al. 2009b). There were no peaks at around 160–163 eV for Ti–S bonds, suggesting no anionic sulfur doping that S^{2-} substituted for the lattice O^{2-} (Ohno et al. 2004, Rengifo-Herrera et al. 2008, Umebayashi et al. 2002). Ohno et al. found that the substitution of Ti^{4+} by S^{6+} would be more favorable than replacing O^{2-} with S^{2-} if thiourea was used (Ohno et al. 2004). And they demonstrated that cationic S–doped TiO_2 absorbed visible light more strongly than N, C and anionic S–doped TiO_2 , leading to high photocatalytic activity under visible light.

Fig. 4.3d demonstrates that peaks around 529 and 531 eV were observed in all the samples. The peaks at ca. 529 eV are ascribed to the Ti–O bonds in the TiO_2 lattice (Górska et al. 2008). The peaks at ca. 531 eV are related to the oxygen in the surface hydroxyl groups (H–O bonds) and/or in the carbonate species or oxynitrides (Chen et al. 2005, Górska et al. 2008). In addition, one weak peak at 533.1 eV was observed for T0.05–450, which is assigned to the oxygen in the carbonate species (Górska et al. 2008). Meanwhile, additional peaks at 528.6 and 527.8 eV were observed for CT and ST, respectively, which are also related to the Ti–O bonds in the TiO_2 lattice (Górska et al. 2008).

As seen in Fig. 4.3e, the core level binding energies of Ti 2p are ca. 456.6–458.8 eV for Ti 2p_{3/2} and 462.1–464.4 eV for Ti 2p_{1/2}. The peaks at ca. 458 and 464 eV are assigned to TiO_2 (Wang and Lim 2010). While the peaks with lower binding

energies, such as 456.6, 457.0, 457.4, 462.1 and 462.6 eV, may be related to the presence of various carbon, nitrogen and sulfur species, such as Ti–C, Ti–N–O, Ti–O–N, O–Ti–N and Ti–O–S bonds (Chen and Burda 2004, Ohno et al. 2004, Wang and Lim 2010). This is in agreement with the results as shown in Figs. 4.3a, 3b and 3c.

4.3.1.4 Optical properties

Fig. 4.4 shows that the C–N–S tridoped TiO₂ exhibited remarkable red shift of absorption edge to the visible–light region with long band tailings and strong absorbance. In addition, CT, NT and ST showed red shift compared to P25. Based on the optical absorption edge obtained from the DRS, the respective band–gap energies (E_g) were calculated using the transformed Kubelka–Munk function (Serpone et al. 1995) as shown in Table 4.1. The red shift of absorption edge, corresponding to the band–gap narrowing, could be attributed to the mixing of C, N and/or S 2p orbitals with O 2p orbitals, the intragap localized states of C, N and/or S, and/or the overlap of the C, N and/or S 2p orbitals with the valence band O 2p orbitals (Asahi et al. 2001, Dong et al. 2008, Umebayashi et al. 2002, Wang and Lim 2010, Yang et al. 2009). The carbonaceous species as photosensitizer might result in the extended band tailing (Górska et al. 2008, Treschev et al. 2008, Tseng et al. 2006, Yang et al. 2009).

Fig. 4.4 DRS of the as-synthesized TiO₂ and P25.

4.3.2 Photocatalytic degradation

4.3.2.1 Photocatalytic performance of various photocatalysts

In dark, TC concentration was remained at the initial concentration of 5.0 mg L^{-1} via hydrolysis (without photocatalyst), indicating that hydrolysis of TC could be negligible. The k_{app} values and PCD efficiencies of TC under various experimental conditions are summarized in Table 4.2. Fig. 4.5a shows that only 10% of TC was photodegraded after 3 h of visible-light irradiation via photolysis (without photocatalyst). The highest photocatalytic activity was shown by T0.05-450 with 97% of TC removal after 3 h of visible-light irradiation. In addition, relatively high TC removal efficiencies were found when NT (88%) and ST (94%) were used, which can be attributed to the doping effect (Figs. 4.3 and 4.4). It can be seen from Fig. 4.5a that the photocatalytic activities of T0.05-550 and T0.05-650 under visible-light irradiation were worse than that of T0.05-450, but were better than that of P25. This can be validated by the result of Fig. 4.4 that the absorbance intensities of the as-synthesized TiO_2 in the visible-light region were in the order of $\text{T0.05-450} > \text{T0.05-550} > \text{T0.05-650} > \text{P25}$. Therefore, PCD of TC under visible-light irradiation using T0.05-450 is a potential treatment alternative for TC removal in the aquatic environment.

The high visible-light photocatalytic activity of T0.05-450 for TC degradation could be attributed to the synergistic effects of adsorption of TC on T0.05-450 due to its high specific surface area, band-gap narrowing resulting from C-N-S tridoping, presence of carbonaceous species serving as photosensitizer, and the well-formed anatase phase. The high specific surface area of T0.05-450 is favorable for the diffusion and adsorption of TC. In this study, ca. 10% and 14% of TC was adsorbed on CT and T0.05-450 at neutral pH, respectively. On the other hand, C-N-S tridoping led to the band-gap narrowing of T0.05-450 (Table 4.1) with corresponding remarkable red shift of absorption edge to the visible-light

region (Fig. 4.4).

Table 4.2 k_{app} and PCD efficiencies of TC under various experimental conditions.

TiO ₂	C_0 (mg L ⁻¹)	Light	pH	k_{app} (min ⁻¹), ×10 ⁻³	PDE ^b (%)
Photolysis				0.629 (0.989) ^a	10
P25				1.87 (0.970)	26
T0.03–450				15.8 (0.999)	95
T0.05–450				20.7 (0.990)	97
T0.10–450				14.2 (0.993)	92
T0.15–450				3.65 (0.985)	45
T0.05–350	5.0	Visible–1	Neutral	5.72 (0.970)	59
T0.05–550				4.05 (0.997)	51
T0.05–650				2.39 (0.997)	35
CT				3.60 (0.977)	44
NT				10.9 (0.993)	88
ST				15.7 (0.994)	94
	5.0			20.7 (0.990)	97
	10			12.0 (0.980)	85
T0.05–450	25	Visible–1	Neutral	6.89 (0.995)	71
	50			3.75 (0.997)	50
			3.0 ± 0.1	6.11 (0.997)	70
			6.0 ± 0.1	16.8 (0.982)	94
T0.05–450	5.0	Visible–1	9.0 ± 0.1	24.6 (0.978)	98
			12.0 ± 0.1	15.4 (0.982)	92
Photolysis				–	41
T0.05–450				–	>99
CT	5.0	Visible–2	Neutral	–	88
NT				–	96
ST				–	99
P25				–	46
Photolysis				–	73
T0.05–450				–	>99
CT	5.0	UV	Neutral	–	81
NT				–	91
ST				–	95
P25				–	89
Photolysis				–	63
T0.05–450				–	>99
CT	5.0	Solar	Neutral	–	97
NT				–	99
ST				–	>99

TiO ₂	C_0 (mg L ⁻¹)	Light	pH	k_{app} (min ⁻¹), ×10 ⁻³	PDE ^b (%)
P25				—	94
T0.05-450:					
BQ = 0 mM	5.0	Visible-1	Neutral	20.7 (0.990)	97
BQ = 0.01 mM				17.7 (0.988)	88
BQ = 0.05 mM				13.9 (0.978)	83
BQ = 0.10 mM				12.2 (0.966)	69

^a R², correlation of determination.

^b PDE, PCD efficiencies of TC after 3.0 h of irradiation.

Fig. 4.5 PCD of TC using the as-synthesized TiO₂ (a) without and (b) with BQ in solution (C_0 : 5.0 mg L⁻¹; photocatalyst dosage: 0.5 g L⁻¹; irradiation light: visible-1; pH: neutral).

It is postulated that the excited photosensitizer, namely the carbonaceous species, could inject an electron into the conduction band of the photocatalyst followed by the reaction between the electron and molecular oxygen adsorbed on the surface of

photocatalysts as shown in Eqs. (4.1)–(4.4). Subsequently, both the formed $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are favorable for the PCD of TC. In order to investigate the role of carbonaceous species, benzoquinone (BQ) was used as an effective quencher of $\bullet\text{O}_2^-$ (Raja et al. 2005) with the result shown in Fig. 4.5b and Table 4.2. It demonstrates that the TC removal efficiencies using T0.05–450 decreased with the increase of BQ concentrations in solution, reflecting that BQ prevented the degradation of TC through consuming $\bullet\text{O}_2^-$. This result confirmed the carbon photosensitizing effect that the carbonaceous species could promote the Eq. (4.1) to produce $\bullet\text{O}_2^-$.

It has been reported that there is an optimal content of C, N and/or S dopant at which they could synergistically serve as electron traps to inhibit the recombination of electron–hole pairs (Asahi et al. 2001, Rengifo-Herrera and Pulgarin 2010). However, an excessive dopant with high content could act as the charge recombination centers. The optimum molar ratio of thiourea to Ti for the C–N–S tridoped TiO_2 was 0.05:1 in this study. The calcination temperature is another factor to affect the photocatalytic activity of the C–N–S tridoped TiO_2 . 450 °C was found to be the optimum calcination temperature due to the well–formed anatase phase (Fig. 4.5a). In this study, the optimum surface elemental contents of C, N and S were found to be 12.56 (excluded adventitious carbon at 284.8 eV), 0.54 and 1.60 % based on the XPS analysis, respectively. Therefore, further evaluations of photocatalytic activity were focused on T0.05–450 in the following sections.

4.3.2.2 Effect of initial TC concentration

Fig. 4.6 and Table 4.2 illustrate the effect of initial TC concentration on its PCD kinetics. For a solution with high TC concentration, it is presumed that a part of light might be absorbed by the TC molecules rather than T0.05–450. The by-products formed during photocatalysis might also compete with the TC molecules for the limited adsorption and photocatalytic sites on the T0.05–450 surface, causing partial inhibition of the PCD of TC to a certain degree. The linear plot of Langmuir–Hinshelwood model is shown in the inset of Fig. 4.6. The Langmuir–Hinshelwood reaction rate constant and Langmuir adsorption equilibrium constant are $0.197 \text{ mg L}^{-1} \text{ min}^{-1}$ and 0.206 L mg^{-1} ($R^2=0.931$), respectively.

Fig. 4.6 Effect of initial TC concentration on the PCD of TC (Inset shows linear plot fitting of Langmuir–Hinshelwood model) (T0.05–450 dosage: 0.5 g L^{-1} ; irradiation light: visible–1; pH: neutral).

4.3.2.3 Effect of solution pH

The PCD efficiencies of TC using T0.05–450 are in the order of $\text{pH } 9 > \text{pH } 6 \approx \text{pH } 12 > \text{pH } 3$ (Fig. 4.7 and Table 4.2). 98% of TC was photodegraded at pH 9 after 3 h of visible–1 irradiation, while only 68% of TC was removed at pH 3 under the same experimental condition.

Fig. 4.7 Effect of solution pH on the PCD of TC (Inset shows equilibrium adsorption isotherms) (C_0 : 5.0 mg L⁻¹; T0.05–450 dosage: 0.5 g L⁻¹; irradiation light: visible–1).

