

Review

Recent developments in photocatalytic water treatment technology: A review

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ABSTRACT

In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the "zero" waste scheme in the water/wastewater industry. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. At present, the main technical barriers that impede its commercialisation remained on the post-recovery of the catalyst particles after water treatment.

This paper reviews the recent R&D progresses of engineered-photocatalysts, photoreactor systems, and the process optimizations and modellings of the photooxidation processes for water treatment. A number of potential and commercial photocatalytic reactor configurations are discussed, in particular the photocatalytic membrane reactors. The effects of key photoreactor operation parameters and water quality on the photo-process performances in terms of the mineralization and disinfection are assessed. For the first time, we describe how to utilize a multi-variables optimization approach to determine the optimum operation parameters so as to enhance process performance and photooxidation efficiency. Both photomineralization and photo-disinfection kinetics and their modellings associated with the photocatalytic water treatment process are detailed. A brief discussion on the life cycle assessment for retrofitting the photocatalytic technology as an alternative waste treatment process is presented. This paper will deliver a scientific and technical overview and useful information to scientists and engineers who work in this field.

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1. Introduction

Increasing demand and shortage of clean water sources due to the rapid development of industrialisation, population growth and long-term droughts have become an issue worldwide. With this growing demand, various practical strategies and solutions have been adopted to yield more viable water resources. The storage of rainwater for daily activities and increasing the catchment capacity for stormwater are just a few examples that could resolve the problems in short-term. Water industries and governments in some arid areas with abundant of sunlight, less rainfall and long-term drought have a challenge to seek viable water resources. It is estimated that around 4 billion people worldwide experience to have no or little access to clean and sanitised water supply, and millions of people died of severe waterborne diseases annually (Malato et al., 2009). These statistical figures are expected to grow in the short future, as increasing water contamination due to overwhelming discharge of micropollutants and contaminants into the natural water cycle (Wintgens et al., 2008; Richardson, 2008; Suárez et al., 2008). In view to suppress the worsening of clean water shortage, development of advanced with low-cost and high efficiency water treatment technologies to treat the wastewater is desirable.

One of a few attractive options is the possible reuse of onsite rural wastewater or the treated municipal wastewater from treatment plants for agricultural and industrial activities (Bradley et al., 2002; Lapeña et al., 1995). Since these wastewaters constitute one of the largest possible water resources, its reuse is anticipated to offset more clean water resource. Recycling wastewaters are usually associated with the presence of suspended solids, health-threat coliforms and soluble refractory organic compounds that are both tedious and expensive to treat (Viessman and Hammer, 1998). Currently available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, but still remain and not being completely "eliminated" or "destroyed" (Padmanabhan et al., 2006). Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem (Gaya and Abdullah, 2008). These concentrated toxic contaminants are highly redundant and have been concerned worldwide due to the increasing environmental awareness and legislations. Chlorination has been the most commonly and widely used disinfection process. The disinfection by-products generated from chlorination are mutagenic and carcinogenic to human health (Yang and Cheng, 2007; Lu et al., 2009; Coleman et al., 2005).

These have lead to the rapid R&D in the field of "Advanced Oxidation Processes (AOPs)" as the innovative water treatment technologies. The rationales of these AOPs are based on the insitu generation of highly reactive transitory species (i.e. H_2O_2 , OH•, $O_2^{\bullet-}$, O_3) for mineralization of refractory organic compounds, water pathogens and disinfection by-products (Esplugas et al., 2002; Pera-Titus et al., 2004). Among these AOPs, heterogeneous photocatalysis employing semiconductor catalysts (TiO₂, ZnO, Fe₂O₃, CdS, GaP and ZnS) has

demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water. Among the semiconductor catalysts, titanium dioxide (TiO₂) has received the greatest interest in R&D of photocatalysis technology. The TiO₂ is the most active photocatalyst under the photon energy of 300 nm < λ < 390 nm and remains stable after the repeated catalytic cycles, whereas Cds or GaP are degraded along to produce toxic products (Malato et al., 2009). Other than these, the multi-faceted functional properties of TiO₂ catalyst, such as their chemical and thermal stability or resistance to chemical breakdown and their strong mechanical properties have promoted its wide application in photocatalytic water treatment.

A number of important features for the heterogeneous photocatalysis have extended their feasible applications in water treatment, such as; (1) ambient operating temperature and pressure, (2) complete mineralization of parents and their intermediate compounds without secondary pollution and (3) low operating costs. The fact that the highly reactive oxygen species (ROS) generated as a result of the photo-induced charge separation on TiO2 surfaces for microbial inactivation and organic mineralization without creating any secondary pollution is well-documented. So far, the application of such TiO₂ catalysts for water treatment is still experiencing a series of technical challenges. The post-separation of the semiconductor TiO₂ catalyst after water treatment remains as the major obstacle towards the practicality as an industrial process. The fine particle size of the TiO₂, together with their large surface area-to-volume ratio and surface energy creates a strong tendency for catalyst agglomeration during the operation. Such particles agglomeration is highly detrimental in views of particles size preservation, surface-area reduction and its reusable lifespan. Other technical challenges include in the catalysts development with broader photoactivity range and its integration with feasible photocatalytic reactor system. In addition, the understanding of the theory behind the common reactor operational parameters and their interactions is also inadequate and presents a difficult task for process optimization. A number of commonly made mistakes in studying kinetic modelling on either the photomineralization or photo-disinfection have also been seen over the years.

This review paper aims to give an overview of the understanding and development of photocatalytic water treatment technology, from fundamentals of catalyst and photoreactor development, to process optimization and kinetics modelling, and eventually the water parameters that affects the process efficiency. A short outlines of the feasible application of photocatalytic water technology via life cycle interpretation and the possible future challenges are also recommended.

2. Fundamentals and mechanism of TiO₂ photocatalysis

2.1. Heterogeneous TiO₂ photocatalysis

The fundamentals of photophysics and photochemistry underlying the heterogeneous photocatalysis employing the semiconductor TiO₂ catalyst have been intensively reported in many literatures (Gaya and Abdullah, 2008; Fujishima et al., 2000). The semiconductor TiO_2 has been widely utilised as a photocatalyst for inducing a series of reductive and oxidative reactions on its surface. This is solely contributed by the distinct lone electron characteristic in its outer orbital. When photon energy (hv) of greater than or equal to the bandgap energy of TiO₂ is illuminated onto its surface, usually 3.2 eV (anatase) or 3.0 eV (rutile), the lone electron will be photoexcited to the empty conduction band in femtoseconds. Fig. 1 depicts the mechanism of the electron-hole pair formation when the TiO_2 particle is irradiated with adequate hv. The light wavelength for such photon energy usually corresponds to $\lambda < 400$ nm. The photonic excitation leaves behind an empty unfilled valence band, and thus creating the electron-hole pair $(e^{-}-h^{+})$. The series of chain oxidative-reductive reactions (Eqs. (2.1)-(2.11)) that occur at the photon activated surface was widely postulated as follows:

Photoexcitation: $TiO_2 + hv \rightarrow e^- + h^+$	(2.1)
Charge-carrier trapping of e–: $e^{CB} \rightarrow e^{TR}$	(2.2)
Charge-carrier trapping of h+: $h^+{}_{VB} \rightarrow h^+{}_{TR}$	(2.3)
Electron-hole recombination: $e^{-}_{TR} + h^{+}_{VB}(h^{+}_{TR}) \rightarrow e^{-}_{CB} + heat$	(2.4)
Photoexcited e ⁻ scavenging: $(O_2)_{ads} + e^- \rightarrow O_2^{-}$	(2.5)
Oxidation of hydroxyls: $\text{OH}^- + h^+ \rightarrow \text{OH}^{\bullet}$	(2.6)

Photodegradation by OH•:
$$R-H + OH• \rightarrow R'• + H_2O$$
 (2.7)



Fig. 1 – Photo-induced formation mechanism of electron-hole pair in a semiconductor TiO_2 particle with the presence of water pollutant (P).

Direct photoholes: $R + h^+ \rightarrow R^{+ \bullet} \rightarrow $ Intermediate(s)/Fir	ıal
Degradation Products	(2.8)

Protonation of superoxides:
$$O_2^{\bullet-} + OH^{\bullet} \rightarrow HOO^{\bullet}$$
 (2.9)

Co-scavenging of e^- : HOO • + $e^- \rightarrow HO_2^-$ (2.10)

Formation of
$$H_2O_2$$
: $HOO^- + H^+ \rightarrow H_2O_2$ (2.11)

The e_{TR}^{-} and h_{TR}^{+} in (Eq. (2.4)) represent the surface trapped valence band electron and conduction-band hole respectively. It was reported that these trapped carriers are usually TiO₂ surface bounded and do not recombine immediately after photon excitation (Furube et al., 2001). In the absence of electron scavengers (Eq. (2.4)), the photoexcited electron recombines with the valence band hole in nanoseconds with simultaneous dissipation of heat energy. Thus, the presence of electron scavengers is vital for prolonging the recombination and successful functioning of photocatalysis. (Eq. (2.5)) depicts how the presence of oxygen in prevents the recombination of electron-hole pair, while allowing the formation of superoxides radical (O_2^{-}). This O_2^{-} radical can be further protonated to form the hydroperoxyl radical (HO₂•) and subsequently H_2O_2 as shown in (Eqs. (2.9) and (2.10)), respectively. The HO2 radical formed was also reported to have scavenging property and thus, the co-existence of these radical species can doubly prolong the recombination time of the h^+_{TR} in the entire photocatalysis reaction. However it should be noted that all these occurrences in photocatalysis were attributed to the presence of both dissolved oxygen (DO) and water molecules. Without the presence of water molecules, the highly reactive hydroxyl radicals (OH•) could not be formed and impede the photodegradation of liquid phase organics. This was evidenced from a few reports that the photocatalysis reaction did not proceed in the absence of water molecules. Some simple organic compounds (e.g. oxalate and formic acid) can be mineralized by direct electrochemical oxidation where the e⁻_{TR} is scavenged by metals ions in the system without water presents (Byrne and Eggins, 1998). Although the h^+_{TR} has been widely regarded for its ability to oxidize organic species directly, this possibility is remained inconclusive. The h^+_{TR} are powerful oxidants (+1.0 to +3.5 V against NHE), while $e_{\rm TR}^-$ are good redundant (+0.5 to -1.5 V against NHE), depending on the type of catalysts and oxidation conditions.

Many elementary mechanistic studies on different surrogate organic compounds (e.g. phenol, chlorophenol, oxalic acid) have been extensively investigated in the photodegradation over TiO_2 surface. Aromatic compounds can be hydroxylated by the reactive OH• radical that leads to successive oxidation/addition and eventually ring opening. The resulting intermediates, mostly aldehydes and carboxylic acids will be further carboxylated to produce innocuous carbon dioxide and water. Since the photocatalysis reaction occurs on the photon activated surface of TiO_2 , the understanding of the reaction steps that involves photodegradation of organics is essential in the formulation of kinetic expression. For heterogeneous photocatalysis, the liquid phase organic compounds are degraded to its corresponding intermediates and further mineralized to carbon dioxide and water, if the irradiation time is extended (Eq. (2.12)).

Organic Contaminants
$$\xrightarrow{\text{TiO}_2/h\nu}$$
 Intermediate(s) \rightarrow CO₂ + H₂O
(2.12)

The overall photocatalysis reaction as portrayed by (Eq. (2.12)) can be divided into five independent steps, which are shown in Fig. 2 (Herrmann, 1999; Fogler, 1999):

- Mass transfer of the organic contaminant(s) (e.g. A) in the liquid phase to the TiO₂ surface.
- 2. Adsorption of the organic contaminant(s) onto the photon activated TiO₂ surface (i.e. surface activation by photon energy occurs simultaneously in this step).
- 3. Photocatalysis reaction for the adsorbed phase on the TiO_2 surface (e.g. A \rightarrow B).
- 4. Desorption of the intermediate(s) (e.g. B) from the ${\rm TiO_2}$ surface.
- 5. Mass transfer of the intermediate(s) (e.g. B) from the interface region to the bulk fluid.