The adsorption mode and the concentration of $\bullet\text{OH}$ are two key factors influencing the PCD efficiencies of TC at different pH values. Batch equilibrium adsorption experiments were carried out in dark with 1 h as adsorption equilibrium time, over a range of initial concentrations with different pH values. The Langmuir adsorption isotherm model was used for kinetics studies (Yu et al. 2009b) with the result shown in the inset of Fig. 4.7. The adsorption capacities of TC on T0.05–450 were in the order of pH 6 > pH 3 > pH 9 > pH 12, which were more than that of TC on CT (pH 6) due to the high specific surface area of T0.05–450. As an amphoteric material, the TiO_2 surface is positively charged at a pH lower than its point of zero charge and negatively charged at a pH higher than its point of zero charge. Zeta potential of T0.05–450 was determined using a Malvern Nano-ZS Zetasizer at different pH. Its point of zero charge was found to be at ca. pH 5.7. Therefore, T0.05–450 was positively charged at pH 3, while negatively charged at pH 6, 9 and 12. On the other hand, TC molecule possesses pK_a values of 3.3, 7.7, 9.7 and 12 (Jiao et al. 2008), and therefore it predominantly exists as H_4TC^+ , H_3TC , H_2TC^- and HTC^{2-} at pH 3, 6, 9 and 12, respectively. The adsorption of TC on T0.05–450 might be inhibited by the enhanced electrostatic repulsion between H_4TC^+ and positively charged T0.05–450 at pH 3, and between $\text{H}_2\text{TC}^-/\text{HTC}^{2-}$ and negatively charged T0.05–450 at pH 9 and 12, respectively. Concomitantly, TC appeared to be

attracted to the negatively charged T0.05–450 at pH 6. On the other hand, the concentration of $\bullet\text{OH}$ also affects the PCD. A higher concentration of $\bullet\text{OH}$ could be generated with the increase of pH. Moreover, negatively charged TC molecules tend to attract the electrophilic $\bullet\text{OH}$ due to the high electrical density on its ring system (Jiao et al. 2008), leading to enhanced photocatalytic activities in the alkaline conditions. Apparently, there may be an optimum condition for PCD of TC based on the adsorption mode and the concentration of $\bullet\text{OH}$. In this study, the slightly alkaline pH condition was favorable to the PCD of TC.

4.3.2.4 Effect of light intensity and light source

Fig. 4.8a shows the effects of light intensity and light source on the PCD of TC using T0.05–450, CT, NT, ST and P25. It indicated that 10%, 41%, 73% and 63% of TC was photocatalytic degraded via photolysis after 3 h of visible–1, visible–2, UV and solar irradiation, respectively. It is postulated that the effect of photolysis would be further reduced in the presence of photocatalyst particles due to the light attenuation in the turbid solution. For the case of P25, a fraction of TC can be removed under visible–light irradiations. However, P25 exhibited higher TC removal efficiencies under solar and UV irradiations than those under visible–light irradiations using P25. This can be attributed to the presence of predominantly anatase–rutile mixture. Under all the irradiations of the light sources investigated in this study, the TC removal efficiencies were in the order of $\text{ST} > \text{NT} > \text{CT}$. This suggests that the sulfur and nitrogen doping exhibited higher photocatalytic activities than that of carbon doping. However, the highest degradation efficiency of TC was achieved by T0.05–450, namely, 97%, >99%, >99% and >99% of TC removal after 3.0 h of visible–1, visible–2, UV and solar irradiation, respectively. According to the reports (Rengifo-Herrera et al. 2009a, Sun et al. 2006), pollutants removal efficiencies using P25 are usually higher than those using the nonmetal doped TiO_2 under UV irradiation. However, under UV irradiation in this study,

T0.05–450 exhibited higher TC removal efficiency than that using P25. It can be explained by the solution opacity. The solution turbidity measured using HACH 2100N Turbidimeter was ca. 1080 and 2480 NTU for the solution with T0.05–450 (0.5 g L^{-1}) and P25 (0.5 g L^{-1}) suspended, respectively. The high solution opacity can lead to a decrease in the penetration of the photon flux through the reactor, inducing an unfavorable condition for the PCD of TC. Therefore, the TC removal efficiency using P25 was lower than that using T0.05–450. In conclusion, T0.05–450 could be photoexcited by both UV and visible light. This is in agreement with the results of XPS and DRS analysis (Figs. 4.3 and 4.4). Therefore, T0.05–450 possesses the potential application for solar photocatalysis of TC in the aquatic environment.

Fig. 4.8 Effect of light intensity and light source on the (a) PCD and (b) mineralization of TC (C_0 : 5.0 mg L^{-1} ; photocatalyst dosage: 0.5 g L^{-1} ; pH: neutral; irradiation time: 3.0 h).

High degree of mineralization of a variety of organic pollutants can be achieved with photocatalysis due to the non-selectivity of $\bullet\text{OH}$. However, the complete mineralization for most antibiotics are difficult due to their structural stability (Westerhoff et al. 2005). The effects of light intensity and light source on the mineralization of TC using T0.05–450, CT, NT, ST and P25 are shown in Fig. 4.8b. The trends of TOC removal agreed with those of TC degradation (Fig. 4.8a). Apparently, the highest TOC removal efficiency was achieved by T0.05–450. In

particular, the TOC removal efficiency using T0.05–450 was 26% after 3 h of visible–1 irradiation, indicating the formation of recalcitrant intermediates as reported in the previous literatures (Dalmázio et al. 2007, Jiao et al. 2008, Khan et al. 2010). The TC naphthol ring remains intact under irradiation, and the intermediates were most likely to be generated via loss of hydroxyl, N–methyl and amino group from TC structure (Dalmázio et al. 2007, Jiao et al. 2008). However, the TOC removal efficiency reached 67%, 82% and 74% after 3 h of visible–2, UV and solar irradiation, respectively. It potentially offers an intriguing possibility for the application of T0.05–450 in organic pollutants removal, such as TC, using solar energy.

4.3.3 Acute toxicity evaluation

The acute toxicity of TC solution during photocatalysis using T0.05–450 was evaluated as a function of irradiation time with triplicate analysis (Fig. 4.9). Before light irradiation, TC solution showed acute toxicity to *V. fischeri* (21–24% bioluminescence inhibition). The acute toxicity of TC solution reached the maximum (36%, 39% and 43% bioluminescence inhibition) after 1.5 h of visible–1, 1.0 h visible–2 and 0.5 h solar irradiation, respectively, indicating formation of the more toxic intermediates. The intermediates generated after losing hydroxyl, N–methyl and amino groups from the TC naphthol ring could result in a lower steric resistance and subsequently easier diffusion through the cell membrane of *V. fischeri* (Lu et al. 2002). However, the inhibition of *V. fischeri* bioluminescence decreased to 25%, 19% and 11%, respectively, after 5 h of visible–1, visible–2 and solar irradiations. It appeared that the decreases in solution toxicity were in tandem with the increased mineralization efficiencies in the order of solar > visible–2 > visible–1. It is postulated that the acute toxicity of TC solution might continue to decrease with further extending the irradiation time. Therefore, the extended solar photocatalysis with T0.05–450 is efficient in the detoxification of TC solution

beyond the threshold period at ca. 2.0 h.

Fig. 4.9 Acute toxicity of TC solution during photocatalysis using T0.05–450 (n = 3).

4.3.4 Comparison of photocatalytic performance of T300 and T0.05–450

In Chapter 3, T300 showed the highest photocatalytic activity for PCD of SNM under LED–W irradiation. In this chapter, T0.05–450 exhibited the highest photocatalytic activity for PCD of TC under visible–1 irradiation. In order to compare the photocatalytic activity of T300 and T0.05–450, the PCD of SNM and TC using both T300 and T0.05–450 under both LED–W and visible–1 irradianations were investigated. Fig. 4.10 shows that the PCD efficiencies of both SNM and TC using T0.05–450 under LED–W irradiation were higher than those using T300. Enhanced PCD efficiencies of both SNM and TC were found under visible–1 irradiation compared to those cases under LED–W irradiation, due to the higher light intensity of visible–1 light (32 W m^{-2}) than that of LED–W light (5 W m^{-2}). In addition, the slight higher PCD efficiencies of both SNM and TC using T0.05–450 under visible–1 irradiation were achieved compared to those using T300. It is concluded that T0.05–450 exhibited higher photocatalytic activity compared to T300.

Fig. 4.10 PCD of SNM and TC using T300 and T0.05-450 under LED-W and visible-1 irradiations ($n=3$) (C_0 : 5.0 mg L⁻¹; photocatalyst dosage: 1.0 g L⁻¹; irradiation time: 3.0 h; pH: neutral).

4.4 Conclusions

A facile, cost-effective and easily scaled-up sol-gel method was developed for synthesizing C-N-S tridoped TiO₂ used for PCD of TC. The highest photocatalytic activity under visible-light irradiation due to the synergistic effects was achieved from the C-N-S tridoped TiO₂ with the thiourea : Ti molar ratio of 0.05:1 and calcination temperature of 450 °C (T0.05-450) which possessed the optimum surface elemental contents of C (12.56 at%, excluded adventitious carbon at 284.8 eV), N (0.54 at%) and S (1.60 at%) based on the XPS analysis. The PCD and mineralization of TC were more efficient under slightly alkaline pH condition and solar irradiation. The extended solar photocatalysis was efficient in the detoxification of TC solution according to the Microtox assay. Compared to T300 described in Chapter 3, T0.05-450 exhibited higher visible-light photocatalytic activity. The C-N-S tridoped TiO₂ has the potential to be used in solar photocatalysis for water purification during which the recalcitrant toxic organics can be substantially mineralized and detoxified.

CHAPTER 5 MEMBRANE VIS-LED PHOTOREACTOR FOR SIMULTANEOUS PENICILLIN G DEGRADATION AND TiO₂ SEPARATION

5.1 Introduction

Chapters 3 and 4 reveal two kinds of visible-light responsive TiO₂ synthesized using facile sol-gel methods, respectively. T300 (C-sensitized and N-doped TiO₂) and T0.05-450 (C-N-S tridoped TiO₂) exhibited high photocatalytic activity for pollutants degradation under visible-light irradiation. However, the key challenge for applying the TiO₂ suspension system is that the TiO₂ particles have to be separated from the product water.

In order to realize the separation of TiO₂ and simultaneous degradation of pollutants, this phase of study presents a hybrid MPR system which comprised a photoreactor irradiated with vis-LED and a separate cross-flow MF membrane module. P25, T300 and T0.05-450 were used as the photocatalysts. PG, a β -lactam antibiotic, was used as the target pollutant, and its chemical structure is shown as follows.

The PCD of PG under visible-light irradiation over P25, T300 and T0.05-450 were compared in the batch photoreactor. The effects of TiO₂ dosage, TMP and CFV on the performances of the closed-loop MPR system with and without backwashing were investigated with regard to the PG degradation, TiO₂ separation and permeate flux. Based on the optimal operating condition obtained from the closed-loop MPR

system, the performances of MPR system operated in the continuous flow-through mode with fractional recirculation were also investigated.

5.2 Experimental

5.2.1 Membrane photoreactor and experimental procedures

The hybrid MPR system consisted of a separate vis-LED photoreactor and a cross-flow MF membrane module (Fig. 5.1). The vis-LED photoreactor has been described in Section 3.2.3, and the LED-W was used as the light source in this study. A commercial flat sheet PVDF MF membrane (mean pore size of $0.22\ \mu\text{m}$) was provided from Millipore. The effective membrane area was $16.76\ \text{cm}^2$. Prior to the experiment, the clean membrane was pre-treated by soaking in MQ water for 12 h, and then mounted into a custom-made cross-flow membrane module.

Fig. 5.1 Schematic diagram of the hybrid MPR system.

A Masterflex peristaltic pump was used to deliver the TiO_2 suspension from the photoreactor to the membrane module. The retentate water was re-circulated to the photoreactor. In the closed-loop mode, the permeate water was recycled to the photoreactor. In the continuous flow-through mode, the permeate water was partially recycled to the photoreactor; and meanwhile, fresh PG ($>99.0\%$ MP Biomedicals) solution ($5.0\ \text{mg L}^{-1}$) was continuously fed into the photoreactor in order to maintain a constant working volume of the photoreactor. The TMP and

CFV (calculated from the feed flow rate) were adjusted by regulating the manual valve in the retentate line and the Masterflex peristaltic pump speed in the feed line, respectively. The permeate flux was measured by gravimetric method using a digital weighing balance (A&D FX-2000i, Japan). The TMP, feed flow rate and permeate flux were auto-recorded at predetermined time intervals by a data logging system. In the case of operation with backwashing, the solenoid valve in the permeate line was closed, while the solenoid valve and Masterflex peristaltic pump in the backwashing line were open to draw permeate water from the permeate side to the feed side.