In terms of rate determination, the overall rate of reaction is equal to the slowest step. When the mass transfer steps (1 and 5) are very fast compared with the reaction steps (2, 3 and 4), the organic concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk liquid phase. In this scene, the mass transfer steps are not rate limiting and do not affect the overall rate of photocatalytic reaction. Vinodgopal and Kamat (1992) reported the dependence of the photodegradation rate of the organic surrogate on surface coverage of the photocatalysts used. This outlines the importance of molecules adsorption or surface contact with the catalyst during the photocatalytic degradation. If the mass transfer steps are rate limiting, a change in the aeration or liquid flow conditions past the TiO₂ photocatalyst may alter the overall photocatalytic reaction rate.

Similarly, the surface interaction of microorganisms with the catalyst used during the photo-disinfection is essential for



Fig. 2 – Steps in heterogeneous catalytic reaction (Fogler, 1999).

enhancing the inactivation rate. When the generated ROS contacts closely with the microorganisms, the cell wall will be the initial site of attacked (Maness et al., 1999). The lipopolysaccharide layer of the cell external wall is the initial site attacked by the photo-induced ROS. This is followed by the site attack on the peptidoglycan layer, peroxidation of the lipid membrane and the eventual oxidation on the proteins membrane. All these will cause a rapid leakage of potassium ions from the bacterial cells, resulting in direct reduction of cell viability. The decrease in cell viability is usually linked to the peroxidation of polyunsaturated phospholipid components of the cell membrane (i.e. loss of essential cell functions) and eventually leads to cell death. The formation of oxidative stress and its effects on the cell membrane can be observed using advanced atomic force microscopy or attenuated total reflection Fourier transform infrared spectroscopy. The rate of adsorption and the eventual photoinactivation is known to positively correlate to the bactericidal effect of TiO₂ catalyst. In this instance, the transfer of bacterial cell to the close vicinity of the surface generated ROS site remains as the rate-limiting step in the photodisinfection reaction.

2.2. Homogeneous photo-Fenton reaction

The Fenton reaction is a process that does not involve any light irradiation as compared with the heterogeneous TiO₂ photocatalysis reaction, whereas the photo-Fenton does react up to a light wavelength of 600 nm. It was first recognised in the 1960s and remains one of the most applied AOPs for its ability to degrade high loading of organic compounds in highly saline conditions (Neyens and Baeyens, 2003; Bacardit et al., 2007; Machulek et al., 2007). Numerous studies on the photo-Fenton degradation of water pollutants such as chlorophenol (Pera-Titus et al., 2004), pesticides (Fallmann et al., 1999; Huston and Pignatello, 1999) and phenolic or aromatic compounds with organic loading of up to 25 g L⁻¹ have been investigated (Gernjak et al., 2004, 2007). A number of literatures (Neyens and Baeyens, 2003; Pignatello et al., 2006; Gogate and Pandit, 2004) have provided a comprehensive review of the basic understanding and clarity of the principles underlying the Fenton reaction.

In the absence of a light source, hydrogen peroxide (H_2O_2) will decompose by Fe²⁺ ions that present in the aqueous phase, resulting in the formation of hydroxyl radicals. The photo-Fenton reaction is expedited when light source present, causing rapid H₂O₂ decomposition by ferrous or ferric ions and resulting in the formation of radicals. All these soluble ironhydroxy or iron complexes can absorb not only UV radiation but also visible light. However, the actual oxidizing species responsible for the photo-Fenton reaction is still under discussion (Pignatello et al., 1999). These Fenton and photo-Fenton reaction could occur simultaneously with TiO₂ photocatalysis during UV-Vis irradiation period, post TiO₂ photocatalysis period or stand-alone photo-Fenton process. The Fenton reaction is seen to strongly correlate with the post TiO₂ photocatalysis reaction and thus, is described in detail here. The mechanism for the Fenton reaction is shown in (Eq. (2.13)):

$$Fe^{2+} (aq) + H_2O_2 \rightarrow Fe^{3+} (aq) + OH^- + HO^{\bullet}$$
 (2.13)

The \mbox{Fe}^{2+} can be reverted back to \mbox{Fe}^{3+} via different mechanisms:

$$Fe^{3+}(aq) + H_2O_2 \rightarrow Fe^{2+}(aq) + HO_2^{\bullet} + H^+$$
 (2.14)

$$Fe^{3+}$$
 (aq) + HO₂• \rightarrow Fe²⁺ (aq) + O₂ + H⁺ (2.15)

When a light source is present, the rate of photo-Fenton was reported to be positively enhanced compared to the dark condition. This is mainly due to the regeneration of Fe^{2+} (aq) from the photochemical effect of light and the concurrent generation of the OH• radicals in the system. Such a reversion cycle of Fe²⁺ (aq) \rightarrow Fe³⁺ (aq) \rightarrow Fe²⁺ (aq) continuously generates OH•, provided that the concentration of H₂O₂ in the system is substantial. The regeneration of the Fe²⁺ (aq) from Fe^{3+} (aq) is the rate-limiting step in the catalytic iron cycle, if small amount of iron is present. This photoassisted reaction is termed as photo-Fenton reaction, where such reaction could be activated by irradiation wavelengths of up to 600 nm. It was known that this reaction is better functional under longer wavelengths as they are able to overcome the inner filter effects by photolysing the ferric iron complexes. The inner filter effects referred to the competitive adsorption if photons by other light absorbing species in the water.

Even if the photo-Fenton has higher photoactivity than the heterogeneous photocatalysis, its feasible operation is largely dependent on several water quality parameters. In the photo-Fenton reaction, the formation of the highly photoactive iron complexes is highly dependent on the water pH and ions content (De Laat et al., 2004). It was reported that the pH 2.8 was the frequent optimum pH for photo-Fenton reaction (Pignatello, 1992). This is owing to the fact that at such low pH 2.8, the precipitation does not take place and further promotes the presence of dominant iron species of [Fe(OH)]²⁺ in water. Such a low optimum pH 2.8, however, is not cost effective for operation as it requires high chemical costs for pH rectification. The presence of different ions such as carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) , sulphate (SO_4^{2-}) and chlorine (Cl^{-}) also affects the iron equilibrium in water. These ions have the potential to raise the water pH and effectively lowered the photo-Fenton reaction rate. Both CO₃²⁻ and PO₄³⁻ have a double detrimental effect on the reaction, as they precipitate the iron and as well as scavenges the OH• radicals. A higher pH of 4.0-5.0 was determined to be sufficient to sustain the photo-Fenton reaction with 2-6 mM of iron for the initiation of the treatment (Gernjak et al., 2007). To date, the maximal iron loading reported was 450 mg L⁻¹ (Oliveros et al., 1997; Torrades et al., 2003).

Although H_2O_2 may be generated via the TiO₂ photocatalysis (Eq. (2.11)), its relative amount in the system may be inadequate to drive the Fenton reaction. Many researchers have reported the addition of H_2O_2 in enhancing both the photo-Fenton and TiO₂ photocatalysis reactions. The H_2O_2 can inhibit the recombination of electron—hole pair, while further provides additional OH• radicals through the following mechanisms:

$$H_2O_2 + e^- \rightarrow HO^{\bullet} + HO^-$$
(2.16)

$$O_2^{*-} + H_2O_2 \rightarrow O_2 + HO^{*} + HO^{-}$$
 (2.17)

This combined TiO₂ photocatalysis - photo-dark-Fenton reaction is particularly useful for the disinfection process (Domínguez et al., 1998; Marugán et al., 2006, 2007). The addition of H₂O₂ to the photocatalysis - and dark-Fenton system results in a residual disinfection to avoid microbial regrowth. Rincón and Pulgarin (2006) performed trials with TiO₂ photocatalysis and photo-Fenton reaction for the disinfection of water contaminated with Escherichia coli. They found that the bacterial inactivation rate was higher than the photocatalysis alone and the decrease in bacterial number continued in the dark conditions without significant regrowth within the following 60 h. However, it was found that such residual disinfection effect was highly dependent on the light intensity used during the irradiation period, as well as the relative concentrations of Fe³⁺ and H₂O₂. Further addition of H₂O₂ was found to decrease the overall reaction rate in several studies, owing to the formation of less penetrative HO₂• radicals, as described by (Eq. (2.18)):

$$HO^{\bullet} + H_2O_2 \to HO_2^{\bullet} + H_2O$$
 (2.18)

Other combined process of photo-Fenton and oxidative processes have also been proposed in the literature, such as ozone (Beltran-Heredia et al., 2001) and ultrasound (Torres et al., 2008). However, their significance as compared to the TiO₂/photo-Fenton will not be discussed in detail.

3. Advancements in photocatalyst immobilization and supports

Since the discovery of photocatalytic effect on water splitting by Fujishima and Honda (1972) using TiO₂ electrode, numerous researches have evolved to synthesis TiO₂ catalyst of different scale, characterise its physical properties and determine its photooxidation performances to the surfaceoriented nature of photocatalysis reaction (Fujishima and Honda, 1972; Kondo et al., 2008; Hosono et al., 2004; Joo et al., 2005; Wang et al., 1999). The TiO₂ catalyst in nanodimensions allows having a large surface area-to-volume ratio and can further promote the efficient charge separation and trapping at the physical surface (Nagaveni et al., 2004a,b). The light opaqueness of this nanoscale TiO₂ catalysts was reported to have an enhanced oxidation capability compared to the bulk TiO₂ catalysts (Siddiquey et al., 2008). Although the nanoscale TiO₂ catalysts show considerable improvement in terms of their physical and chemical properties, their particle size and morphology remains the main problem in a largescale water treatment process (Byrne et al., 1998b; Yu et al., 2002). In this section, the current technical challenges that prevent the application of slurry TiO₂ photocatalytic system are discussed together with the possible engineering solutions to resolve the problem. We will have a brief discussion on the modified TiO₂ catalyst with dopants for enhanced photoactivity under solar irradiation.

3.1. Challenges in the development of photocatalytic water treatment process

To date, the most widely applied photocatalyst in the research of water treatment is the Degussa P-25 TiO₂ catalyst. This catalyst is used as a standard reference for comparisons of photoactivity under different treatment conditions (Serpone et al., 1996). The fine particles of the Degussa P-25 TiO₂ have always been applied in a slurry form. This is usually associated with a high volumetric generation rate of ROS as proportional to the amount of surface active sites when the TiO₂ catalyst in suspension (Pozzo et al., 1997). On the contrary, the fixation of catalysts into a large inert substrate reduces the amount of catalyst active sites and also enlarges the mass transfer limitations. Immobilization of the catalysts results in increasing the operation difficulty as the photon penetration might not reach every single surface site for photonic activation (Pozzo et al., 1997). Thus, the slurry type of TiO₂ catalyst application is usually preferred.

With the slurry TiO₂ system, an additional process step would need to be entailed for post-separation of the catalysts. This separation process is crucial to avoid the loss of catalyst particles and introduction of the new pollutant of contamination of TiO₂ in the treated water (Yang and Li, 2007b). The catalyst recovery can be achieved through process hybridization with conventional sedimentation (Fernández-Ibáñez et al., 2003), cross-flow filtration (Doll and Frimmel, 2005) or various membrane filtrations (Choo et al., 2001; Zhao et al., 2002; Zhang et al., 2008a). Coupled with the pH control strategy close to the isoelectric point for induced coagulation, it was reported the microfiltration (MF) hybridization can recover the remaining 3% of the catalyst particles for reuse (Malato et al., 2009). Several important operating issues with slurry TiO₂ still remain even with a membrane integration process. These include the types of membrane, pore size and blockage, regeneration or back-washing and fouling (Lee et al., 2001; Molinari et al., 2002; Xi and Geissen, 2001). A number of studies have utilised microns size immobilizers for catalyst fixation that enhance surface contact with contaminants and prevented the membrane fouling or pores blocking with rapid back-washing (Xi and Geissen, 2001; Zhang et al., 2009). These immobilisers include catalyst fixation onto activated carbon (Lee et al., 2004), mesoporous clays (Chong et al., 2009a), fibers (Zhu et al., 2004) or even onto the membrane itself (Kwak and Kim, 2001). The following subsections outline a few catalyst immobilization strategies that are suitable for the use of slurry reactor or membrane reactor or both.

3.2. Mesoporous clays

Natural clays have been used intensively as the support for TiO_2 owing to their high adsorption capacity and costeffectiveness. Fig. 3 shows the TiO_2 crystal being deposited on a clay material (Chong et al., 2009a). Different types of clays have been investigated, which includes bentonite (Sun et al., 2002), sepiolite (Xie et al., 2009), montmorillonite (Kun et al., 2006), zeolite (Fukahori et al., 2003) and kaolinite (Chong et al., 2009a). Although these clays are catalytically inactive, their superior adsorption capacity has been



Fig. 3 – Nanocrystal of TiO₂ deposited on clay materials by SEM imaging. (a) 10 μ m resolution; (b) 3 μ m resolution.

attractive for increasing the surface contact during photocatalysis reaction. It was proposed that the natural clays should not be used directly to immobilise TiO₂. This is owing to the presence of different surface or lattice-bounded impurities that might diffuse and further affects the TiO₂ efficiency of the immobilised layer (Chong et al., 2009a). In addition, if these impurities are not removed, the polar molecules in the aqueous environment might initiate an internal reaction within the clay structure that result in clay swelling (Chong et al., 2009a). The swelling will be profound in certain type of clays, where Van der Waals forces held the entire clay in a turbostatic array. This is undesirable, particularly if the photocatalytic reactions take place in a reactor where the hydrodynamics may be strongly affected and consequently leading to the loss of photoactivity. Other factors that might need to be taken into a consideration if pillared clays are used as the immobilizer substrate include the density of the clays, particle size distribution range and the complementary photoreactor system used. The use of mesoporous clays as the support for nano-size TiO₂ have been successfully demonstrated in a number of studies, including the slurry or membrane processes (Chong et al., 2009b; Sun et al., 2004).

3.3. Nanofibers, nanowires or nanorods

Glass, optical, carbon, titanate and woven cloths fibers have also been studied as support materials in the photooxidation of various organic contaminants for water purification (Pozzo et al., 1997). Most of these fibers have a protruded rod-shape or longitudinal morphology. Using the nanofibers, nanowires or nanorods, mass transfer limitation can be resolved by their thin longitudinal morphology. The use of less durable immobilizer fibers (e.g. of glass or woven cloths) however, may lead to a low durability as the deposited anatase crystals might wear-off, resulting in a loss of photoactivity over reaction time. Such immobilizer fibers also increase pressure drop in the reactor system. On the contrary, a good benefit of nanofibers with commercial success is that they can be fabricated into MF, ultrafiltration (UF) and photocatalytic membranes (PMs). The MF fibers membrane is of particular interest as it shows high pollutant removal rate at low transmembrane pressure (<300 kPa). A commercial success of such fabricated MF and UF membranes has been demonstrated by Zhang and co-workers (Zhang et al., 2008a,b). Further details on the fabricated nanofibers or nanowires MF membranes can be obtained in the literatures.

3.4. Photocatalytic membrane

Recently the use of the PMs has been targeted owing to the photocatalytic reaction can take place on the membrane surface and the treated water could be continuously discharged without the loss of photocatalyst particles. The PMs can be prepared from different materials and synthesis methods. These include the TiO₂/Al₂O₃ composite membranes (Bosc et al., 2005; Zhang et al., 2006a,b; Choi et al., 2005, 2007), TiO₂ supported on polymer and metallic membranes (Kim et al., 2003; Bellobono et al., 2005a,b) or doted polymer membranes containing TiO₂ particles entrapped within the membrane structure during the membrane fabrication process (Artale et al., 2001; Kleine et al., 2002; Molinari et al., 2004). Also, the possible TiO₂ organic and inorganic ceramic membranes have been investigated (Kwak and Kim, 2001; Kim et al., 2003; Yang and Wang, 2006). Fig. 4 shows different types of PMs for water treatment application (Zhang et al., 2008b; Albu et al., 2007). In most studies, however, PMs may encounter various technical problems such as membrane structure deterioration, low photocatalytic activity and loss of deposited TiO2 layer over time. To prevent the problems associated with the TiO₂ membrane coating, an approach of using membranes without any deposited TiO₂ layer can be configured into a slurry-membrane hybrid system, which will be outlined in Section 4.

3.5. Photocatalyst modification and doping

As TiO₂ photocatalytic reactions take place under ambient operating conditions, photoactivity is usually constrained by the narrow wavelength spectrum for photonic activation of catalysts. The higher-end of UV spectrum required for catalysts activation is usually accompanied by high operating costs. One attractive option is to utilize the vast abundance of outdoor solar irradiation for catalyst activation in a suitably



Fig. 4 – (a) FESEM images of the TiO_2 nanowire membrane (Zhang et al., 2008b); (b) SEM images of TiO_2 nanotube layer formed free-standing membrane (Albu et al., 2007).

designed photoreactor system. To broaden the photoresponse of TiO_2 catalyst for solar spectrum, various material engineering solutions have been devised, including composite photocatalysts with carbon nanotubes (Yu et al., 2005), dyed sensitizers (Vinodgopal et al., 1996), noble metals or metal ions incorporation (Ni et al., 2007), transition metals (Litter, 1999) and non-metals doping (Fujishima et al., 2008).

The rationale in utilizing these material engineering strategies is to balance both the half-reaction rates of the photocatalytic reaction by adding electron acceptor, or modifying the catalyst structure and composition. Fig. 5 presents the use of different mechanisms to enhance the photoactivity of the catalysts. The presence of electron acceptors could scavenge the excited electrons and altogether prevent the recombination of electron—hole pairs. Recent studies shown that modified TiO_2 catalysts have an enhanced photoactivity under solar irradiation (Li et al., 2006; Ishibai et al., 2008; Shaban and Khan, 2008). CNTs coupling with TiO_2 have shown potential prolongation of electron—hole pairs by capturing the electron within their structure (Yu et al., 2005). As for dye sensitized coupling, the excited dye molecules under solar illumination can provide additional electrons to the CB for enhancing the formation of electron—hole pairs (Fig. 5a) (Vinodgopal et al., 1996). Dyes such as Methylene Blue, Azure, Erythosin, Rhodamin and Crystal Violet have been widely functionalised under solar irradiation (Vinodgopal et al., 1996).

Similarly, noble metals (e.g. Ag, Ni, Cu, Pt, Rh, and Pd) with Fermi level lower than TiO_2 catalyst have also been deposited



Fig. 5 – (a) Steps of excitation with a sensitizer in the presence of an adsorbed organic electron acceptor (EA); (b) Scheme of TiO_2 band structures, chemically ion-doped TiO_2 and physically ion-implanted TiO_2 ; (c) Electron capture by a metal in contact with a semiconductor surface (Malato et al., 2009).

on the TiO₂ surface for enhanced charge separation (Fig. 5b) (Ni et al., 2007). These metals were reported to enhance electron transfer, but require good knowledge on the optimal deposited amount needed during the fabrication process. Although noble metals coupling could be efficient in prolonging the surface charge separation, their cost-effectiveness for an industrial application is usually replaced by more economical transition or non-metals doping. The mechanism of such transition and non-metals doping, however, is different from the noble metals coupling as the TiO₂ is incorporated into the TiO₂ crystal lattice (Asahi et al., 2001; Irie et al., 2003; Ihara et al., 2003). Such incorporation introduces impurity in the bandgap of TiO₂ and thus, reduces the photonic energy requirements (Fig. 5c). More recently, the use of non-metal dopants (e.g. N, C, F, S and etc.) can improve the photoactivity and feasibility of TiO₂ catalysts for industrial application (Fujishima et al., 2008). Further research efforts may be needed to get a better understanding of the photoactivity kinetics, so as to improve the photooxidation efficiency for water treatment.

4. Photocatalytic reactor configuration

Photocatalytic reactors for water treatment can generally be classified into two main configurations, depending on the deployed state of the photocatalysts: (1) reactors with suspended photocatalyst particles and (2) reactors with photocatalyst immobilised onto continuous inert carrier (Pozzo et al., 2000). Various types of reactors have been used in the photocatalytic water treatment, including the annular slurry photoreactor (Chong et al., 2009b), cascade photoreactor (Chan et al., 2003), downflow contactor reactor (Ochuma et al., 2007) and, etc. The disparity between these two main configurations is that the first one requires an additional downstream separation unit for the recovery of photocatalyst particles while the latter permits a continuous operation.

Pareek et al. (2008) addressed that the most important factors in configuring a photocatalytic reactor are the total irradiated surface area of catalyst per unit volume and light distribution within the reactor. Slurry-type photocatalytic reactor usually performs a high total surface area of photocatalyst per unit volume, while the fixed-bed configuration is often associated with mass transfer limitation over the immobilised layer of photocatalysts. The light photon distribution through either direct or diffuse paths within the reactors needs to be decided (Cassano and Alfano, 2000). Direct photon utilization means that the photocatalysts are directly activated with light photon, rather with the assistance of various parabolic light deflectors to transfer the photons. To achieve uniformity in photon flux distribution within the reactor, a correct position of light source is essential to ensure maximal and symmetrical light transmission and distribution. The use of photo-reactors with assisted parabolic light deflectors nowadays has become unfavourable, owing to the need of special configuration and high operating costs. This type of reactor needs to be specifically designed to ensure the maximal illuminated reactor volume with minimal pressure requirement for good catalyst mixing and dispersion. Until recently, the slurry photocatalytic reactor was still the preferred configuration owing to its high total surface area of photocatalyst per unit volume and ease of photocatalysts reactivation. The photocatalyst particles can be separated by settling tanks or external cross-flow filtration system to enable continuous operation of the slurry reactor. A technically promising solution for solving the downstream separation of photocatalyst particles after treatment is via the application of hybrid photocatalysis-membrane processes. Application of such a hybrid system prevents the use of a coagulation, flocculation or sedimentation to separate the catalyst particles from the treated water stream. Other benefits include further energy saving and size of process installation and site area required.

The hybrid photocatalytic-membrane reactor system is generally known as the "photocatalytic membrane reactors" (PMRs). This is owing to the nature of the hybrid system where the membrane filtration unit could be configured into different positioning with the photocatalytic reactor. Fu et al. (2006) designed a submerged membrane reactor (Fig. 6) with two different reaction zones; UV slurry TiO₂ zone with a movable baffle that separates the submerged membrane module. These PMRs can be generalised by (1) irradiation of the membrane module and (2) irradiation of a feed tank containing photocatalyst in suspension (Molinari et al., 2001, 2002). For the former configuration, the photocatalyst could be either deposited onto the membrane or suspended in the reaction water. The PMRs allow a continuous operation of the



Fig. 6 - Schematic of submerged membrane photocatalytic reactor (Fu et al., 2006).

slurry-type reactor without any loss of photocatalyst particles as well as to control the water residence time independently. This enables the treated water to achieve the predefined level before being filtered through the hybrid membrane system. In the PMRs with immobilised PMs, the membrane module functionalised as the support for the photocatalyst particles and barrier against the different organic molecules in the reaction water. Similarly, the membrane also acts as a physical barrier against the photocatalyst particles and organic molecules or intermediate compounds to be degraded in the slurry PMRs.