In a typical operation, 500 mL of TiO_2 suspension with initial PG concentration of 5.0 mg L^{-1} was stirred in dark to reach its adsorption equilibrium (achieved within 1 h). Meanwhile, the MPR system was equilibrated with MQ water under the desired TMP and CFV for 1 h to compress the membrane and reach a stable permeate flux which represented the initial permeate flux. Subsequently, the 500 mL of the equilibrated suspension replaced the MQ water in the MPR system under the same TMP and CFV, and then the LED-W was switched on. Sample aliquots of permeate water in the permeate/backwashing tank as well as in the photoreactor were collected at predetermined time intervals for analysis. After each run, the MPR system was emptied and thoroughly rinsed with MQ water. For comparison, the PCD of PG was also carried out in the batch photoreactor without the membrane module. Blank experiments were conducted without photocatalyst to investigate the hydrolysis (in dark) and photolysis (under LED-W irradiation) of PG.

5.2.2 Analytical method

The HPLC analysis was similar to that described in Section 4.2.3. The differences included: (1) methanol and 0.05 M KH_2PO_4 buffer solution was used as mobile phase A and B ($v_A/v_B = 70/30$), respectively; and (2) the detector wavelength was set at 215 nm. TOC was measured with a Shimadzu ASI-V TOC Analyzer.

Particle size distribution of TiO_2 in suspension was determined using a Malvern Mastersizer 2000 equipped with a Hydro 2000SM sample dispersion unit. Turbidity was measured using a HACH 2100N turbidimeter.

5.2.3 Acute toxicity test

The acute toxicity of PG solution during photocatalysis was evaluated with *Vibrio fischeri* using a Microtox Model 500 Analyzer. The detailed procedure is described in Section 3.2.6.

5.2.4 Hydraulic resistance

The resistance-in-series model was used to evaluate the membrane fouling characteristics during the separation of TiO_2 in the MPR system. Based on this model, the permeate flux of membrane could be expressed as follows (Drioli and Giorno 2009):

$$J = \frac{TMP}{\mu R_t} = \frac{TMP}{\mu (R_m + R_c + R_p)} \quad (5.1)$$

where J is the permeate flux ($\text{L m}^{-2} \text{h}^{-1}$), TMP is the transmembrane pressure (kPa), μ is the viscosity of permeate water, and R_t is the total resistance (m^{-1}) which comprises three components: the membrane resistance (R_m), the cake resistance (R_c) and the pore blockage resistance (R_p). R_m could be obtained based on the MQ water permeate flux. R_t could be calculated using the steady-state flux after filtration of the TiO_2 suspension. Then, the membrane surface was rinsed with MQ water and cleaned with sponge to remove the cake layer, followed by the permeate flux measurement using MQ water to obtain $(R_m + R_p)$. Finally, R_c and R_p could be calculated.

5.3 Results and discussion

5.3.1 Batch photoreactor without membrane module

5.3.1.1 Photocatalytic degradation of PG

The k_{app} values and PCD efficiencies of PG under various experimental conditions are summarized in Table 5.1. Fig. 5.2a and Table 5.1 show that the PG concentration decreased by 15% and 19% after 4 h in the hydrolysis and photolysis experiment, respectively. The presence of TiO_2 enhanced the PG degradation with the order of significance following $\text{T0.05-450} > \text{T300} > \text{P25}$. The PCD of PG efficiency increased with TiO_2 dosage for both T300 and T0.05-450, as the photocatalyst surface area available for adsorption and degradation was increased. The PG degradation efficiencies reached 97% and >99% after 4 h of LED-W irradiation with 1.0 g L^{-1} of T300 and T0.05-450, respectively. Therefore, T300 and T0.05-450 were chosen as the photocatalysts for the investigation using the MPR system.

Reactive oxygen species (ROSs), such as hydroxyl radical ($\bullet\text{OH}$), superoxide radical ($\bullet\text{O}_2^-$) and singlet oxygen ($^1\text{O}_2$), could be generated during photocatalysis involving a series of chemical reactions (Fujishima and Zhang 2006). In order to understand the roles of ROSs in the visible-light PCD of PG, potassium iodide (KI), dimethyl sulfoxide (DMSO), benzoquinone (BQ) and sodium azide (NaN_3) were used as scavenging species of h^+ , $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and $^1\text{O}_2$, respectively. As shown from Fig. 5.2b, the degradation of PG was inhibited in the presence of the ROS with the order of significance following $\text{DMSO} > \text{BQ} > \text{KI} > \text{NaN}_3$ for both T300 and T0.05-450 systems. Obviously, it is postulated that $\bullet\text{OH}$ significantly contribute to the degradation of PG followed by $\bullet\text{O}_2^-$, while the role of h^+ and $^1\text{O}_2$ in PG degradation was found to be much less significant.

Table 5.1 k_{app} and PCD efficiencies of PG under various experimental conditions.

TiO ₂	TiO ₂ dosage (g L ⁻¹)	TMP (kPa)	CFV (m s ⁻¹)	Backwashing pressure (kPa)	k_{app}^a ($\times 10^{-3} \text{ min}^{-1}$)	PCD at 4 h ^c (%)
Hydrolysis/Photolysis/PCD in the batch photoreactor						
Hydrolysis	—	—	—	—	0.708 (0.993)	15
Photolysis	—	—	—	—	0.934 (0.992) ^b	19
P25	0.3	—	—	—	1.37 (0.957)	25
P25	0.5	—	—	—	2.07 (0.968)	35
P25	1.0	—	—	—	1.69 (0.967)	30
T300	0.3	—	—	—	4.61 (0.997)	65
T300	0.5	—	—	—	7.83 (0.995)	84
T300	1.0	—	—	—	12.7 (0.998)	97
T0.05–450	0.3	—	—	—	7.33 (0.993)	81
T0.05–450	0.5	—	—	—	10.4 (0.997)	92
T0.05–450	1.0	—	—	—	16.0 (0.998)	99
Closed-loop MPR system without backwashing						
T300	0.3	10	0.15	—	3.93 (0.999)	43
T300	0.5	10	0.15	—	7.01 (0.989)	58
T300	1.0	10	0.15	—	9.89 (0.989)	75
T0.05–450	0.3	10	0.15	—	6.48 (0.999)	61
T0.05–450	0.5	10	0.15	—	8.90 (0.992)	70
T0.05–450	1.0	10	0.15	—	13.2 (0.995)	84
T300	1.0	10	0.15	—	9.89 (0.989)	75
T300	1.0	20	0.15	—	8.04 (0.957)	69
T300	1.0	30	0.15	—	7.47 (0.964)	62

TiO ₂	TiO ₂ dosage (g L ⁻¹)	TMP (kPa)	CFV (m s ⁻¹)	Backwashing pressure (kPa)	k_{app}^a ($\times 10^{-3} \text{ min}^{-1}$)	PCD at 4 h ^c (%)
T0.05–450	1.0	10	0.15	–	13.2 (0.995)	84
T0.05–450	1.0	20	0.15	–	11.6 (0.991)	78
T0.05–450	1.0	30	0.15	–	10.3 (0.992)	77
T300	1.0	10	0.09	–	8.90 (0.976)	67
T300	1.0	10	0.12	–	9.24 (0.982)	71
T300	1.0	10	0.15	–	9.89 (0.989)	75
T0.05–450	1.0	10	0.09	–	10.7 (0.994)	82
T0.05–450	1.0	10	0.12	–	12.2 (0.994)	83
T0.05–450	1.0	10	0.15	–	13.2 (0.995)	84
Closed-loop MPR system with backwashing						
T300	0.3	10	0.15	24	4.26 (0.994)	61
T300	0.5	10	0.15	27	7.38 (0.992)	81
T300	1.0	10	0.15	34	11.7 (0.997)	93
T0.05–450	0.3	10	0.15	27	7.19 (0.995)	80
T0.05–450	0.5	10	0.15	30	10.0 (0.999)	90
T0.05–450	1.0	10	0.15	35	13.7 (0.983)	95
T300	1.0	10	0.15	34	11.7 (0.997)	93
T300	1.0	20	0.15	41	10.7 (0.997)	91
T300	1.0	30	0.15	64	10.3 (0.997)	89
T0.05–450	1.0	10	0.15	35	13.7 (0.983)	95
T0.05–450	1.0	20	0.15	45	12.9 (0.978)	92
T0.05–450	1.0	30	0.15	68	12.3 (0.972)	92
T300	1.0	10	0.09	44	11.3 (0.998)	92

TiO ₂	TiO ₂ dosage (g L ⁻¹)	TMP (kPa)	CFV (m s ⁻¹)	Backwashing pressure (kPa)	k_{app}^a ($\times 10^{-3} \text{ min}^{-1}$)	PCD at 4 h ^c (%)
T300	1.0	10	0.12	38	11.7 (0.995)	91
T300	1.0	10	0.15	34	11.7 (0.997)	93
T0.05–450	1.0	10	0.09	48	12.8 (0.981)	92
T0.05–450	1.0	10	0.12	40	13.4 (0.989)	94
T0.05–450	1.0	10	0.15	35	13.7 (0.983)	95

^a Apparent rate constant: calculated after 4 h of LED–W irradiation both in the batch photoreactor and in the closed–loop MPRs with backwashing; while calculated after 2 h of LED–W irradiation in the closed–loop MPRs without backwashing.

^b R^2 , coefficient of determination.

^c Calculated after 4 h of LED–W irradiation.

Fig. 5.2 PCD of PG in the (a) absence and (b) presence of radical scavenging species in the batch photoreactor.

5.3.1.2 Mineralization of PG and acute toxicity evaluation

The TOC removal efficiency was 6%, 16% and 25% after 4 h of LED–W irradiation using P25, T300 and T0.05–450, respectively (Fig. 5.3a). It reached 16%, 44% and 55% after 24 h of LED–W irradiation using P25, T300 and T0.05–450, respectively. This indicated the formation of recalcitrant organic intermediates during the LED–W irradiation. It has been reported that penillic acid, penilloic acid, penicilloic acid, isopenillic acid and penicilloaldehyde could be formed during PG degradation (Blaha et al. 1976, Li et al. 2008a, Trovó et al. 2011) through (i) hydroxylation with

hydroxyl groups added to the PG molecule in the position of thiazolidine ring, benzoic ring and/or nitrogen atom, and/or (ii) opening of the four-membered β -lactam ring with further arrangement of the PG molecule. On the other hand, $\bullet\text{OH}$ could react with both the aromatic ring and the β -lactam ring of PG to form isomeric monohydroxyl derivatives, followed by the formation of phenolic compounds with further irradiation (Song et al. 2008). In the present study, to investigate the extent of ring-opening reactions and PG mineralization, the DOC of the PG solution was determined along with the UV absorbance at 254 nm (UV254) during the PCD experiment. The SUVA ($= \text{UV254}/\text{DOC}$) indicates the degree of aromaticity of the DOC remained in the solution. As could be seen from Fig. 5.3b, the UV254 values decreased with the irradiation time, suggesting a decrease of the aromatic content in the solution. In view of the SUVA analysis, the opening of aromatic ring contributed more significantly to the PG mineralization after 4 h of irradiation.

Fig. 5.3 (a) Mineralization and acute toxicity of PG solution, and (b) changes of UV254 and SUVA during photocatalysis of PG in the batch photoreactor.

The formation of intermediates would result in changes of solution toxicity during the PCD of PG. It is highly desirable to evaluate the transient toxicity of PG solution during the course of its PCD. Fig. 5.3a shows the 15- and 30-min *V. fischeri* bioluminescence inhibition of PG solution with P25, T300 and T0.05-450 as the photocatalysts respectively, as a function of irradiation time. For the P25

system, no significant change in the acute toxicity was observed during the 24 h of irradiation. While for the T300 and T0.05–450 systems, no significant change in the acute toxicity was observed during the first 3 h of irradiation, and then the toxicity gradually decreased with the extended irradiation time. The reason might be that the intermediates formed during photocatalysis lost the antibacterial activity of their parent compound PG due to the opening of β -lactam rings (Cha et al. 2006, Hou and Poole 1971). Therefore, the visible-light photocatalysis with T300 and T0.05–450 was efficient to detoxify the PG solution.