In the PMRs with immobilised photocatalysts, the photocatalytic reaction takes place on the surface of the membrane or within its pores. The PMs used may be of MF (Ryu et al., 2005; Meng et al., 2005; Rivero et al., 2006; Jung et al., 2007; Chin et al., 2007; Huang et al., 2007), UF (Molinari et al., 2002; Tsarenko et al., 2006; Sun et al., 2004; Sopajaree et al., 1999a, b) and nanofiltration (NF) (Molinari et al., 2001, 2002, 2004, 2006; Augugliaro et al., 2005), depending on the targeted colloidal size and final water quality requirement. The MF membrane is useful when the colloidal size is in the range of $0.1-5 \mu m$, while both UF and NF target a smaller particle size ranges. The photooxidation efficiency of the contaminants was reported to be higher when an immobilised PM was used, rather than in the case of PMRs with suspended catalyst particles (Molinari et al., 2004). It was, however, reported that immobilising the photocatalyst particles might cause severe destruction to the membrane structure owing to their close contact with both UV light and hydroxyl radicals (Chin et al., 2006). In view of this, the hybridization configuration of the membrane process using photocatalysts in suspension appears to be the more promising arrangement. This PMR configuration has been well described in the literature for water phase degradation of humic (Sun et al., 2004; Ryu et al., 2005; Jung et al., 2007; Tsarenko et al., 2006) and fulvic acids (Fu et al., 2006), bisphenol A (Chin et al., 2006), phenol (Molinari et al., 2002), 4-nitrophenol (Molinari et al., 2001), 4chlorophenol (Ryu et al., 2005), grey water (Rivero et al., 2006), para-chlorobenzoate (Huang et al., 2007), river water (Meng et al., 2005) and dyes (Molinari et al., 2002, 2004; Ryu et al., 2005; Sopajaree et al., 1999a,b).

With these PMRs, one of the main operational issues is the transmembrane pressure, which determines both the filtration rate and operating costs. It was known that the PMR treatment costs increase if the photocatalysts with small particle and colloidal size are used. With both the MF and UF membrane filtration, the fine photocatalyst particles can cause membrane fouling and subsequently reducemembrane permeate flux. Fu et al. (2006) utilised a spherical ball-shaped TiO₂ particles that promotes separation, recovery and reused while prolonging the membrane lifespan as the particles do not cause pore blockage. Besides, the surface charge properties of the photocatalyst particles can also be manipulated to prevent membrane pore blockage. Xi and Geissen (2001) integrated a thermoplastic membrane module of cross-flow MF and found that the low permeate flux occurred when the operating pH varied from the isoelectric point of the TiO₂ particles used. This is owing to the pH induced coagulation-flocculation state of TiO2 that declines the rate of permeate flux. This was resolved by maintaining the operating pH close to the isoelectric point of TiO₂ by adding certain electrolytes to the TiO₂ slurry. Even with such control strategies, the quality of permeate is low owing to the rapid penetration of small molecules through the membrane used.

Recently, different hybridization of PMRs with dialysis (Azrague et al., 2006), pervaporation (Camera-Roda and Santarelli, 2007) and direct contact membrane distillation (MD) (Mozia et al., 2009) have been used (Fig. 7). Pervaporation is a physical process where usually a selective organophilic membrane was used to act as a selective barrier for the molecules to be degraded. Augugliaro et al. (2006) observed that a synergistic effect occurs when pervaporation was used, where the intermediates from the degradation of 4-chlorophenol (i.e. hydroquinone, benzoquinone) could be



Fig. 7 – Schematic diagram of the apparatus for hybrid photocatalysis–MD process: (1) membrane module; (2) distillate tank; (3) feed tank ($V = 2.9 \text{ dm}^3$); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp; T_{Fin} , T_{Din} , T_{Fout} , T_{Dout} – inlet and outlet temperatures of feed and distillate, respectively (Mozia et al., 2009).

selectively permeable without competing with 4-chlorophenol for photocatalytic reaction. Other types of organophilic membrane have also been investigated, such as polymeric UF membranes and polyethersulfonate NF membranes (Bae and Tak, 2005; Lee et al., 2008). A stronger rejection impact on the membrane is usually associated with the use of the UF or NF membranes. The choice of membrane for an efficient hybridization depends on the organic molecular size, pH or electrostatic interaction and Donnan exclusion phenomenon (Meares, 1986).

The MD is a process where the feed volatile components in water are evaporated through a porous hydrophobic membrane to produce high quality distillate products (Mozia et al., 2009). Its main advantage is that there is no membrane fouling when TiO_2 is present. During the process, the volatile stream is maintained inside the membrane pores. The difference in vapour pressure on both sides of the porous membrane remains as a driving force for the process. This force, however, largely depends on the temperatures and solution composition in the layer adjacent to the membrane (Tomaszewska et al., 1998; Gryta et al., 2001). It was reported that the feeding temperature in MD can range from 303 to 363 K. Similar scaling-up operational constraints of low permeate flux and high energy demand have redundant its current full-scale development. However, some efforts to utilize alternative energy source such as solar energy to enable MD application was found in the literature (Lawson and Lloyd, 1997; Bouguecha et al., 2005).

Among all the hybrid PMR systems, the pilot Photo-CatTM system (Fig. 8) (manufactured by Purifics Inc., Ontario, London) has shown the potential application. Benotti et al. (2009) has evaluated its ability in the removal of 32 pharmaceuticals, endocrine disrupting compounds and estrogenic

activity from water. They found that 29 targeted compounds and estrogenic activity of greater than 70% were removed while only 3 compounds were less than 50% removed at the highest number of UV passes. In the Photo-CatTM system, the water stream passes through a pre-filter bag and a cartridge filter before being mixed with a nanoparticle TiO₂ slurry stream. The mixed stream then passes through the reactor within the 3 mm annulus of the 32 UV lamps aligned in series, which can be individually controlled for the varying water quality. The overall hydraulic residence time for the 32 UV passes between 1 and 32 s, depending on the number of UV lights being turned on. A cross-flow ceramic membrane TiO₂ recovery unit is hybridized downstream of the reactor to remove the TiO₂ from the flow stream, while allowing the treated water to exit. The retentate TiO₂ stream is recycled and remixed with the fresh TiO2 slurry stream that enters the reactor stream.

5. Operational parameters of the photocatalytic reactor

After the integration of the semiconductor catalyst with a photoreactor, the oxidation rates and efficiency of the photocatalytic system are highly dependent on a number of the operation parameters that govern the kinetics of photomineralization and photo-disinfection. This section will discuss the significance of each operation parameters on the corresponding kinetics and some recent methods to optimize the photocatalytic system via response surface analysis. The followings outline a range of photoreactor operating parameters that affects the photocatalytic performance of TiO_2 photocatalysts in water treatment.



Fig. 8 - General schematic of photocatalytic reactor membrane pilot system (Benotti et al., 2009).

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5.1. TiO₂ loading

Concentration of TiO₂ in the photocatalytic water treatment system affects the overall photocatalysis reaction rate in a true heterogeneous catalytic regime, where the amount of TiO₂ is directly proportional to the overall photocatalytic reaction rate (Gaya and Abdullah, 2008). A linear dependency holds until certain extent when the reaction rate starts to aggravate and becomes independent of TiO₂ concentration. This is attributed to the geometry and working conditions of the photoreactor where the surface reaction is initiated upon light photon absorption (Bamba et al., 2008). When the amount of TiO₂ increases above a saturation level (leading to a high turbidity state), the light photon absorption coefficient usually decreases radially. However, such a light attenuation over the radial distance could not be well correlated with the Beer-Lambert Law owing to the strong absorption and scattering of light photons by the TiO₂ particles (Chen et al., 2007). The excess TiO₂ particles can create a light screening effect that reduces the surface area of TiO₂ being exposed to light illumination and the photocatalytic efficiency. Therefore, any chosen photoreactor should be operated below the saturation level of TiO₂ photocatalyst used to avoid excess catalyst and ensure efficient photons absorption. In this sense, both catalyst loading and light scattering effect can be considered as a function of optical path length in the reactor.

A large number of studies have reported the effect of TiO_2 loadings on the process efficiency (Gaya and Abdullah, 2008; Herrmann, 1999; Chong et al., 2009b,c; Ochuma et al., 2007; Chin et al., 2006). These results are mostly independent and a direct comparison cannot be made, as the working geometry, radiation fluxes, intensity and wavelengths used were different. It was reported that the optimum catalyst loading for photomineralization and photo-disinfection are varied, and mainly depend on the dimension of the photoreactor. In addition, the determination of photoreactor diameter is crucial in not only the effective photons absorption but also the water flow hydrodynamics (Malato et al., 2009). Uniform

flow region can ensure that a steady state residence time is obtained, while turbulence flow removes catalyst deposition or reaction dead zone (Malato et al., 2003). Reactor diameters smaller than 20-25 mm were not feasible for turbulent flow while diameter larger than 50-60 mm is impractical. This is because large diameters usually have lower saturated catalyst loading and efficiency. In this instance, the amount of catalyst should be considered. Usually the TiO₂ catalysts can be mixed uniformly with the targeted water prior to the introduction into the reactor system. During the dark homogenization period of the catalyst, a lower initial concentration of organic pollutants is observed owing to the strict adsorption of organics onto the catalysts surface (Xu and Langford, 2000). Similarly, catalysts-bacteria interaction was reported in the photo-disinfection treatment of microorganism (Gogniat et al., 2006).

5.2. pH

In heterogeneous photocatalytic water system, pH is one of the most important operating parameters that affect the charge on the catalyst particles, size of catalyst aggregates and the positions of conductance and valence bands. Due to the nature of TiO₂ catalyst used, any variation in the operating pH is known to affect the isoelectric point or the surface charge of the photocatalyst used. Many reports have used the point of zero charge (PZC) of TiO₂ to study the pH impact on the photocatalytic oxidation performance (Chong et al., 2009b,c; Ochuma et al., 2007; Chin et al., 2006; Toor et al., 2006). The PZC is a condition where the surface charge of TiO₂ is zero or neutral that lies in the pH range of 4.5-7.0, depending on the catalysts used. At PZC of TiO₂, the interaction between the photocatalyst particles and water contaminants is minimal due to the absence of any electrostatic force. When operating $pH < PZC(TiO_2)$, the surface charge for the catalyst becomes positively charged and gradually exerted an electrostatic attraction force towards the negatively charged compounds. Such polar attractions between TiO₂ and charged anionic

organic compounds can intensify the adsorption onto the photon activated TiO_2 surface for subsequent photocatalytic reactions (Xu and Langford, 2000; Gogniat et al., 2006). This is particularly significant when the anionic organic compounds present in a low concentration level. At pH > PZC(TiO₂), the catalyst surface will be negatively charged and repulse the anionic compounds in water. Different pH will affect the surface charge density of the TiO₂ catalyst (Rincón and Pulgarin, 2004), according to the following water equilibrium equations (Eqs. (5.1) and (5.2));

At pH < PZC:
$$TiOH + H^+ \leftrightarrow TiOH_2^+$$
 (5.1)

At pH > PZC: TiOH + OH⁻
$$\leftrightarrow$$
 TiO⁻ + H₂O (5.2)

The surface charge density distribution for these $\rm TiO_2$ catalyst clusters is highly dependent on the operating pH. It was reported that the distribution of TiOH is \geq 80% at $3 < pH < 10; TiO^- \geq$ 20% at pH > 10 and $\rm TiOH_2^+ \geq 20\%$ at pH < 3. The equilibrium constants for these reactions at different pH are $pK_{\rm TiOH_2}+=$ 2.4 and $pK_{\rm TiOH}=$ 8.0 (Kormann et al., 1991). During photocatalytic reaction, the initial operating pH usually drops slightly from the formation of multitude intermediate by-products that may pose different chemical functional groups and affect the water pH indifferently (Stylidi et al., 2003).

A similar electrostatic interaction enhancement for photodisinfection of microorganisms was observed during the photocatalytic process (Gogniat et al., 2006). During the photodisinfection, the initial photo-induced damage to the microorganisms takes place on the lipopolysaccharide layer of the external cell wall and on the peptidoglycan layer. This is followed by lipid membrane peroxidation and the subsequent oxidation of the membrane protein and polysaccharides. An increased density of TiOH₂⁺ (at low pH) can form electrostatic link with the bacteria of negatively charged surfaces, resulting in increasing rate of photo-disinfection. Herrera Melián et al. (2000) observed that the bacterial inactivation rate was enhanced at pH 5.0. It should be noted that the enhanced bactericidal activity of TiO₂ at a low pH is due solely to the TiO₂ mediated photo-killing and not acidification of the cell. Heyde and Portalier (1990) explained that the negligible E. coli reaction to acid conditions was from the presence of an acid tolerance response to the bacterium itself, which secreted acid-induced proteins for acid-shock protection. However, Rincón and Pulgarin (2006) did not find any differences in E. coli inactivation rates when the initial pH varied between 4.0 and 9.0. To date, various types of microorganisms have been successfully inactivated using TiO₂ photocatalysis, which include Lactobacillus acidophilus, E. coli, Saccharomyces cerevisiae, Chlorella vulgaris, Streptococcus faecalis and aureus, Enterobacter cloacae, total coliforms, Candida albicans, Fusarium solami, Aspergillus niger and others (Matsunaga et al., 1985; Herrera Melián et al., 2000; Ibáñez et al., 2003; Seven et al., 2004; Lonnen et al., 2005).

Although the electrostatic link between the catalyst particles and microorganisms were reported to exist, a subsequent microbial cell adsorption and eventual penetration of the catalysts through the cell wall are highly dependent on the

mean particle size. Since the relative sizes between the bacteria and catalysts are significantly different, the charged TiOH₂⁺ clusters might not come into full contact with the bacteria. Sichel et al. (2007) found that the TiO₂ catalyst is actually adsorbed onto fungal spores rather than the reverse setting. This is owing to the fact that the fungal spores arelarger (a few order of magnitudes) than the catalyst particles. A small decrease in microbial loadings was observed during the initial dark homogenization period with catalyst particles. This is owing to the catalyst agglomeration and subsequent sedimentation of the agglomerates. The rate of bacterial adsorption in this instance was found to directly relate to the bactericidal activity of the catalyst used. It was also reported that the adsorption phenomena during the dark and irradiated phase will act indifferently and thus, a strong conclusion cannot be made.

Besides, the interaction between the catalyst particles itself also exists and is dependent on the operating pH. The particle size of the same catalysts can vary from 300 nm to $4 \,\mu\text{m}$ depending on the distant from the PZC of TiO₂ (Malato et al., 2009). At pH = PZC, the neutral surface charge of the catalyst particles is unable to produce the interactive rejection for solid-liquid separation. Thus, this induces catalyst aggregation where the catalyst becomes larger, leading to catalyst sedimentation (Blanco and Malato, 2001). This physical property is usually manipulated in the hybridized PMR system, where the pH of the treated wastewater is neutralized to pH 7 for the subsequent recovery of catalyst particles. The larger TiO₂ clusters can settle faster than the smaller one. It was reported that with such neutralisation strategy, almost 97% of the catalysts can be recovered in the settling tank. The remaining TiO₂ catalysts can be recovered via the downstream MF system. Similarly, the water pH will also affect the effective separation in the PMR system where inappropriate control of water pH promotes the electrostatic repulsion, the Donnan exclusion phenomena and thus, the rejection tendency for the membrane used (Seffaj et al., 2005; Molinari et al., 2008). It must be stressed that appropriate pH control strategies must be implemented at every different location of a photocatalytic water treatment process for efficient photocatalytic reaction to proceed.

5.3. Temperature

Numerous studies have been conducted on the dependence of photocatalytic reaction on the reaction temperature (Muradov et al., 1996; Fu et al., 1996; Chen and Ray, 1998; Rincón and Pulgarin, 2003; Evgenidou et al., 2005). Although heat energy is inadequate to activate the TiO₂ surface, the understanding on such dependency could be extrapolated when operating the process under natural sunlight illumination. Most of the previous investigations stated that an increase in photocatalytic reaction temperature (>80 °C) promotes the recombination of charge carriers and disfavour the adsorption of organic compounds onto the TiO₂ surface (Gaya and Abdullah, 2008). At a reaction temperature greater than 80 °C, the photocatalytic reaction is interpreted with Langmuir-Hinshelwood (L-H) mechanism where the adsorption of the reactants is disfavoured resulting in KC becomes "1. This will reduce the L-H expression (Eq. (6.1)) into the apparent rate equation

 $r = k_{apparent}C$. All these drastically reduce the photocatalytic activity of TiO₂ when the reaction temperature rises. The desorption of degraded products from the TiO₂ surface is the rate-limiting step when temperatures rise. On the contrary, a low temperature below 80 °C actually favours adsorption which is a spontaneous exothermic phenomenon, resulting in getting KC of L–H model " 1, enhancing the adsorption of final reaction products. A further reaction in temperature down to 0 °C will cause an increase in the apparent activation energy. As a consequence, the optimum reaction temperature for photomineralization is reported to be in the range of 20–80 °C (Malato et al., 2009).

For photo-disinfection using TiO_2 photocatalysis, the increase in the reaction temperature increased the inactivation rate of microorganisms (Rincón and Pulgarin, 2003). This is consistent with the Van't Hoff–Arrhenius equation (Eq. (5.3)), where the rate constant k is linearly proportional to the exponential (-1/T);

$$\ln\left(\frac{k_{1}}{k_{2}}\right) = -\frac{E_{a}}{R}\left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$$
(5.3)

in which k_1 and k_2 are the constants for temperatures T_1 and T_2 , E_a is the energy of activation and R is the universal gas constant. The viability of a microbe to the catalyst activity depends on its incubation temperature, type and resistance to temperature change. The order of resistance of microorganisms to conventional disinfection treatment is of: Non-forming spores bacteria < Viruses < Forming spores bacteria < Helminths < Protozoa (oocysts). To date, there is no comprehensive study conducted to compare the effect of TiO₂ photo-disinfection on each microorganism types under different operating temperature. Thus, the photo-disinfection using TiO₂ catalyst is usually conducted below ambient temperature of 80 °C to prevent high water heating costs (high heat capacity) (Herrmann, 2005).

5.4. Dissolved oxygen

Dissolved oxygen (DO) plays an important role in TiO₂ photocatalysis reaction to assure sufficient electron scavengers present to trap the excited conduction-band electron from recombination (Chong et al., 2009b). The oxygen does not affect the adsorption on the TiO_2 catalyst surface as the reduction reaction takes place at a different location from where oxidation occurs (Malato et al., 2009). Other roles for DO may involve in the formation of other ROS and the stabilization of radical intermediates, mineralization and direct photocatalytic reactions. The total amount of DO in a reactor depends on a few technical considerations. For a photoreactor, the total delivered DO not only acts as an electron sink but also provides sufficient buoyant force for complete suspension of TiO₂ particles. Photoreactor sparging with pure oxygen in TiO2 slurry reactor is usually a cost-ineffective solution, as the amount of DO being held-up is a function of the photoreactor geometry. The difference between the two sparging media of air and oxygen is usually not very drastic as the mass transfer of oxygen to the close vicinity of the surface is the rate dependent step (Habibi et al., 2005). Generally the Henry's Law can be assumed to give a good approximation of the amount of oxygen dissolved under the experimental

conditions, provided the oxygen sparging rate and the photoreactor gas hold-up are known (Chong et al., 2009c). In this equilibrium law, it is also necessary to account for the decrease in oxygen solubility with increasing reaction temperature. As discussed, it is preferential to operate the photoreactor under ambient conditions to prevent the elevate cost of air or oxygen sparging for enhanced electron sink.

The presence of dissolved oxygen is also suggested to induce the cleavage mechanism for aromatic ringsin organic pollutants that are present in the water matrices. Wang and Hong (2000) proposed that during aromatic ring cleavage in the degradation of a dioxyl compound, the molecular oxygen will follow the cleaving attack of a second hydroxyl radical. The analogous partial pressure of oxygen applied during the reaction for a closed reactor system is also important. A significantly higher partial pressure of oxygen will result in a higher initial organics photomineralization rate than its structural transformation (Chen and Ray, 1998; Wang and Hong, 2000). It was reported that at low oxygen pressure of 0.5 kPa, 75% of the original 2-CB compounds were transformed, but only 1% of them was mineralized to CO₂ after 5 h of UV irradiation (Wang and Hong, 2000). Though elevated partial pressure of oxygen is imperative, it is difficult to quantify their specific influence on the surface activity of TiO₂. owing to the polyphasic nature of the photocatalytic liquid phase reaction (Herrmann, 1999).

The detrimental effect of DO on the photocatalysis reaction was reported by Shirayama et al. (2001). They observed an elevated photodegradation rate of chlorinated hydrocarbons in the absence of DO. This could be explained by the strong absorption characteristics for UV photons at intensities of 185 and 254 nm, respectively. The DO molecules act as an inner filter in this case and cause a sharp attenuation in UV light intensity mainly at UV-C germicidal region. There is no report found to determine the DO impact on a photocatalysis process using UV-A or UV-B light sources. To date, the effect of DO on the efficiency of photo-disinfection rate has been paid little attention. The formation of various ROS under the series of redox reactions on the catalysts surface was assumed to be similar in both photomineralization and photo-disinfection reaction. If sufficient nutrients are available, the constant sparging of DO will generally promote microbial growth and offset the photo-disinfection rate. This indirectly prolongs the irradiation time necessary to achieve the desired inactivation level. It is thus recommended that the effect of DO on the microbial inactivation should be investigated thoroughly in a particular photoreactor system before improvising the DO sparging strategy.

5.5. Contaminants and their loading

Previous investigations have reported the dependency of the TiO_2 photocatalytic reaction rate on the concentration of water contaminants (Ochuma et al., 2007; Toor et al., 2006; Chong et al., 2009b,c). Under similar operating conditions, a variation in the initial concentration of the water contaminants will result in different irradiation time necessary to achieve complete mineralization or disinfection. Owing to the photonic nature of the photocatalysis reaction, excessively high concentration of organic substrates is known to

simultaneously saturate the TiO_2 surface and reduce the photonic efficiency leading to photocatalyst deactivation (Saquib and Muneer, 2003).

Not all organic substrates will have such profound effect on the irradiation time, and this also depends on the corresponding chemical nature of the targeted compounds for TiO₂ photocatalysis reaction. For instances, 4-chlorophenol will undergo a degradation pathway with constant evolution of intermediate(s) product (i.e. hydroguinone and benzoguinone) while oxalic acid will undergo direct transformation to carbon dioxide and water (Bahnemann, 2004). In the case of 4-chlorophenol, such evolution of intermediate(s) will further prolong the irradiation time necessary for total mineralization owing to the direct competition over unselective TiO₂ surfaces. In the development of mathematical model that represents the kinetics of mineralization while relating to the TiO2 loading required, commonly used water quality parameters such as chemical oxygen demand (COD), total organic carbon (TOC) or dissolved organic carbon (DOC) could be more appropriate to account for such competitiveness of intermediate(s) with its predecessor compounds. Also organic substrates with electron-withdrawing nature such as benzoic acid and nitrobenzene were found to strongly adhere and more susceptible to direct oxidation than those with electron donating groups (Bhatkhnade et al., 2004). Most of the TiO₂ studies conducted to date, utilises a range of model organic substrates with different substituent groups but these rarely convey any useful information and merely test on the photo-efficiency of a new photocatalyst or an integrated reactor column. Some field kinetics of the photomineralization of real wastewater has also been reported (Marugán et al., 2007; Radjenovíc et al., 2009; Vilar et al., 2009; Malato-Rodríguez et al., 1996). It was observed that owing to the persistency of the dissolved organic in the real wastewater, a slow photomineralization kinetics are attained with prolong irradiation times to achieve complete mineralization. Slow kinetics turnover of the photocatalytic water treatment as a stand-alone process means a higher initial cost on the reactor volume and site area is required. Recently, this heterogeneous photocatalytic technology has been coupled with biological treatment to increase its industrial feasibility (Parra et al., 2002). Such coupling allows the retention time in biological treatment stages to be reduced, where the non-biodegradable compounds of the wastewater can be turned into biodegradable compounds with the aid of photocatalytic treatment.