5.3.2 Membrane module for PG rejection and TiO₂ separation

5.3.2.1 Membrane permeability using MQ water

MQ water permeability of membrane was investigated at different TMPs and CFVs. It was found that the permeate flux was independent of CFV which was in agreement with the result reported by Sopajaree et al. (Sopajaree et al. 1999). It also showed that the permeate flux was linearly dependent on the applied TMP ($R^2 = 0.998$). This indicated that there was no phenomenon of membrane compaction or swelling, and the membrane structural integrity was maintained at the applied TMP. The hydraulic permeability ($L_p = J\mu/R_m$, m Pa⁻¹ s⁻¹) using MQ water was 2.14×10^{-8} m Pa⁻¹ s⁻¹.

5.3.2.2 Rejection test of PG solution

Preliminary test indicated that the adsorption of PG on the membrane and tubing surface could be ignored. The rejection test of PG solution by the membrane showed that the PG concentration in the permeate water was similar to that in the feedwater. This is anticipated as the molecular size of PG (MW = 334.39 g mol⁻¹) is much smaller than the mean pore size of MF membrane (0.22 μ m).

5.3.2.3 TiO₂ separation by membrane

The particle size distributions of T300 and T0.05–450 in suspensions after 4-h mixing were determined in triplicate, and the average result is presented in Fig. 5.4. As a comparison, the particle size distribution of P25 in suspension was also determined (Fig. 5.4). It shows that the particle size of T0.05–450 in suspension was slightly smaller than that of T300, both of which were larger than that of P25 in suspension. Moreover, almost all the T300, T0.05–450 and P25 particles were larger than the MF membrane pore size. TiO₂ particles with the size smaller than the pore size of membrane might have a chance to pass through the membrane. Nevertheless, the larger TiO₂ particles could form a porous cake layer (secondary dynamic membrane) on the membrane surface during MF process, which would be effective for the retention of the smaller particles.

Fig. 5.4 Particle size distribution of TiO₂ in suspension.

The turbidity of permeate water was measured in order to investigate the effectiveness of TiO₂ separation by the MF membrane operated at different TMPs and CFVs. The initial turbidities of T300 suspensions with dosages of 0.3, 0.5 and 1.0 g L⁻¹ in the photoreactor were 560, 1000 and 2070 NTU, respectively, while they were 620, 1070 and 2150 NTU for T0.05–450 suspensions with dosages of 0.3, 0.5 and 1.0 g L⁻¹, respectively. However, the turbidities of permeate water were

consistently <0.2 NTU for both T300 and T0.05–450 suspensions. While for P25 suspensions with initial turbidities of 1110, 2060, 4210 NTU at dosages of 0.3, 0.5 and 1.0 g L^{-1} , respectively, the turbidities of permeate water were <0.4 NTU. It indicated that the MF membrane for the separation of T300 and T0.05–450 particles was slightly more efficient than that of P25 particles. Therefore, the MF membrane could be successfully applied for TiO_2 separation.

5.3.3 PG degradation and membrane permeability in the MPR system

5.3.3.1 Effect of TiO_2 dosage on the closed-loop MPR system

The PCD efficiency of PG in the closed-loop MPR system using T0.05–450 was higher than that using T300 (Figs. 5.5a and 5b and Table 5.1), and it increased with the dosage of the photocatalysts from 0.3 to 1.0 g L^{-1} . The PCD efficiency of PG in the closed-loop MPR system without backwashing was found to be lower than that of the case with backwashing. The PCD of PG followed the pseudo-first-order kinetics in the first 2 h in the closed-loop MPR system without backwashing (Fig. 5.5a). Subsequently, the reaction rate decreased which could be attributed to the loss of TiO_2 from the photoreactor (as indicated by the decrease of turbidity). The adsorption of TiO_2 (1.0 g mL^{-1}) on the tubing surface were found to be negligible. Therefore, the loss of TiO_2 from the photoreactor could be resulted from the TiO_2 deposition on the membrane surface, which could not be returned to the photoreactor for photoactivation.

The turbidities of TiO_2 suspensions are linearly correlated with their concentrations in the range of $0.1\text{--}1.2 \text{ g L}^{-1}$. Calibration curves for T300 and T0.05–450 suspensions were established as shown in Eqs. (5.2) and (5.3), respectively:

(1) For T300 suspension:

$$D = 0.0005T + 0.0319 \quad (R^2 = 0.998) \quad (5.2)$$

(2) For T0.05–450 suspension:

$$D = 0.0005T + 0.0026 \quad (R^2 = 0.998) \quad (5.3)$$

where D is the TiO_2 concentration (g L^{-1}), and T is the turbidity of TiO_2 suspension (NTU).

Fig. 5.5 Effect of TiO_2 dosage on the performance of the closed-loop MPR system (TMP: 10 kPa; CFV: 0.15 m s^{-1}) (1) without backwashing: (a) PCD of PG, (c) TiO_2 concentration in the photoreactor, and (e) permeate flux; and (2) with backwashing: (b) PCD of PG, (d) TiO_2 concentration in the photoreactor, and (f) permeate flux.

The TiO₂ concentration in the photoreactor continuously decreased in the first 2 h, and then reached an almost constant value which was only 11–27% of the initial TiO₂ concentration (Fig. 5.5c). The TiO₂ deposition on the membrane surface induced permeate flux decline (Fig. 5.5e). A higher rate of permeate flux decline was observed at a higher TiO₂ dosage, which was attributed to the greater amount of TiO₂ deposited on the membrane surface. The permeate flux decline for T0.05–450 was more significant than that for T300, and the steady-state permeate flux with T0.05–450 was lower than that with T300. Since the particle size of T300 was slightly larger than that of T0.05–450 (Fig. 5.4), it is expected that the cake layer with T300 particles was likely to be more porous than that with T0.05–450 particles. In addition, TiO₂ with larger particle sizes would lead to larger pore sizes (flow channels). Consequently, water could more easily pass through T300 cake layer than that of T0.05–450.

After 4 h of operation in the closed-loop MPR system without backwashing, the membrane surface was rinsed with MQ water, cleaned with sponge to remove the cake layer, and then determined for its MQ water permeate flux for 1 h. The recovery of permeate flux was found to be >95% (Fig. 5.5e), suggesting that the cake layer was the main reason for the permeate flux reduction. Table 5.2 shows that the cake resistance was more significant than the pore blockage resistance. In addition, the total resistance, cake resistance and pore blockage resistance increased with the TiO₂ dosage. The total resistance and cake resistance of T300 system were lower than those of T0.05–450 system due to the larger particle size of T300.

Table 5.2 Effect of TiO₂ dosage, TMP and CFV on the hydraulic resistance in the closed-loop MPR system without backwashing.

TiO ₂	Parameter	R_t ($\times 10^{10} \text{ m}^{-1}$)	R_m ($\times 10^{10} \text{ m}^{-1}$)	R_c ($\times 10^{10} \text{ m}^{-1}$)	R_p ($\times 10^{10} \text{ m}^{-1}$)
T300					
	Dosage (g L ⁻¹)				
	0.3	4.74	4.43	0.260	0.0522
	0.5	5.10	4.42	0.591	0.0915

TiO ₂	Parameter	R _t (×10 ¹⁰ m ⁻¹)	R _m (×10 ¹⁰ m ⁻¹)	R _c (×10 ¹⁰ m ⁻¹)	R _p (×10 ¹⁰ m ⁻¹)
	1.0	5.50	4.41	0.949	0.138
	TMP (kPa)				
	10	5.50	4.41	0.952	0.135
	20	5.60	4.42	1.10	0.0852
	30	5.81	4.42	1.29	0.0985
	CFV (m s ⁻¹)				
	0.09	5.64	4.42	1.05	0.188
	0.12	5.54	4.41	0.961	0.171
	0.15	5.50	4.41	0.952	0.135
T0.05–450					
	Dosage (g L ⁻¹)				
	0.3	4.89	4.42	0.403	0.0656
	0.5	5.41	4.43	0.900	0.0794
	1.0	5.92	4.41	1.36	0.146
	TMP (kPa)				
	10	5.92	4.41	1.36	0.143
	20	6.11	4.41	1.59	0.109
	30	6.53	4.42	2.00	0.106
	CFV (m s ⁻¹)				
	0.09	6.07	4.41	1.47	0.194
	0.12	5.97	4.42	1.38	0.181
	0.15	5.92	4.41	1.36	0.143

In order to enhance the PCD of PG in the photoreactor, TiO₂ deposition on the membrane surface should be prevented. This could be realized by periodical backwashing of the membrane. As different amounts of TiO₂ particles were deposited on the membrane surface for different TiO₂ types and dosages, preliminary test was carried out to find out the efficient operating condition for backwashing. It showed that the TiO₂ deposition on the membrane surface could be efficiently minimized when backwashing was conducted every 10 min for a duration of 5 s with different backwashing pressures (Table 5.1). The turbidity of TiO₂ suspension in the photoreactor of the closed-loop MPR system with backwashing was measured every 10, 20 or 30 min before backwashing. The TiO₂ concentration in the photoreactor was higher than the case without backwashing, and remained almost constant during the process (Fig. 5.5d). The permeate flux was

also monitored every 5 min before backwashing, and it was rather stable throughout the experimental period (Fig. 5.5f). It could be concluded from Figs. 5.5d and 5f that the backwashing was efficient to dislodge the TiO_2 particles from the membrane surface back to the photoreactor. With backwashing, the PCD of PG was enhanced to be almost comparable to those achieved in the batch photoreactor without the membrane module.

5.3.3.2 Effect of TMP on the closed-loop MPR system

A higher PG degradation efficiency was found at a lower TMP (Figs. 5.6a and 6b and Table 5.1). The PCD of PG in the closed-loop MPR system with backwashing was more efficient than that without backwashing. This was attributed to the TiO_2 deposition on the membrane surface resulting in the decrease of TiO_2 concentration in the photoreactor. The TiO_2 concentration in the photoreactor of the closed-loop MPR system without backwashing continuously decreased (Fig. 5.6c), and an almost constant TiO_2 concentration value (8–13% of the initial value) was achieved after 2 h. It suggested that the TiO_2 deposition rate on the membrane surface was higher at the higher TMP. Accordingly, the permeate flux decreased more rapid as TMP increased (Fig. 5.6e). The steady-state permeate flux was achieved sooner at a higher TMP, and it was higher for T300 suspension than T0.05–450 suspension. >95% of permeate flux was recovered after MQ water rinse and cake layer removal of the membrane (Fig. 5.6e). This indicated that the cake resistance was the dominant component of the fouling resistance which was in agreement with the result in Table 5.2. Moreover, Table 5.2 shows increasing cake resistance with increasing TMP, attributable to the formation of denser cake layer on the membrane surface due to the higher driving force.

Fig. 5.6 Effect of TMP on the performance of the closed-loop MPR system (TiO_2 dosage: 1.0 g L^{-1} ; CFV: 0.15 m s^{-1}) (1) without backwashing: (a) PCD of PG, (c) TiO_2 concentration in the photoreactor, and (e) permeate flux; and (2) with backwashing: (b) PCD of PG, (d) TiO_2 concentration in the photoreactor, and (f) permeate flux.

In order to realize on/in site recovery of TiO_2 particles, backwashing of the membrane was performed with backwashing frequency of 10 min, backwashing

duration of 5 s and different backwashing pressures (Table 5.1). An almost constant TiO_2 concentration in the photoreactor (Fig. 5.6d) and a rather sustainable permeate flux (Fig. 5.6f) were found throughout the experimental period with backwashing. The PCD of PG was enhanced by backwashing (Fig. 5.6b and Table 5.1) due to the higher TiO_2 concentration in the photoreactor compared to that without backwashing.