Similarly, the photo-disinfection efficiency of various microorganisms has been assessed for the possible application of photocatalytic technology to replace the chemical disinfectant methods. In general, the mechanism involved in the microbial disinfection includes the destruction of the microbial protein structures and inhibition of their enzymatic activities (Maness et al., 1999). Compared to the persistency during organic photomineralization, a general classification in the bacterial resistance to the disinfectant used has also been proposed. Among all, the most resistance infectious type of microorganisms are prions, followed by coccidia (*Cryptosporidium*), bacterial endospores (*Bacillus*), mycobacteria (M. *tuberculosis*), viruses (poliovirus), fungi (*Aspergillus*), Gramnegative (*Pseudomonas*) and eventually Gram-positive bacteria (*Enterococcus*) (Malato et al., 2009). Their differences in resistance are explained by their cell wall permeability, size and complexity of the specific microorganisms. Each microorganism might also be of infectious nature, which causes epidemic diseases when they multiply in water. Most bacteria can be killed easily with TiO₂ photocatalysis, but a complete inactivation might have to be ensured as they are highly infectious. Similarly, this infectious nature can also be found in viruses (adenoviruses, enteroviruses, hepatitis A and E viruses, noroviruses and saproviruses, rotaviruses) and the most in protozoa (Acanthamoeba spp, Cryptosporidium parvum, Cyclospora cayetanensis, Entamoeba histolytica, Giardia intestinalis, Naegleria fowleri, Toxoplasma gondii (WHO, 2006). All these protozoa are highly infectious in low concentration and the photocatalytic treatment should be targeted on these microorganisms as the surrogate indicators. This is to ensure that adequate photocatalytic treatment to prevent the outbreak of the epidemic diseases in the treated water, if photocatalytic treatment is chosen.

5.6. Light wavelength

The photochemical effects of light sources with different wavelength emitting ranges will have a profound consequence on the photocatalytic reaction rate, depending on the types of photocatalysts used – crystalline phase, anatase-to-rutile composition and any state of photocatalyst modifications. Using commercial Degussa P-25 TiO₂, which has a crystalline ratio of anatase 70/80: 20/30, a light wavelength at $\lambda < 380$ nm is sufficient for photonic activation (Herrmann, 1999; Bahnemann, 2004). The crystalline phase of rutile TiO₂ has a smaller bandgap energy of $E_{\rm B} \sim 3.02$ eV, compared to the anatase TiO₂ of 3.2 eV (Gaya and Abdullah, 2008). This dictates that rutile TiO₂ can be activated with light wavelength of up to 400 nm, depending on the bandgap threshold for the type of rutile TiO₂ used.

For UV irradiation, its corresponding electromagnetic spectrum can be classified as UV-A, UV-B and UV-C, according to its emitting wavelength. The UV-A range has its light wavelength spans from 315 to 400 nm (3.10-3.94 eV), while UV-B has wavelength range of 280-315 nm (3.94-4.43 eV) and the germicidal UV-C ranges from 100 to 280 nm (4.43-12.4 eV) (Rincón and Pulgarin, 2005). In most of the previous studies, the UV-A light provides light photons sufficient for photonic activation of the catalyst (Bhatkhnade et al., 2004; Chin et al., 2006; Ochuma et al., 2007). As with outdoor solar irradiation, the UV-C is usually absorbed by the atmosphere and not reaching the earth surface. Only the lamp-driven photoreactor system can utilize UV-C irradiation artificially for photonic activation of catalyst and reduction of viable microorganisms. The mechanism of UV-C cell destruction involves the direct induction on pyrimidine and purine and pyrimidine adducts on the cell DNA. However, not all microorganisms are susceptible to the UV-C radiation and some highly resistant microorganisms can survive through disinfection process. These include Legionella pneumonphila and Cryptosporidium parvum oocysts (Malato et al., 2009).

The natural UV radiation that reaches the surface of the earth consists of both UV-A and UV-B spectrums. The photolysis mechanism for both UV irradiations on cell inactivation is dissimilar to the discussed UV-C mechanism. Both UV-A and UV-B irradiations can be absorbed by cellular components called intracellular chromophores. L-trytophan is the best known intracellular chromophore and is thought to contain unsaturated bonds such as flavins, steroids and quinines (Tyrrell and Keyse, 1990). Among these UV irradiations, the UV-A irradiation is toxic only in the presence of oxygen. The ROS or oxidative stress generated from the chromophore light absorption can damage cells and cell components, leading to lipid peroxidation, pyrimidine dimer formation and eventually DNA lesions. The contact between the ROS and DNA results in single strand breaks and nucleic acid modifications. Such damages on the DNA are usually lethal or mutagenic irreversible. With the presence of TiO2 catalyst as the light sensitizers, a high degree of cell damages is seen as the amount ROS generated increases accordingly. A few microorganisms that are resistant to UV-A photolysis have been inactivated successfully by TiO₂ photocatalysis, namely; E. cloacae, E. coli, P.aeruginosa and S. typhimurium (Ibáñez et al., 2003).

A longer wavelength of solar irradiation ($\lambda > 400$ nm) has also been used in solar disinfection (SODIS) study (Sichel et al., 2007; Lonnen et al., 2005; Berney et al., 2006; Kehoe et al., 2004; McGuigan et al., 2006. However, the photo-killing mechanism is as yet unclear as it involves a variety of microbial and a larger mixed spectrum of UV-A and solar irradiation. A similar cell destruction mechanism to the one proposed for UV-A irradiation is thought to take place in this mixed light spectrum. In the SODIS, the pathogens in the drinking water contained in PET bottles were found to be inactivated within 6 h of sunlight exposure. However, significant research and developments on the disinfection using photocatalyticmediated process need to be conducted to broaden the photoactivity of current TiO₂ catalysts used.

5.7. Light intensity

The photonic nature of the photocatalysis reaction has outlined the dependency of the overall photocatalytic rate on the light source used. Light intensity is one of the few parameters that affect the degree of photocatalytic reaction on organic substrates. Fujishima et al. (2000) indicated the initiation of TiO₂ photocatalysis reaction rates is not highly dependent on light intensity, where a few photons of energy (i.e. as low as 1 μ W cm⁻¹) can sufficiently induce the surface reaction. To achieve a high photocatalytic reaction rate, particularly in water treatment, a relatively high light intensity is required to adequately provide each TiO2 surface active sites with sufficient photons energy required. However, when using the nominal TiO₂ particles without modifications, the surface reaction is restricted to photons with wavelengths shorter than the absorption edge of approximately 400 nm. The organic conversion in the presence of UV wavelength $(\lambda < 400 \text{ nm})$ in many studies obeyed the linear proportionality correlation to the incident radiant flux. This was evidenced by Glatzmaier et al. (1990) and Glatzmaier (1991), where they observed that the destruction of dioxin and polychlorinated biphenyls was significantly enhanced in the presence of high intensity photons. A similar finding was reported in Magrini and Webb (1990) where the organic decomposition rate was reported to increase with the radiation intensity.

Later, it was discovered that the dependency of the reaction rate on radiant intensity behaves indifferently under different lighting conditions (Curcó et al., 2002; Qamar et al., 2006; Karunakaran and Senthilvelan, 2005). The linear dependency of the photocatalytic reaction rate on radiant flux (Φ) changed to a square-root dependency ($\Phi^{0.5}$) above certain threshold value. Such a shift in dependency form was postulated owing to the amount of photo-generated holes available during the electron-hole pair formation. In the TiO₂ catalyst used, the photo-induced generation of valence band holes are much less than the conduction-band electrons available. In this instance, the photo-generated holes are the rate-limiting step and the details derivation of the square-root dependency can be obtained from Malato et al. (2009). At high intensities, the dependency of the photocatalytic reaction rate on radiant flux reduced to zero (Φ^0). This was explained by the saturated surface coverage of the catalyst, resulting in a mass transfer limitation in the adsorption and desorption and thus, preventing the effect of light intensity to set in. An increase in the fluid turbulency in this case might help to alleviate the mass transfer problem on the surface of the catalyst. The desorbed final products might also affect the dependency of reaction rate on radiant flux, as they might scavenge the electron acceptors and further promote the electron-hole pair recombination.

Rincón and Pulgarin (2004) reported that the residual disinfecting ability of the photocatalyst largely depends on the duration of light intensity without any temporal interruptions. They investigated the effect of light intensities at 400 and 1000 W/m² on bacterial lethality and regrowth, and found that the higher intensity without any temporal interruptions can cause irreversible damage to the E. coli. In the intermittent light irradiations with constant interruptions, the bacteria were seen to regrow during the subsequent 24 or 48 h. Some studies suggested that this regrowth is due to the dark-repair mechanism where the partially damaged cells recover in the presence of nutrients (Sun et al., 2003; Shang et al., 2009). Others have suggested that the damaged but not totally inactivated cells could recover its viability through photo-repairing under radiation of 300–500 nm or on the re-synthesis and post replication of cells (Rincón and Pulgarin, 2003; Sichel et al., 2007). It must be noted in this case that for photo-disinfection using different light intensity, a final conclusive point cannot be made directly. The disinfection results of 400 W/m² at 2.5 h irradiation might not be the same as the result arose from 1000 W/m^2 for 1 h. Thus, in order to predict the minimum irradiation required at constant irradiance, preliminary studies into both the photoreactor performance and microbial consortia (different resistants) presents is important.

5.8. Response surface analysis

From the earlier discussions on the effect of the operation parameters on the photocatalytic reaction rate, it can be seen that these parameters would affect the system indifferently. In overall, it can be interpreted that a multi-variable (MV) optimization approach is actually required to optimize a photoreactor system as parameter interaction might exist. Parameter interactions refer to the relationship between operating parameters such as TiO_2 loading on pH or pH on radiant flux. For the optimization of a photoreactor system, the conventional one-parameter-at-a-time approach is mostly used to unveil the effects of one parameter after another. Although this conventional optimization approach is widely acceptable, the reported outcomes could be of insignificant and have less predictive power if the condition for one operating parameter changes.

This has lead to the application of effective design of experiments (DOE), statistical analysis and response surface analysis for photocatalytic studies (Chong et al., 2009d; Liu and Chiou, 2005; Lizama et al., 2002; Körbahti and Rauf, 2008; Calza et al., 2006; Fu et al., 2007). Using this approach, different permutations of experimental design are involved and the operational parameters and spans are defined. As compared to the conventional one-parameter-at-a-time approach, the MV optimization approach has pre-determined experimental points that are dispersed uniformly throughout the study domain, i.e. only a small region is covered in the domain of conventional study. This allows the optimization process to be more timeeffective and enhances the identification of parameter interactions, where they can be interpreted using commercial statistical software such as Design Expert[®] software.

Chong et al. (2009d) proposed the use of Taguchi-DOE approach, together with analysis of variance, statistical regression and response surface analysis to study the combined effects of four key operation parameters that affect the photocatalytic reaction rate in an annular photoreactor. They utilised 9 experimental permutations to analyse the 81 possible parameters combination. It was reported that the interaction between the TiO_2 loading and aeration rate had a positive synergistic effect on the overall reaction rate. A response surface model was developed to correlate the reaction rate dependency on the four different parameters according to the statistical regression as shown in (Eq. (5.4));

$$R_{o} = b_{0} + \sum_{i=1}^{k} b_{i}X_{i} + \sum_{i=1}^{k} b_{ij}X_{i}^{2} + \sum_{i_{i< j}}^{k} \sum_{j}^{k} b_{ij}X_{i}X_{j}$$
(5.4)

where R_o is the predicted response output of the photomineralization rate, and i, *j* are linear, quadratic coefficients, respectively. The parameters of *b* and *k* are regression coefficient and the number of parameters studied in the experiment, respectively, and X_i , X_j ($I = 1, 4; j = 1, 4, i \neq j$) represent the number of independent variables in the study. This model (Eq. (5.4)) is empirical and independent for each photoreactor system. Subsequent verification works are required to determine the accuracy and applicability of such model for the prediction of photoreaction rate under the variation of its parameters. Other DOE approach to photocatalytic reactor optimization has also been applied over the years, such as central composite design (Cho and Zoh, 2007), Bayesian (Jaworski et al., 2008) and Plackett–Burman designs (Wu et al., 2006).

6. Kinetics and modelling

Kinetics and mechanistic studies on the photomineralization or photo-disinfection rate of the water contaminants are useful for process scale-up. The appropriate utilization of kinetic models for the interpretation of experimental data enables the design and optimization of photoreactor system with sufficient capacity and minimal non-illuminated reactor volume. In this section, the different kinetics and rate model for both photomineralization and photo-disinfection will be discussed along with the common misconceptions in kinetic modelling.

6.1. Photomineralization kinetics

In most of the photocatalytic studies, kinetic or mechanistic studies over the irradiated TiO₂ surfaces usually only involve a single constituent model organic compound. The kinetics of different organic compounds ranging from dye molecules, pesticides, herbicides and phenolic compounds to simple alkanes, haloalkanes, aliphatic alcohols and carboxylic acids have been investigated (Herrmann, 1999; Bahnemann, 2004; Gaya and Abdullah, 2008; Malato et al., 2009). The nonselective nature of the OH· radicals means that the disappearance rate of the studied compound with irradiation time should not be referenced as a standard for reactor design purpose. This is because that numerous intermediates are formed en-route to complete mineralization and neglecting this aspectisa common mistake in portraying the photomineralization kinetics. In this instance, the organic concentrations can be expressed collectively in COD or TOC to yield an in-depth understanding on the photomineralization kinetics.

As the L—H model is a surface-area dependent, the reaction rate is expected to increase with irradiation times since less organic substrate will remain after increased irradiation times with higher surface availability. A zero rate of degradation is associated with the total decomposition achieved. Numerous assumptions for the L—H saturation kinetics type exist and for the applicability in the rate of photomineralization, any of the four possible situations is valid: (i) reactions take place between two adsorbed components of radicals and organics; (ii) the reactions are between the radicals in water and adsorbed organics; (iii) reactions take place between the radical on the surface and organics in water; (iv) reaction occurs with both radical and organics in water.

Some researchers found that simpler zero- or first-order kinetics is sufficient to model the photomineralization of organic compounds. This was, however only applicable for limited conditions where the solute concentration is inadequately low. In most kinetic studies, a plateau-type of kinetic profile is usually seen where the oxidation rate increases with irradiation time until the rate becomes zero (Minero, 1999; Cunningham and Sedlak, 1996). The appearance of such kinetics regime usually fits the L–H scheme. According to the L–H model (Eq. (6.1)), the photocatalytic reaction rate (r) is proportional to the fraction of surface coverage by the organic substrate (θ_x), k_r is the reaction rate constant, C is the concentration of organic species and K is the Langmuir adsorption constant:

$$\mathbf{r} = -\frac{\mathrm{d}C}{\mathrm{d}t} = \mathbf{k}_r \theta_{\mathrm{x}} = \frac{\mathbf{k}_r \mathrm{K} \mathrm{C}}{1 + \mathrm{K} \mathrm{C}} \tag{6.1}$$

The applicability of (Eq. (6.1)) depends on several assumptions, which include (i) the reaction system is in dynamic equilibrium; (ii) the reaction is surface mediated; (3) the

competition for the TiO₂ active surface sites by the intermediates and other reactive oxygen species is not limiting (Chong et al., 2009c). If these assumptions are valid, the reactor scheme only consists of adsorption surface sites, organic molecules and its intermediates, electron-hole pairs and the reactive oxygen species. The rate constant (k_r) for most of the photocatalytic reaction in water is usually reported to be in the order of $10^6 - 10^9$ (Ms)⁻¹ (Malato et al., 2009). This k_r-value is the proportionality constant for the intrinsic reactivity of photo-activated surface with C. Others have also related the k_r is proportional to the power law of effective radiant flux (i.e. Φ_{e}^{n}) during the photomineralization reaction (Cunningham and Sedlak, 1996; Monllor-Satoca et al., 2007). The K-parameter is the dynamic Langmuir adsorption constant (M⁻¹) that represents the catalysts adsorption capacity. (Eq. (6.1)) can be solved explicitly for t using discrete change in C from initial concentration to a reference point:

$$\ln\left(\frac{C}{C_o}\right) + K(C - C_o) = -k_r Kt$$
(6.2)

The K-value can be obtained using a linearized form of (Eq. (6.1)), where 1/r is plotted against 1/C:

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K C_0} \tag{6.3}$$

It was reported that the real K-value obtained from the linearized plot of 1/r against 1/C is significantly smaller (Malato et al., 2009). This was explained by the differences in adsorption—desorption phenomena during dark and illuminated period. When the organics concentration is low (in mM), an "apparent" first-order rate constant (Eq. (6.4)) could be expressed where k' (min⁻¹) = k_r K:

$$r = -\frac{dC}{dt} = k_r KC = k'C$$
(6.4)

Rearranging and integration of (Eq. (6.4)) yields the typical pseudo-first-order model as in (Eqs. (6.5) and (6.6)):

$$C = C_o e^{-k't} \tag{6.5}$$

$$\ln\left(\frac{C_0}{C}\right) = -k_r K t = -k't \tag{6.6}$$

The apparent rate constant however, is only served as a comparison and description for the photocatalytic reaction rate in the reactor system. Fig. 9 shows a typical saturation kinetic plot for the degradation of organic dye molecules in an annular photoreactor system where the reaction rate increases to a point where the rate plateaus off. To interpret the maximal photomineralization rate, the tailing regime of the L–H saturation profile should be neglected. Only the slope of the tangent to the inflexion point should be used to obtain the maximal photomineralization rate. In this instance, the unit for the slope has the same chemical reaction order as the zero-order rate constant.

A lump-sum L-H saturation kinetics profile has also been used to simplify the approximation for a specific photocatalytic reactor system (Minero et al., 1996). In such an empirical lump-sum L-H approach, the degree of organics mineralization is actually expressed in terms of TOC (Eq. (6.7)):



Fig. 9 – Typical saturation kinetics plot for the degradation of organic dye molecules in an annular photoreactor system (Chong et al., 2009b).

$$r_{\text{TOC},0} = \frac{\beta_1[\text{TOC}]}{\beta_2 + \beta_3[\text{TOC}]} \tag{6.7}$$

This (Eq. (6.7)) allows the prediction of TOC degradation as a function of irradiation time. Similar reciprocal plots of 1/r against 1/[TOC] can be used to determine the empirical parameters, β_1 , β_2 and β_3 as in (Eq. (6.3)). The irradiation time taken to achieve the fractional degradation of TOC can also be estimated when (Eq. (6.7)) is expressed as in (Eq. (6.2)). Such an empirical lump-sum L–H model has greatly summarized the needs for precise kinetics measurement and made a great approximation for any particular photoreactor system, provided sufficient data are collected for the determination of rate parameters.

6.2. Photo-disinfection kinetics

Since the first application of semiconductor catalysts for disinfection by Matsunaga et al. (1985), few studies have been found in the literatures which comprehensively study the kinetic modelling of photo-disinfection of microorganisms in a water treatment process. Empirical kinetic models have been the mostly applied for interpretation of photodisinfection data, because of process complexity and variability. The general expression for the empirical photodisinfection models for demand-free conditionis expressed in (Eq. (6.8)). In this instance, demand-free conditions assume that the catalyst concentration is constant with irradiation time.

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -kmN^{\mathrm{x}}C^{n}T^{m-1} \tag{6.8}$$

where dN/dt = rate of inactivation; N = number of bacterial survivors at irradiation time t; k = experimental reaction rate; C = concentration of photocatalyst used; m, n and x are the empirical constants. However, the most commonly employed disinfection model in photo-disinfection studies to date is the simple mechanistic Chick–Watson (C–W) model (Eq. (6.9)) (Cho et al., 2004; Cho and Yoon, 2008).

$$\log \frac{N}{N_{\rm O}} = -k'T \tag{6.9}$$

In this C–W model, the photo-disinfection rate is expressed as a linear function of the enumerated bacteria and catalyst loading. The combined kinetic parameter of CT between the catalyst concentration and irradiation time required to achieve complete inactivation is widely used as a reference for process design. Other than this, this CT-values concept is usually used to compare the efficacy of different disinfectant used in water treatment (Finch et al., 1993). This C-W model however, may not always be applicable as many studies may have experienced a curvilinear or non-linear photo-disinfection profile. Hom (1972) reproduced a useful empirical modification on C-W model after having observed that the disinfection plots of natural algal-bacterial systems were curvilinear, rather than typical log-linear type (Eq. (6.10)). In the Hom model, the bacterial inactivation level is predicted in a non-linear function of C and T, depending on the empirical parameters of n and m respectively. Since this Hom model is a two-parameter model, it should be stressed that the model is only applicable to a photo-disinfection profile with a maximum of two different non-linear regions. For m-value greater than unity, the inactivation curve displays an initial "shoulder" while "tailing" is seen when the m-value is less than unity.

$$\log \frac{N}{N_0} = -k'C^n T^m \tag{6.10}$$

Marugán et al. (2008) have outlined the common nonlinearity found in the photo-disinfection kinetics profile using Degussa P-25 TiO₂ catalyst fitted with common disinfection models (Fig. 10). In their study, they found that three different inactivation regions in the photo-disinfection profile, namely (i) a lag or initial smooth decay, known as the "shoulder", followed by (ii) a typical log-linear inactivation region and ends with (iii) a long deceleration process at the end of the disinfection, which is known as the "tailing". The presence of "shoulder" was justified by the cumulative damage nature of photo-disinfection treatment on the cytoplasmic membrane rather than an instantly lethal (Gyürék and Finch, 1998). However, the "tailing" during the photo-disinfection is not well understood. Benabbou et al. (2007) proposed that the "tailing" region was related to the competition for photocatalysis between organic products released from constant cell lyses and the remaining intact cells. Others have proposed that the "tailing" deviations from the log-linear reduction were due to the presence of variations in the bacterial population resistant to the disinfectant used (Lambert and Johnston, 2000). Nevertheless, the use of CT concept or Hom model can lead to an over-design for a photo-disinfection system (Gyürék and Finch, 1998). A further modification to the Hom model was made to account for the simultaneous presence of shoulder, log-linear reduction and tailing (Eq. (6.11)) (Marugán et al., 2008; Cho et al., 2003);

$$\log \frac{N}{N_0} = -k_1 [1 - \exp(-k_2 t)]^{k_3}$$
(6.11)

Eq. (6.11) is known as the modified Hom model and it expands the applicability of the Hom model for the fitting of the initial shoulder, log-linear reduction and prolonged tailing behaviours. Another detailed empirical model that can detail

Fig. 10 – Common non-linearity in the photo-disinfection kinetics profile using TiO_2 catalyst, along with the appropriate disinfection models used (Marugán et al., 2008).

the different bacterial inactivation regions is a power law expression (Eq. (6.12)), when m = 1 for the generalised differential equation (Eq. (6.8)) (Gyürék and Finch, 1998);

$$\frac{\mathrm{dN}}{\mathrm{dt}} = -kN^{\mathrm{x}}C^{n} \tag{6.12}$$

Integration of (Eq. (6.12)) yields the Rational model (Eq. (6.13)). If x = 1, this Rational model can be reverted back to the C–W model. In this instance, the Rational model assumes that $x \neq 1$;

$$\log \frac{N}{N_0} = -\frac{\log \left[1 + N_0^{x-1} (x-1) k C^n T\right]}{(x-1)}$$
(6.13)

The Rational model (Eq. (6.13)) can describe both "shoulder" and "tailing" characteristics for x less than or greater than unity respectively. Similarly, the Hom model (Eq. (6.10)) can also be integrated according to the Rational Model with the introduction of both x and $m \neq 1$ to yield the Hom–Power model (Eq. (6.14)):

$$\log \frac{N}{N_{\rm O}} = -\frac{\log \left[1 + N_{\rm O}^{\rm x-1}({\rm x}-1)kC^{n}T^{m}\right]}{({\rm x}-1)} \tag{6.14}$$

Anotai (1996) reported that this Hom–Power model may provide a better fit than both the Hom and Rational models. However, the existence of four empirical parameters in the model may result in an over-parameterization with null physical meanings for each parameter within the model. To



reduce the number of null parameters, the Selleck model (Eq. (6.15)) was proposed. This model assumes that the catalyst concentration remains constant during the irradiation period:

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{\mathrm{kCS}}{1 + \mathrm{KCT}} \tag{6.15}$$

where S is the survival ratio $= N/N_o$ at irradiation time t; k and K are the rate constants. In this model, the "shoulder" was assumed to be a result of cumulative effects of the chemical disinfectant on the microbial target during the contact time. A gradual decrease in the permeability of the outer cell membrane of *E. coli* as an action of the catalysts can be idealized by a series of first-order reaction steps on a single *E. coli* cell that leads to lethality. This model can be modified to account for the disinfection of coliform bacteria in water/ wastewater effluent (Eq. (6.16)) (Gyürék and Finch, 1998):

$$\log \frac{N}{N_o} = -n \log \left[1 + \frac{CT}{K} \right]$$
(6.16)

Although empirical models provide a simple correlation of the photo-disinfection data, the mathematical nature of their relevant terms yields null or misinterpret physical meaning. For instance, the *m*-value > 1 in the Hom model actually suggests that photocatalytic reactivity increases with irradiation time in the ASP. If the vitalistic assumption of bacterial population resistance distribution is valid, this actually indicates that the most resistant bacteria are killed first prior to the least resistant one (Lambert and Johnston, 2000). This shows that the rationale for the applicability of Hom model is contradictory.