5.3.3.3 Effect of CFV on the closed-loop MPR system

A higher PCD efficiency of PG was found at a higher CFV (Figs. 5.7a and 7b and Table 5.1). Due to the loss of TiO_2 from the photoreactor resulting from the TiO_2 deposition on the membrane surface, the PCD efficiency of PG in the closed-loop MPR system without backwashing was lower than that with backwashing. At a lower CFV, a more rapid decrease of TiO_2 concentration in the photoreactor of the closed-loop MPR system without backwashing was observed in the first 2 h (Fig. 5.7c). This indicated a higher rate of TiO_2 deposition on the membrane surface at a lower CFV. Subsequently, the TiO_2 concentration in the photoreactor remained almost constant (10–14% of the initial value). The reduction rate of permeate flux increased with decreasing CFV (Fig. 5.7e), and then the permeate flux remained almost constant after 2 h. The steady-state permeate flux for T300 suspension was higher than that for T0.05–450 suspension, and was higher at higher CFV. >95% recovery of permeate flux (Fig. 5.7e), achieved after MQ water rinse and cake layer removal of the membrane, suggested that the cake layer was significantly related to the permeate flux reduction. Correspondingly, Table 5.2 shows decreasing total resistance and cake resistance with increasing CFV. It is postulated that high CFV with high shear stress could flush the TiO_2 particles on the membrane surface back to the photoreactor, resulting in the reduction of the thickness of cake layer followed by the lower total resistance and cake resistance.

Fig. 5.7 Effect of CFV on the performance of the closed-loop MPR system (TiO_2 dosage: 1.0 g L^{-1} ; TMP: 10 kPa) (1) without backwashing: (a) PCD of PG, (c) TiO_2 concentration in the photoreactor, and (e) permeate flux; and (2) with backwashing: (b) PCD of PG, (d) TiO_2 concentration in the photoreactor, and (f) permeate flux.

Backwashing of the membrane was carried out with backwashing frequency of 10 min, backwashing duration of 5 s and different backwashing pressures (Table 5.1).

With backwashing, TiO_2 particles were efficiently dislodged from the membrane

surface back to the photoreactor, resulting in an almost constant TiO_2 concentration in the photoreactor (Fig. 5.7d) and an almost constant permeate flux (Fig. 5.7f) over the experimental period. Accordingly, the PCD efficiency of PG was enhanced by backwashing (Fig. 5.7b and Table 5.1).

5.3.3.4 Performance of continuous flow-through MPR system

Based on the investigation of the closed-loop MPR system, TiO_2 dosage of 1.0 g L^{-1} , TMP of 10 kPa and CFV of 0.15 m s^{-1} were chosen as the optimal operating condition for the investigation of PG removal with the continuous flow-through MPR system. The membrane was backwashed every 10 min for a duration of 5 s with 34 and 35 kPa of backwashing pressures for the T300 and T0.05–450 suspensions, respectively. In order to prolong the photocatalytic reaction time for PG, the permeate water was partially recycled to the photoreactor. In this operating mode, different volumetric percents of permeate water were recycled to the photoreactor to examine the PCD of PG with different HRTs in the photoreactor. The HRT could be expressed as follows:

$$HRT = \frac{V}{Q(1 - V_r / 100)} \quad (5.4)$$

where V is the working volume of the photoreactor (mL), Q is the flow rate of the permeate water (mL min^{-1}), and V_r is the volumetric percent of permeate water recycled to the photoreactor (%), $0 < V_r < 100$). It should be noted that Eq. (5.4) with $V_r = 100$ is not applicable which should be the closed-loop operating mode.

The TiO_2 concentration in the photoreactor was monitored every 10, 20 or 30 min before backwashing and found to remain almost constant during the 6 h of operation (Fig. 5.8a). The permeate flux monitored every 5 min before backwashing was rather stable throughout the experimental period (Fig. 5.8b). This further confirmed the effectiveness of the backwashing operation to reduce membrane fouling and recover TiO_2 . With the increase of V_r , increased PCD efficiency of PG

Fig. 5.8 (a) TiO_2 concentration in the photoreactor, (b) permeate flux, and (c) PCD of PG in the closed-loop and continuous flow-through MPR systems with backwashing (TiO_2 dosage: $1.0 g L^{-1}$; TMP: 10 kPa; CFV: $0.15 m s^{-1}$).

could be achieved due to the longer HRT of PG in the photoreactor (Fig. 5.8c). After 6 h of operation, the PCD efficiencies of PG using $1.0 g L^{-1}$ of T300 were 82%, 90%, 95% and >99% for V_r of 50, 75, 90 and 100, respectively, while they were 85%, 92%, 97% and >99% for that using $1.0 g L^{-1}$ of T0.05-450, respectively.

It indicated that the PCD efficiency of PG in the continuous flow-through MPR system was lower than that in the closed-loop MPR system. Although the continuous flow-through MPR system was less efficient for the PCD of PG compared to the closed-loop MPR system, it seems more promising from the practical application point of view.

5.4 Conclusions

Effective separation of TiO_2 by the MF membrane was achieved in the hybrid MPR system. The loss of TiO_2 from the photoreactor due to the TiO_2 deposition on the membrane surface induced the decrease of PCD efficiency of PG in the closed-loop MPR system without backwashing. With backwashing operation, the TiO_2 particles were efficiently dislodged from the membrane surface back to the photoreactor, hence enhancing the PCD of PG to be almost comparable to that achieved in the batch photoreactor without the membrane module. In the MPR system operated under continuous flow-through mode, the PG degradation efficiency increased with the volumetric percent of permeate water recycled to the photoreactor due to the longer HRT of PG in the photoreactor. This vis-LED irradiated MPR system investigated in this study allows optimization for process design and operation of both visible-light photoreactor and membrane separation process. It shows practical application in treating antibiotics-polluted water.

CHAPTER 6 SUBMERGED MEMBRANE VIS-LED PHOTOREACTOR FOR SIMULTANEOUS CARBAMAZEPINE DEGRADATION AND TiO₂ SEPARATION

6.1 Introduction

Chapter 5 describes a hybrid MPR system combining a photoreactor irradiated with vis-LED and a separate cross-flow MF membrane module. The PG degradation, TiO₂ separation and permeate flux have been evaluated for the MPR system operated in both the closed-loop mode (with and without backwashing) and the continuous flow-through mode with fractional recirculation. The effects of TiO₂ dosage, TMP and CFV on its performances were systematically investigated. It is noted that the separated MPR system has an inherent drawback because it requires a larger facility footprint, which might not be suitable for an urban setting or in the premises with space restrictions. Moreover, its operation is more complicated compared to the combined MPR system.

The submerged membrane photoreactor (sMPR) system is more compact with the membrane module submerged into the photoreactor. Nevertheless, it is rather challenging to design such sMPR system due to the inherent complexities associated with the membrane module and light distribution therein. LEDs with flexible configuration show a good potential to be used as the light source for the sMPR system, without significantly reducing the membrane packing density. One inherent problem for this combined MPR system is associated with the deterioration of the polymeric membrane if irradiated by UV. In this context, the application of

vis-LED has the potential to alleviate this inherent problem.

This chapter illustrates a novel sMPR system comprising a photoreactor irradiated with vis-LED and a submerged hollow fiber MF membrane module. This system had a rather different flow hydrodynamics compared to that of the separated MPR system as described in Chapter 5. P25 and T0.05-450 were used as the photocatalysts. CBZ was used as the target pollutant, which is an antiepileptic pharmaceutical and considered as one of the most frequently detected pharmaceuticals in sewage water, sludge, surface water, groundwater and even drinking water (Kümmerer 2009a). Its chemical structure is shown as follows.

The effects of HRT, TiO_2 dosage and visible-light intensity on the performances of the sMPR system operated in the continuous flow-through mode were investigated. Inorganic anions are omnipresent in aquatic systems with different pH values. Humic acid (HA), one of the most significant fractions of NOMs, is ubiquitous in nearly all the natural waters and municipal wastewaters. Therefore, in order to simulate real surface waters or wastewaters, the effects of solution pH, inorganic anions and HA on the performances of the sMPR system were also elucidated. The effectiveness of sMPR in retaining the powdered TiO_2 while allowing continuous PCD of CBZ was evaluated. The membrane fouling propensity was also examined. In order to evaluate the effects of visible-light photocatalytic process, solution pH, inorganic anion and HA on the membrane property, the membranes before and after use were characterized for their morphologies, contact angles and chemical structures. The long-term performance of the sMPR system was also evaluated.

6.2 Experimental

6.2.1 Submerged membrane photoreactor and experimental procedures

In general, the sMPR system was a modification of MPR system investigated in Chapter 5. In the sMPR system, a hollow fiber MF membrane module was submerged into a vis-LED photoreactor (Fig. 6.1). The fabrication of vis-LED photoreactor was similar to that described in Section 3.2.3, while the difference was the property of the vis-LED flexible strip (i.e. light power and light intensity). In this study, vis-LED that emitted white light (SMD 5050, 60 unit m^{-1} , 15 W m^{-1}) was used as the visible-light source. The beam angle of the light source from vis-LED was 120° (vis-LED unit size was $4 \text{ mm} \times 4 \text{ mm}$) and the LED array was not contagious but they spaced out at average 1.7 cm. A tubular borosilicate glass photoreactor with a working volume of 1000 mL was wrapped with a 4 m long vis-LED flexible strip comprising 240 vis-LED units. A commercial hollow fiber PVDF MF membrane (mean pore size of $0.1 \mu\text{m}$, inner and outer diameter of 0.6 and 1.2 mm, respectively) was provided by Memstar Technology Ltd. (Singapore). Four hollow fibers with effective length of 15 cm each were formed into a membrane module. The effective membrane area was 22.61 cm^2 . Prior to the experiment, the clean membrane was pre-wetted by soaking in 50% ethanol solution for 12 h.

Fig. 6.1 Schematic diagram of the hybrid sMPR system.

The pre-wetted membrane module was rinsed with MQ water, and then mounted to the permeate line by connecting the Masterflex tubing side of the membrane module to the pressure transducer, followed by a Masterflex peristaltic pump. The sMPR system was operated at a constant flux in a continuous flow-through mode. Fresh CBZ (>99.0%, Sigma–Aldrich) solution (5.0 mg L^{-1}) was continuously fed into the photoreactor in order to maintain a constant working volume of the photoreactor. The permeate flux was measured by gravimetric method using a digital weighing balance (A&D FX–2000i, Japan). The TMP and permeate flux were auto-recorded at predetermined time intervals by a data logging system.

In a typical operation, 1000 mL of TiO_2 suspension with initial CBZ concentration of 5.0 mg L^{-1} was stirred in the dark to reach its adsorption equilibrium (achieved within 1 h). Meanwhile, the pre-wetted and rinsed membrane module was mounted onto the sMPR system and then submerged into MQ water. In order to realize the equilibration of the membrane module at a constant flux, the Masterflex peristaltic pump was used to drive a constant flow from the outside into the hollow fiber for 1 h. This completely removed the ethanol from the membrane surface and pores, and also compressed the membrane to reach a stable TMP which represented the initial TMP. Subsequently, the 1000 mL of the equilibrated TiO_2 –CBZ suspension replaced the MQ water in the sMPR system at the same constant flux and then the vis-LED was switched on. Sample aliquots of permeate water were collected at predetermined time intervals for HPLC analysis. The HPLC analysis was similar to that described in Section 4.2.3. The differences included: (1) methanol and MQ water was used as mobile phase A and B ($v_A/v_B = 80/20$), respectively; and (2) the detector wavelength was set at 210 nm. The procedures for particle size distribution and turbidity measurements are described in Chapter 5.

The effects of HRT, TiO_2 dosage, visible-light intensity, solution pH, inorganic anion, and HA on the performance of the sMPR system were investigated. The HRT

was controlled by varying the permeate flow rate (permeate flux) and/or changing the working volume of the photoreactor. The visible–light intensity was controlled by covering up different numbers of vis–LED units with aluminium foil, and was labeled as I–x where x indicated the numbers of vis–LED units in use. The powers of I–240, I–180, I–120 and I–60 were 60, 45, 30 and 15 W, respectively, and their visible–light intensities were ca. 15, 11, 8 and 4 W m⁻² as measured by a digital power meter SP 1065 (Janco Impex) when the power meter was placed in the middle of the spiral LED strips. The UV intensity was < 0.5 W m⁻² as measured by an Accumax XRP–3000 radiometer. Solution pH was adjusted using 1 M HCl and 1 M NaOH solutions. The inorganic anions investigated in this study included Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, H₂PO₄⁻, SiO₃²⁻ and silica which were added as sodium salts into the suspension. HA sodium salt (Sigma–Aldrich) was dissolved in MQ water (pH 11 adjusted by 1 M NaOH solution), filtered through a 0.45 µm cellulose acetate syringe membrane filter, and then stored in dark at 4 °C as stock solution. Different amounts of HA stock solutions were added to the photoreactor followed by pH adjustment to pH 6.9. The HA concentration was expressed in terms of TOC concentration (mg C L⁻¹) measured using a Shimadzu ASI–V TOC Analyzer. For comparison, the PCD of CBZ was also carried out in the batch photoreactor without the membrane module. Blank experiments were also conducted without photocatalyst to investigate the hydrolysis (in the dark) and photolysis (under vis–LED irradiation) of CBZ.

6.2.2 Photocatalytic degradation kinetics

The ideal continuous stirrer tank reactor (CSTR) model was used to evaluate the PCD of CBZ in the sMPR system (Schmidt 2011):

$$C_p = \left(C_0 - \frac{C_l}{1 + k\tau} \right) e^{-\left(\frac{1}{\tau} + k\right)\tau} + \frac{C_l}{1 + k\tau} \quad (6.1)$$

where C_P is the concentration of CBZ (mg L^{-1}) in the permeate water at the reaction time t (min), C_0 is the initial concentration of CBZ (mg L^{-1}) in the photoreactor, C_I is the concentration of CBZ (mg L^{-1}) in the feedwater, $\bar{t}$ is HRT (min), and k is the PCD rate constant (min^{-1}). At steady state, the CSTR model can be simplified to:

$$C_P = \frac{C_I}{1 + k_s \bar{t}} \quad (6.2)$$

where k_s is the PCD rate constant (min^{-1}) at steady state.

6.2.3 Characterization of membrane

The cross-section and outer surface morphologies of hollow fiber PVDF membranes were observed using a Zeiss EVO 50 scanning electron microscopy (SEM, Carl Zeiss AG). Prior to the test, the hollow fibers were dried in vacuum at room temperature for at least 24 h. Subsequently, the hollow fibers were broken in liquid nitrogen and then sputtered with a thin layer of gold using EMITECH SC7620 sputter coater (Quorum Technologies Ltd., UK).

In order to evaluate the effects of ROSs, (i.e. $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and $^1\text{O}_2$) on the chemical structure of the membrane, the attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) was carried out using an IRPrestige21 spectrophotometer (Shimadzu, Japan). The surface infrared spectra were recorded at room temperature over a scanning range of $650\text{--}4000\text{ cm}^{-1}$ with 45 scans at a resolution of 4.0 cm^{-1} in an ATR mode. Spectral analysis was performed using FTIR software (IR Solution, Shimadzu).

In order to evaluate the overall change of the hydrophilicity and hydrophobicity of the membrane surface before and after use, the contact angle was measured using a tensiometer (DCAT11 Dataphysics, Germany). The sample was fixed by the sample holder, and then lifted from the arm of an electronic balance. Subsequently, it experienced a cycle of immersion into MQ water and successive emersion. Three

immersion–emersion cycles were carried out for each sample, and the weight difference was continuously recorded by the electronic balance. The contact angle was calculated from the wetting force based on the Wilhelmy method. The reported contact angle is the average of at least 8 measurements for each sample.

6.2.4 Hydraulic resistance

The membrane fouling was evaluated by hydraulic resistance based on the resistance–in–series model. The detailed calculations could be found in Section 5.2.4.

6.3 Results and discussion

6.3.1 Photocatalytic degradation of CBZ in the sMPR system

In the absence of photocatalyst in the batch photoreactor, the CBZ concentration remained at the initial concentration of 5.0 mg L^{-1} both in the dark and under vis–LED irradiation, indicating that both hydrolysis and photolysis of CBZ could be negligible. The adsorption of CBZ on the membrane surface was insignificant. The rejection tests in dark showed that <3% and <8% of CBZ were rejected by the membrane in the case of CBZ–MQ and CBZ–TiO₂ solutions after 10–h operation of the sMPR system, respectively.

Fig. 6.2a shows the PCD of CBZ at different HRTs in the continuous flow–through sMPR system, and the corresponding k_s values are shown in Table 6.1. A global k_s value of $(19.4 \pm 2.35) \times 10^{-3} \text{ min}^{-1}$ was achieved for the range of HRTs investigated. The permeate quality reached almost a steady state after ca. 10–h operation of the sMPR system. The PCD efficiency of CBZ was higher for the case with longer HRT (lower permeate flux), which was attributed to the longer reaction time of CBZ in the photoreactor. The PCD of CBZ as a function of HRT in the sMPR system was compared with that in the batch photoreactor (Fig. 6.2b). The apparent rate constant,

k_{app} , was calculated using the Langmuir–Hinshelwood model. A slightly lower k_{app} value was obtained in the sMPR system, which could be attributed to the operating complexity of the sMPR system, such as the deposition of TiO_2 particles on the membrane surface along with the decline of photocatalyst concentration in the irradiated suspension.

Fig. 6.2 (a) PCD of CBZ as a function of HRT in the continuous flow-through sMPR system, and (b) Comparison of PCD of CBZ in the sMPR system with that in the batch photoreactor. The experimental conditions were as follows: T0.05–450 dosage: 1.0 g L^{-1} ; visible-light intensity: I-240; pH: 5.1 ± 0.1 .

Table 6.1 k_s values for the PCD of CBZ at different HRTs in the continuous flow-through sMPR system.

HRT (min)	$k_s^a (\times 10^{-3} \text{ min}^{-1})$	R^{2b}
30	14.9	0.982
60	20.3	0.984
90	17.9	0.985
120	21.0	0.995
180	21.8	0.993
240	19.4	0.997
300	20.5	0.995

^a PCD of CBZ rate constant at steady state calculated using CSTR model.

^b Coefficient of determination.

The PCD of CBZ was investigated using P25 and T0.05–450 as photocatalyst with different dosages, respectively. The CBZ removal rate and efficiency increased with the T0.05–450 dosage (Fig. 6.3a). In the sMPR system with HRT of 120 min, the CBZ removal efficiencies at the steady states were 44%, 60% and 68% with

T0.05–450 dosages of 0.3, 0.5 and 1.0 g L⁻¹, respectively. P25 exhibited a much lower visible–light photocatalytic activity which could be attributed to its larger band–gap energy of 3.0–3.2 eV compared to 2.67 eV of T0.05–450.

Fig. 6.3b shows the PCD of CBZ during 10–h operation of the sMPR system with different visible–light intensities. The PCD efficiency of CBZ increased with the visible–light intensity. Compared to 68% removal of CBZ (at $21.0 \times 10^{-3} \text{ min}^{-1}$) under irradiation with 240 vis–LED units at the steady state, only 28% of CBZ was photocatalytic degraded (at $4.99 \times 10^{-3} \text{ min}^{-1}$) with 60 vis–LED units.

Fig. 6.3c presents that the PCD of CBZ was slightly favorable in the alkaline conditions (76% of steady–state CBZ removal (at $26.7 \times 10^{-3} \text{ min}^{-1}$) at pH 12 while 64% (at $17.6 \times 10^{-3} \text{ min}^{-1}$) at pH 3). It was found that the CBZ adsorption on T0.05–450 was insignificantly affected by solution pH in the range of 3–12. This could be explained by their charging status. The T0.05–450 with its point of zero charge at pH 5.7 was positively charged at pH 3, and negatively charged at pH 6, 9 and 12. For the CBZ molecule which possesses pK_a values of 2.3 and 13.9 (Yu et al. 2008), it is mainly neutral at pH 3–12. Therefore, the electrostatic repulsion and attraction were insignificant between T0.05–450 and CBZ at pH 3–12. The concentration of $\bullet\text{OH}$ is another key factor influencing the PCD of CBZ. A higher concentration of $\bullet\text{OH}$ could be generated with the increase of pH (Wang and Lim 2010), leading to the enhanced PCD of CBZ in the alkaline conditions.

Though the presence of various inorganic anions had negligible influence on CBZ adsorption by T0.05–450, they have significant impact on PCD of CBZ. The anions can be ranked in the order of silica > phosphate > nitrate > bicarbonate > sulfate > chloride, based on their inhibitory effects on the CBZ degradation (Fig. 6.3d). It has been reported that the anions could act as the scavengers of h^+ and $\bullet\text{OH}$ (Eqs. (3.14) and (3.15)) (Rincón and Pulgarin 2004). The various ionic radicals formed are less oxidative than h^+ and $\bullet\text{OH}$, and thus would inevitably inhibit the CBZ degradation

to varying extents.

Fig. 6.3 Effect of (a) TiO_2 dosage, (b) visible-light intensity, (c) solution pH, (d) inorganic anion and (e) HA on the PCD of CBZ in the sMPR system. Unless otherwise indicated in the figures, the experimental conditions were as follows: T0.05-450 dosage: 1.0 g L^{-1} ; visible-light intensity: I-240; HRT: 120 min; permeate flux: 220 L $\text{m}^{-2} \text{h}^{-1}$; pH: 5.1 $\pm$ 0.1.

Silica is ubiquitous in the surface waters, groundwaters and wastewaters, and they

are originated from weathering of minerals. It is worth noting that the dissolved silica can undergo polymerization and forming polymeric and colloidal silica, through condensation of its monomers even at a relatively low concentration (Kohn et al. 2003, Yang et al. 2008b). Thus, the inhibitory effect induced by silica on PCD of CBZ as a function of its concentration was further investigated. Fig. 6.3d shows increased inhibitory effects on the PCD of CBZ with increasing silica concentration. This could be attributed to the increased deactivation of the photocatalyst surface sites by the deposited silica. In addition, the vis-LED light could be substantially attenuated in the photoreactor containing suspended polymeric and/or colloidal silica.

The PCD of CBZ was investigated with the presence of HA. It was found that 12% of CBZ was adsorbed on TiO_2 in the presence of 5.0 mg C L^{-1} of HA, and the CBZ adsorption increased with HA concentration. The rejection test in dark showed that <15% of CBZ in the TiO_2 -HA (5.0 mg C L^{-1}) suspension was retained by the membrane after 10 h of operation. Fig. 6.3e shows that the CBZ degradation rates increased in the presence of HA with concentration up to 5.0 mg C L^{-1} , while a further increase of HA concentration would inhibit the CBZ degradation. This reversible trend could be explained as follows. On the one hand, as an electron shuttle (Lovley et al. 1996), HA could transfer conduction band electrons to oxygen dissolved in bulk water, thereafter promoting the generation of $\bullet\text{O}_2^-$ and meanwhile reducing the electron-hole recombination (Fig. 6.4). On the other hand, HA could compete with CBZ for the active sites of the photocatalyst. Furthermore, HA could contribute to the light attenuation in the photoreactor. Therefore, the overall effect of HA on the CBZ degradation would depend on the net effect of the aforementioned competitive phenomena.

Fig. 6.4 Proposed mechanism of CBZ degradation in the TiO₂-HA suspension under vis-LED irradiation.

6.3.2 Effectiveness of TiO₂ separation by the membrane

Preliminary tests showed that the membrane structural integrity was maintained at the applied permeate flux with insignificant membrane compaction or swelling. The hydraulic permeability ($L_p = 1/\mu R_m$, m Pa⁻¹ s⁻¹) using MQ water was 3.21×10^{-9} m Pa⁻¹ s⁻¹. Membrane photostability tests demonstrated no changes in the contact angle and chemical structure (Fig. 6.5a) for the membrane after 10-day vis-LED irradiation, moreover, no release of organic species from the polymeric membrane was found according to the TOC measurement. This confirmed the excellent photoresistance of the membrane to visible light.

For both T0.05-450 suspensions (pH 5.1, with initial turbidities of 620, 1070 and 2150 NTU at dosages of 0.3, 0.5 and 1.0 g L⁻¹, respectively) and P25 suspensions (pH 5.5, with initial turbidities of 1110, 2060, 4210 NTU at dosages of 0.3, 0.5 and 1.0 g L⁻¹, respectively), the turbidities of permeate water were consistently <0.1 NTU. This indicated that the MF membrane was effective for the retention of TiO₂. This could be further confirmed by the results of the particle size distributions of T0.05-450 and P25 in suspensions (Fig. 6.6a and Table 6.2). Obviously, the particle size of T0.05-450 in suspension was larger than that of P25 in suspension. For both P25 and T0.05-450, there were only slight shifts in the respective particle size distributions as their dosages were increased. The particle sizes of T0.05-450 after

72-h mixing were slightly larger than those after 10-h and 1-h mixings due to aggregation of particles. In conclusion, almost all the T0.05–450 and P25 particles were much larger than the mean pore size of the MF membrane. In addition, the larger TiO_2 particles could form a porous cake layer (secondary dynamic membrane) on the membrane surface during MF process, which would be effective for the further rejection of the smaller particles.

Fig. 6.5 ATR-FTIR spectra of membrane: (a) before and after use in the sMPR system; effect of (b) pH; (c) inorganic anion; and (d) HA.

The particle size distributions of T0.05–450 in suspensions with pH in the range of 3–12 are compared in Fig. 6.6b and Table 6.2. Apparently, the largest TiO_2 particles were observed at pH 6. This was because at pH 6 ($\geq$ point of zero charge of T0.05–450), the electrostatic repulsion between the TiO_2 particles was the smallest, and thus the TiO_2 particles tended to agglomerate easily. The TiO_2 particle sizes

were smaller at pH far away from the point of zero charge of T0.05–450 due to the enhanced electrostatic repulsion. While the particle sizes of T0.05–450 in suspensions at pH 9 and 12 were slightly smaller than those at pH 3, they were still much larger than the MF membrane pore size.

The effects of inorganic anions (except silica) on the particle size distributions of T0.05–450 were much less profound (Fig. 6.6c and Table 6.2). Silica could be the most influential in promoting aggregation of TiO_2 particles. In the sMPR system with solution containing both TiO_2 and HA, the particle sizes of TiO_2 were slightly larger with higher concentration of HA in the solution (Fig. 6.6d and Table 6.2). It is postulated that the adsorption of HA on TiO_2 occurred, hence HA could act as bridge to enhance the agglomeration of TiO_2 particles.

Fig. 6.6 Particle size distribution of T0.05–450 (pH 5.1) and P25 (pH 5.5) in suspension: effect of (a) dosage and mixing time; (b) solution pH; (c) inorganic anion; and (d) HA.

Table 6.2 Particle size of TiO₂ in suspension after 10-h mixing, and effect of TiO₂ dosage, solution pH, inorganic anion and HA on the hydraulic resistance in the continuous flow-through sMPR system.

Parameter	R _t (×10 ¹¹ m ⁻¹)	R _m (×10 ¹¹ m ⁻¹)	R _c (×10 ¹¹ m ⁻¹)	R _p (×10 ¹¹ m ⁻¹)	Particle size of TiO ₂ (μm)		
					d(0.1) ^b	d(0.5) ^c	d(0.9) ^d
TiO ₂ dosage (g L ⁻¹)							
0.3 (pH 5.5) ^a	4.11	2.99	0.844	0.279	0.947	3.154	16.907
0.5 (pH 5.5) ^a	4.88	2.97	1.46	0.452	0.938	3.241	18.069
1.0 (pH 5.5) ^a	6.84	2.95	3.20	0.694	0.937	3.515	23.143
0.3 (pH 5.1)	3.46	2.98	0.360	0.118	2.189	11.682	42.712
0.5 (pH 5.1)	3.71	2.97	0.601	0.139	2.102	12.255	43.016
1.0 (pH 5.1)	4.09	2.99	0.936	0.166	2.230	14.546	51.717
Solution pH							
3	3.48	2.96	0.351	0.173	3.044	11.255	35.249
6	3.20	2.98	0.116	0.104	2.159	12.719	38.727
9	3.67	2.99	0.491	0.190	2.428	9.106	27.150
12	3.74	2.99	0.518	0.239	2.021	8.986	28.029
Inorganic anion (pH 6.9)							
Cl ⁻ (1 mM)	3.38	2.97	0.292	0.118	3.065	8.386	20.712
NO ₃ ⁻ (1 mM)	3.37	2.99	0.266	0.111	3.150	8.743	21.906
SO ₄ ²⁻ (1 mM)	3.38	2.96	0.298	0.123	3.053	8.589	21.490
HCO ₃ ⁻ (1 mM)	3.39	2.98	0.279	0.134	3.508	9.511	25.400
H ₂ PO ₄ ⁻ (1 mM)	3.38	2.99	0.266	0.123	3.248	9.385	26.624
Silica (0.1 mM)	3.37	2.96	0.286	0.120	2.616	8.408	23.374
Silica (1 mM)	3.47	2.97	0.312	0.186	3.964	10.960	29.118

Parameter	R_t ($\times 10^{11} \text{ m}^{-1}$)	R_m ($\times 10^{11} \text{ m}^{-1}$)	R_c ($\times 10^{11} \text{ m}^{-1}$)	R_p ($\times 10^{11} \text{ m}^{-1}$)	Particle size of TiO_2 (μm)		
					d(0.1) ^b	d(0.5) ^c	d(0.9) ^d
Silica (5 mM)	3.55	2.98	0.358	0.212	4.725	14.112	42.507
HA (mg C L ⁻¹) (pH 6.9)							
1.5	3.44	2.97	0.304	0.164	2.425	7.737	18.321
3.0	3.56	2.96	0.378	0.226	2.513	7.391	18.050
5.0	3.72	3.00	0.463	0.260	2.638	7.774	19.061
14.5	3.92	2.98	0.564	0.374	3.053	9.229	23.048

^a Parameters investigated with P25, while others investigated with T0.05–450.

^{bcd} Particle size of TiO_2 in suspension after 10-h mixing at the cumulative volumetric percentage of 10, 50 and 90%, respectively.

6.3.3 Membrane fouling evaluation in the sMPR system

Membrane fouling was evaluated through monitoring the TMP changes throughout the experimental period. It can be observed from Fig. 6.7a that the TMP increased in the first 2 h for all the TiO_2 dosages investigated. It is postulated that the increase of TMP was mainly attributed to the TiO_2 cake layer deposited on the membrane surface. The steady state TMP observed implies that the cake build-up became limited. This could be due to a finite inventory of particles most likely to deposit, which would tend to be the smaller particles as can be seen from the particle size distribution (Fig. 6.6a and Table 6.2). Alternatively, the modest stirring at the bottom of the reactor could have induced circulation flows which would limit particle deposition. It would be possible to reduce cake build-up by more vigorous stirring, bubbling etc, at some energy penalty. Because of its smaller particle sizes, the P25 cake layer was expected to be less permeable than T0.05–450 cake layer (as can be inferred from Figs. 6.8b1 and 8c1), resulting in a much higher steady-state TMP. In addition, the higher steady-state TMP could be attributed to the thicker cake layer for the higher TiO_2 dosage. After 10-h operation of the sMPR system, the membrane was rinsed with MQ water and then the TMP was measured for 1 h using MQ water as feedwater. It was found that the reinstated TMPs for all the TiO_2 dosages decreased to some extent, namely, 23% and 6% higher than the initial value for the 1.0 g L^{-1} P25 and T0.05–450 cases, respectively (Fig. 6.7a). The reason might be that, compared to the T0.05–450 particles, the P25 particles were smaller which could enter into the membrane pores more easily and caused irreversible pore blockings, as can be observed from Figs. 6.8b2 and 8c2. Table 6.2 further shows that, although the pore blockage resistances for both P25 and T0.05–450 were insignificant, they were slightly more significant for the cases with P25 than those with T0.05–450. In addition, the total resistance and cake resistance for P25 were higher than those for T0.05–450. The total resistance, cake resistance and pore

blockage resistance increased with the TiO_2 dosage.

Fig. 6.7 Effect of (a) TiO_2 dosage, (b) solution pH, (c) inorganic anion and (d) HA on the TMP change in the sMPR system. Unless otherwise indicated in the figures, the experimental conditions were as follows: T0.05–450 dosage: 1.0 g L⁻¹; visible–light intensity: I–240; HRT: 120 min; permeate flux: 220 L m⁻² h⁻¹; pH: 5.1 ± 0.1.

Fig. 6.8 SEM images of hollow fiber PVDF membrane: (a) clean membrane; used in the P25 suspension (1.0 g L^{-1}) for 10 h (b1) before and (b2) after water rinse; used in the T0.05–450 suspension (1.0 g L^{-1}) for 10 h (c1) before and (c2) after water rinse.

Similarly, the steady-state TMP was achieved after the slight increase in the first 2 h at all the solution pH investigated (Fig. 6.7b). The lowest steady-state TMP was found at pH 6 because the TiO₂ particles were the largest (Fig. 6.6b and Table 6.2) and the associated cake layer would be the most permeable compared to the other pH conditions (note: cake resistance is proportional to (particle size)⁻², $\alpha_c = 180(1 - \varepsilon_c) / \rho_p d_p^2 \varepsilon_c^3$) (Drioli and Giorno 2009). After water rinse, the reinstated TMPs were only 4–9% higher than the initial values, indicating a rather effective membrane cleaning with water rinse. Correspondingly, Table 6.2 shows lowest hydraulic resistance at pH 6, and the cake resistances contributed more to the membrane fouling than the pore blockage resistances in pH 3–12. Analysis with ATR–FTIR showed that there was insignificant change of the chemical structures for the membranes after use in the solution with pH in the range of 3–9 (Fig. 6.5b). However, the intensities of the bands at 1182 and 1277 cm⁻¹ attributed to the asymmetrical and symmetrical stretching of CF₂, respectively, and the band at 1402 cm⁻¹ assigned to the vibration of CH₂ decreased for the membrane used at pH 12. The contact angles for the membranes used in the solutions with pH of 3, 6, 9 and 12 were 71°, 73°, 72° and 67°, respectively. Compared to the contact angle of 79° for the clean membrane, the membrane tended to be slightly more hydrophilic after use due to the adsorption of TiO₂ on it.

There were no noticeable differences both in the TMP (Fig. 6.7c) and in the hydraulic resistance (Table 6.2) with respect to the various anions added at 1 mM. However, slightly higher steady-state TMP and hydraulic resistance were observed when the silica concentration was increased to 5 mM, and the reinstated TMP was 10% higher than the initial value after water rinse of the membrane. This indicated that the polymeric and colloidal silica might deposit on the membrane surface, and water rinsing was not totally effective to remove it. As shown in Table 6.2, the cake resistance was the dominant component of the fouling resistance. There was no noticeable evidence showing the presence of chloride, nitrate, sulfate, bicarbonate,

phosphate and silica on the membrane surface. The ATR–FTIR spectra intensities of the bands at 1182, 1277 and 1402 cm^{-1} were slightly lower after its use in the solution with relatively higher silica concentration than lower silica concentration and in solution containing other inorganic anions (Fig. 6.5c). The contact angles after use were in the range of 69° – 73° , indicating slightly enhanced hydrophilicity of the membrane surface due to the adsorption of TiO_2 and inorganic anions (contact angle of 79° for the clean membrane).

In the sMPR system with solution containing both TiO_2 and HA, the steady–state TMP was achieved after its increase in the first 2 h (Fig. 6.7d). The steady–state TMP and hydraulic resistance (Table 6.2) were slightly higher for the case with a higher HA concentration. The schematic diagrams of membrane fouling caused by TiO_2 alone and mixture of HA and TiO_2 are shown in Fig. 6.9. It is postulated that a porous TiO_2 alone cake layer was gradually generated on the membrane surface, while a denser HA– TiO_2 cake layer was formed due to the adsorption of HA on TiO_2 during which HA could occupy the vacancies between the TiO_2 particles. On one hand, the adsorption of HA on TiO_2 would be inhibited in the alkaline solution due to the negative–negative electrostatic repulsion between the negatively charged HA and TiO_2 . On the other hand, most of HA would be fully protonated and scarcely soluble in the acidic solution, which could induce a significantly increase of the adsorption of HA on TiO_2 .

Fig. 6.9 Schematic diagrams of membrane fouling caused by TiO_2 alone and mixture of HA and TiO_2 .

The SEM images of membrane after use in the T0.05–450 suspension (1.0 g L^{-1}) with presence of HA (5.0 mg C L^{-1}) for 10 h is present in Fig. 6.10a. After water rinse, the reinstated TMP was 7–13% higher than the initial values (Fig. 6.7d). This suggested that HA combined with TiO_2 deposited on the membrane surface could not be removed so easily by water rinse (Fig. 6.10b). Therefore, chemical cleaning was performed at pH 11 using NaOH and 0.5 mM ethylenediaminetetraacetic acid (EDTA) as cleaning agents, respectively. On the one hand, HA is more soluble at high pH. On the other hand, NaOH (Yu et al. 2010) and EDTA (Ang et al. 2011) have been reported to be efficient in cleaning hydrophobic fouling. Based on the TMP monitoring (Fig. 6.7d) and the observed membrane morphology (Figs. 6.10c and 10d), both NaOH (pH = 11) and 0.5 mM EDTA (pH = 11) were efficient for cleaning the membrane fouled by HA. According to the ATR–FTIR analysis (Fig. 6.5d), the spectra intensities of membranes used in the presence of HA were slightly lower after water rinse than that of the clean membrane. This could be due to the HA deposited on the membrane surface. After chemical cleaning with NaOH (pH = 11) and 0.5 mM EDTA (pH = 11), the spectra intensities were almost identical to that of the clean membrane. After water rinse of the membranes used in the HA solutions of 0, 1.5, 3.0, 5.0 and 14.5 mg C L^{-1} concentrations, the contact angles were 72° , 74° , 76° , 78° , and 81° , respectively, and decreased to 72° – 73° after chemical cleaning. The hydrophobic portions of HA deposited on the membrane surface could possibly contribute to the slightly higher contact angles of the membranes.

Fig. 6.10 SEM images of hollow fiber PVDF membrane: (a) after use in the T0.05–450 suspension (1.0 g L^{-1}) with presence of HA (5.0 mg C L^{-1}) for 10 h, (b) after water rinse, (c) after NaOH ($\text{pH} = 11$) cleaning and (d) after 0.5 mM EDTA ($\text{pH} = 11$) cleaning.

6.3.4 Long-term performance of the sMPR system

The sMPR system was operated using 1.0 g L^{-1} of T0.05–450 under vis-LED irradiation (I-240) at a permeate flux of $220 \text{ L m}^{-2} \text{ h}^{-1}$ for 72 h without intermittent physical and chemical cleaning. It was found that the steady-state permeate quality could be achieved within 10 h with a CBZ removal efficiency of $>69\%$ (Fig. 6.11a). However, the PCD efficiency of CBZ started to decrease slightly after 36 h of sMPR operation. This reduction was possibly attributed to the continuous deposition of TiO_2 particles on the photoreactor wall surface and membrane surface over time, resulting in the decreased photocatalyst concentration in the irradiated suspension. Another possible explanation might be the aggregation of TiO_2 particles during the prolonged operation of sMPR (Fig. 6.6a and Table 6.2). In a separate experiment in which 6-h batch experiment was carried out using the photoreactor (without membrane module) over 12 cycles (inset of Fig. 6.11a), $>87\%$ of CBZ degradation was still achieved after 7 cycles (total 42 h), and then decreased to 70% after 12 cycle (total 72 h), indicating some degree of TiO_2 deactivation. From a practical point of view, attention should be paid to the permeate quality during the sMPR operation. It is recommended that backwashing, air bubbling, membrane module vibration, and/or intermittent membrane cleaning could be performed in order to dislodge the TiO_2 particles from the membrane surface back to the suspension, thus the PCD efficiency of CBZ could be maintained steady.

Fig. 6.11b shows that the TMP increased in the first 2 h due to the TiO_2 cake layer (8–18% of the total TiO_2 particles) formed on the membrane surface. It indicated that this loss of TiO_2 from the irradiated suspension could not induce a significant reduction of CBZ degradation efficiency. Subsequently, the established steady-state TMP remained almost constant throughout the subsequent 70 h of experimental run. The cake layer was removed after water rinse, obtaining a reinstated TMP which was 7% higher than the initial value. There was insignificant change of the chemical

structures according to the ATR–FTIR analysis (Fig. 6.5a). The contact angles for the membranes after 10-h and 72-h sMPR operations were 72° and 71°, respectively. Compared to the contact angle of 79° for the clean membrane, the membrane tended to be slightly more hydrophilic after use in the sMPR system with TiO₂ suspension.

Fig. 6.11 Long-term experiment results: (a) PCD of CBZ (Inset shows the deactivation test of T0.05–450 in the 6-h batch photoreactor without membrane module), and (b) TMP change in the sMPR system. The experimental conditions were as follows: T0.05–450 dosage: 1.0 g L⁻¹; visible-light intensity: I-240; HRT: 120 min; permeate flux: 220 L m⁻² h⁻¹; pH: 5.1 ± 0.1.

6.4 Conclusions

The hybrid submerged membrane vis-LED photoreactor with a visible-light responsive TiO₂ and a PVDF MF membrane module realized effective CBZ degradation and simultaneous TiO₂ separation without significant membrane deterioration and fouling. In the presence of HA, intermittent chemical cleaning is necessary in order to remove the fouling caused by HA. An alkaline pH condition was favorable for the PCD of CBZ. Silica showed more significant inhibitory effects on the PCD of CBZ than the other common anions. As an electron shuttle, HA could enhance the CBZ degradation through promoting the generation of $\cdot\text{O}_2^-$ along with reducing the recombination of electron-hole pairs, while HA could inhibit its degradation through competing with CBZ for the active sites of the

photocatalyst and contributing to the light attenuation in the photoreactor. This sMPR system has the scientific merit and is promising for treating real waters using visible–light photocatalysis and low–pressure membrane process with an advantage of low energy consumption.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Overall conclusions

Two kinds of visible–light responsive TiO_2 were synthesized using facile sol–gel methods. They were characterized using XRD, porosimetry, SEM/EDX, TEM, XPS and DRS. Their photocatalytic activities were evaluated in the batch photoreactors with the effects of calcination temperature for TiO_2 synthesis, initial pollutant concentration, TiO_2 dosage, solution pH, inorganic anions, light intensity and light source. It was found that T300, a novel C–sensitized and N–doped TiO_2 , exhibited high photocatalytic activity for SNM degradation under visible–light irradiation due to the synergistic effects of carbon–sensitizing and nitrogen–doping. In addition, T0.05–450, a novel C–N–S tridoped TiO_2 , exhibited high photocatalytic activity for TC degradation due to the synergistic effects of carbon, nitrogen and sulfur tridoping. The acute toxicity of SNM and TC solution could be reduced over prolonged photocatalysis as could be inferred from the Microtox assay. The comparison of the PCD of SNM, TC and PG using T300 and T0.05–450 showed that T0.05–450 exhibited higher visible–light photocatalytic activity than T300.

Two hybrid membrane photoreactor systems, namely separated system and combined system, were developed and evaluated with regard to the pollutants degradation, TiO_2 separation and membrane fouling propensity. Both systems could realize effective separation of powdered TiO_2 and PCD of pollutants. The first type of MPR system was a separated system, which was investigated in both closed–loop (with/without backwashing) and continuous flow–through modes with PG as the target pollutant and T300 and T0.05–450 as the photocatalysts. It was found that the

operations at a higher TMP and a lower CFV were more prone to induce TiO_2 deposition on the membrane surface, which resulted in the membrane fouling, the loss of TiO_2 from the photoreactor and the decrease of PCD efficiency of PG. These problems can be alleviated through backwashing of the membrane. This separated MPR system can achieve the optimization for design and operation of both visible–light photoreactor and membrane separation process. It is worth noting that the separated MPR system requires a large footprint which might not be suitable for an urban setting or in the premises with space restrictions. Therefore, the combined sMPR system was investigated in a continuous flow–through mode with CBZ as the target pollutant and T0.05–450 as the photocatalyst. The effects of solution pH and inorganic anions on the membrane deterioration and fouling were insignificant in this combined sMPR system. With the presence of HA, intermittent chemical cleaning is necessary in order to remove the fouling caused by HA. For the long–term operation of the sMPR system, the reduction of PCD efficiency of CBZ could be attributed to the decrease of the photocatalyst dosage in the suspension, and the aggregation and deactivation of TiO_2 particles during the prolonged operation. In summary, the two vis–LED irradiated MPR systems show practical application in treating real water/wastewaters.

7.2 Recommendations for future research

To further extend the potential practical application of visible–light responsive TiO_2 in the hybrid MPR systems for the water treatment and reclamation, several recommendations for the future study have been proposed.

1. Visible–light responsive TiO_2

- Novel synthesis techniques should be developed to prepare visible–light responsive TiO_2 with potentially further enhanced visible–light photocatalytic activity and up–scalability for mass production. Other types

of characterization techniques can be used to gain in-depth insights into the characteristics of the visible-light responsive TiO_2 , such as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR).

- Several other analytical techniques can be carried out to investigate the formation of ROSs for the further understanding of the photocatalytic mechanism. For example, electron spin resonance (ESR) spectroscopy can be used for the detection and identification of low concentration of $\bullet\text{OH}$.
- The performances of the visible-light responsive TiO_2 can be examined in the simulated real waters with a wide range of recalcitrant organic pollutants in solution with different pH and various aqueous matrix species, which can indicate their feasibility for practical application for treating real water/wastewaters. In addition, real sunlight and real water/wastewaters can also be utilized to evaluate their practical solar photocatalysis application.
- Prior to the practical solar photocatalysis application of visible-light responsive TiO_2 , some potential challenges should be considered, such as cost-effectiveness, up-scalability, photocatalyst deactivation and the need for pretreatment of the water/wastewaters. Furthermore, the continuous use and saturation problem of visible-light responsive TiO_2 have to be addressed.

2. Hybrid membrane photoreactor (MPR)

- The configuration of photoreactor can be further investigated with different light intensities, light sources and light positions (including real sunlight). The fabrication of the hybrid MPR systems can be further improved through varying the relative position of the light source, photoreactor and membrane module.

- Membranes with different properties (pore size, hydrophilicity and hydrophobicity, etc) and different configurations (flat sheet/hollow fiber) in different membrane modules can be evaluated. The long-term membrane stability should be monitored (e.g. FTIR spectra and contact angle measurements, etc), especially when the real sunlight is used.
- Similarly, the removal efficiency of a wide range of recalcitrant organic pollutants can be examined in the MPR systems, along with the effects of solution pH and various aqueous matrix species. When considering a large-scale application of MPR system, the inherent drawbacks associated with application of photocatalysis for treating real water/wastewaters (e.g. photocatalyst deactivation and the need for pretreatment of feedwater) should be addressed.
- Some additional operations can be conducted to minimize membrane fouling, such as backwashing, air bubbling, membrane module vibration, and/or intermittent membrane cleaning, etc., in order to further improve its performance and realize its industry-scale application. In addition, the capital and operating costs have to be considered in comparison with the currently available treatment options.

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