It was proposed that the mechanistic models could convey a better physical meaning in their kinetic terms. It was hypothesized that the photo-disinfection mechanism can be viewed as a pure physicochemical phenomenon and precedes in a similar way to a chemical reaction (Lambert and Johnston, 2000). The classical C–W model is a typical example of the mechanistic photo-disinfection kinetics model. In the model, the apparent exponential decay curves for bacterial survival ratios with irradiation times follow a similar decay mechanism of a chemical reaction, and are thus applicable under both phenomena. This can be visualised when the C–W model is integrated mathematically, with N assuming to be the number of moles of reactant to yield the log-linear curve of a first-order reaction.

To formulate a mechanistic model for photo-disinfection kinetics, the occurrence of both "shoulder" and "tailing" region should be rationalized idealistically. The presence of "shoulder" can be justified mechanistically by the single-hit multiple targets or a serial phenomenon event (Gyürék and Finch, 1998). Under mechanistic assumption, the damage to the microbial cell is viewed as cumulative rather than instantly lethal. This dictates that a large number of critical molecules need to be denatured prior to cell inactivation (Gyürék and Finch, 1998). Severin et al. (1984) proposed that the cumulative inactivation of a single bacterium can be collectively represented by a series of integer steps. These disinfection steps were thought to pass on a bacterium from one level to another in a first-order reaction with respect to the catalyst used until a finite number of lethal (l) events was reached. The microorganisms which accumulate less than the

postulated number of lethal steps are considered to survive the photo-disinfection process. As for the "tailing" region, many have regarded that it was owing to the presence of a microbial subpopulation resistant to thermal sterilisation. Najm (2006) also suggested that the "tailing" is due to the intrinsic distribution of bacterial resistance to the sterilisation method, making the bacteria more resistant, adapted and inaccessible to heat treatment. Marugán et al. (2008) reviewed that such "tailing" was not a common phenomenon in water disinfection treatment. So far, no justifiable explanation has been proposed to account for the occurrence of "tailing" in the water disinfection treatment with well-mixed conditions and equally resistant cloned-bacterial population. It was suggested that the "tailing" was a result of gradual deterioration in the rate of disinfection, and total inactivation was achievable only after a sufficient retention time. The random collisions between the catalyst and bacteria can be expressed by the Poisson probability, as the number of collisions supersede prior to the number of microbial death (Gyürék and Finch, 1998). If the destruction rate of the microorganisms is assumed to be the same for the first and l th target at the kth bacteria site, thus the rate of destruction for the microorganisms is given by;

$$\frac{\mathrm{d}N_{\mathrm{K}}}{\mathrm{d}t} = \mathrm{k}C\mathrm{N}_{\mathrm{K}-1} - \mathrm{k}C\mathrm{N}_{\mathrm{K}} \tag{6.17}$$

Solving for K = 0 to K = l - 1 gives the log fraction of microbial survival, not exceeding l - 1 at the end of the contact time;

$$\ln \frac{N}{N_{o}} = -kCT + \ln \left[\sum_{K=0}^{l-1} \frac{(kCT)^{K}}{K!} \right]$$
(6.18)

Lambert and Johnston (2000) stated in the formulation of all mechanistic models that take into account the "shoulder" and "tailing", an intermediate population stage is usually suggested with different rates of disinfection for each microbial state. Typically, two different microbial states for the number of damaged bacterial and undamaged bacteria (i.e. $C_{dam} + C_{undam}$) were introduced to account for such non-linearity in bacterial survivor curves. A similar Langmuir–Hinshelwood (L–H) type of mechanistic model (Eqs. (6.19) and (6.20)) can also be applied to represent the photodisinfection kinetics to yield more meaningful kinetic terms (Marugán et al., 2008). Johnston et al. (2000) showed that the inoculum size of the bacteria has a large impact on resistance distribution and thus, the errors associated with this term should be given attention during the mechanistic modelling.

$$\frac{\mathrm{d}C_{\mathrm{undam}}}{\mathrm{d}t} = \frac{-k_1 K_{\mathrm{undam}} C_{\mathrm{undam}}^{\eta_{\mathrm{undam}}}}{1 + K_{\mathrm{undam}} C_{\mathrm{undam}}^{\eta_{\mathrm{undam}}} + K_{\mathrm{dam}} C_{\mathrm{dam}}^{\eta_{\mathrm{dam}}}} \tag{6.19}$$

$$\frac{\mathrm{d}C_{\mathrm{dam}}}{\mathrm{d}t} = \frac{k_1 K_{\mathrm{undam}} C_{\mathrm{undam}}^{\eta_{\mathrm{undam}}} - k_2 K_{\mathrm{dam}} C_{\mathrm{dam}}^{\eta_{\mathrm{dam}}}}{1 + K_{\mathrm{undam}} C_{\mathrm{undam}}^{\eta_{\mathrm{undam}}} + K_{\mathrm{dam}} C_{\mathrm{dam}}^{\eta_{\mathrm{dam}}}}$$
(6.20)

where k_i is the true log-linear deactivation rate constant for the reaction between generated ROS with bacteria. The pseudo-adsorption constant, K_i , represents the surface interaction between the catalyst and bacteria. This constant is similar to the adsorption equilibrium constant in the conventional L–H model. Due to the significant size differences between E. coli cells and the catalyst agglomerates, these constants do not represent strict adsorption phenomena but a more general surface interaction during photo-disinfection. These adsorption constants allow the "shoulder" representation in the photo-disinfection kinetics data. The inhibition coefficient, η_i is a power coefficient that accounts for the "tailing" in the bacteria inactivation curve. Marugán et al. (2008) proposed that η_i is needed to account for the inhibition produced by the increasing concentrations in the medium of cell lysis and oxidation products competing for the ROS. This is particularly important towards the end of photo-disinfection, as high concentrations of these compounds and small numbers of viable bacteria are present in the suspension. In this instance, the η_i in the proposed L–H model essentially means that the reaction order with respect to the microbial population is higher than one.

Both (Eqs. (6.19) and (6.20)) have six independent parameters that describe photo-disinfection rates. This constitutes a high risk of over-fitting the experimental data, where the statistical significance of parameters and the plausibility of the model are low. By taking into account the intrinsic kinetics of ROS attack, the catalyst-bacteria interaction and the inhibition by-products are similar for both undamaged and damaged bacteria, the following are assumed:

$$k_1 = k_2 = k$$
 (6.21)

$$K_{\rm undam} = K_{\rm dam} = K \tag{6.22}$$

$$\eta_{\rm undam} = \eta_{\rm dam} = \eta \tag{6.23}$$

With these, (Eqs. (6.19) and (6.20)) are reduced to (Eqs. (6.24) and (6.25)). The three independent parameters allow a simultaneous fitting of three different inactivation regimes of "shoulder", "log-linear" and "tailing". Fitting of (Eqs. (6.24) and (6.25)) to the experimental measurements of ($C_{undam} + C_{dam}$)/ C_o can be achieved using a non-linear regression algorithm coupled with a fifth-order Runge–Kutta numerical approach. Marugán et al. (2008) showed a good fitting of such mechanistic L–H model to the photo-disinfection of *E. coli* under different loadings of Degussa P25 TiO₂ catalyst.

$$\frac{\mathrm{d}C_{\mathrm{undam}}}{\mathrm{d}t} = \frac{-kKC_{\mathrm{undam}}^{\eta}}{1+KC_{\mathrm{undam}}^{\eta}+KC_{\mathrm{dam}}^{\eta}} \tag{6.24}$$

$$\frac{\mathrm{d}C_{\mathrm{dam}}}{\mathrm{d}t} = k \frac{KC_{\mathrm{undam}}^{\eta} - KC_{\mathrm{dam}}^{\eta}}{1 + KC_{\mathrm{undam}}^{\eta} + KC_{\mathrm{dam}}^{\eta}} \tag{6.25}$$

7. Water quality

In a full-scale plant for water treatment, a number of technical issues have to be sorted out. Water quality of the influents in the treatment plant can vary with time. In this section, the implication of TiO_2 photocatalytic processes for treatment of water sources of different qualities will be discussed. This enables a fuller understanding on the effects of various key water quality parameters on the suitability of applying such advanced TiO_2 photocatalytic processes.

7.1. Turbidity

Turbidity often refers to the insoluble particulates that are present in the targeted water (Viessman and Hammer, 1998). The presence of such insoluble particulate matters are highly detrimental to the TiO₂ photocatalysis based process, as they can affect the optical properties and further impede the penetration of UV light by strong scattering and absorption of the rays (Chin et al., 2004; Tang and Chen, 2004). This will cause a variation in the predicted use of TiO2 loading, UV penetration path and light intensity. Also, excessive levels of turbidity can reduce both the photomineralization and photodisinfection efficiency of the pollutants that present in water owing to the shielding effects that attenuate the light penetration causing those pollutants to flee from the treatment (Rincón and Pulgarin, 2005; Chin et al., 2004; Tang and Chen, 2004). Suspended solids will also shield target pollutants from oxidation reactions. In this instance, the suspended solids refer to the non-filterable residue that is retained on the filter medium after filtration. All these factors ultimately decrease the overall photocatalytic efficiency for water treatment. To ensure rapid photocatalytic reaction rate, the turbidity of the targeted water should be kept below 5 nephalometric turbidity units (NTU) for optimal UV light utilization and photocatalytic reaction (Gelover et al., 2006; Fernándezs-Ibáñez et al., 2009). Rincón and Pulgarin (2003) observed that the water turbidity higher than 30 NTU will negatively affect the rate of photocatalytic disinfection. The limit of 5 NTU is arbitrary and depends on the receiving water bodiesand the treatment levels required. Since TiO₂ photocatalytic processes are retrofitted to advanced water treatment stage, prior reduction in turbidity could be achieved via conventional treatment processes such as screening, filtration, sedimentation, coagulation and flocculation. The standard for 1 NTU is a 1.0 mg L^{-1} of specified size of silica suspension and can be prepared for laboratory investigation. The turbidity standard can be calibrated with a photoelectric detector or nephalometry for the intensity of scattered light.

7.2. Inorganic ions

The presence of inorganic ions in the targeted water for TiO₂ photocatalytic treatment is expected. To functionalise a TiO₂ water treatment process, the basic understanding of these inorganic ions on the photocatalytic performance is essential. Crittenden et al. (1996) reported that when a photocatalyst is utilised in either slurry or fixed-bed configuration to treat real waters with different inorganic ions, photocatalyst deactivation was usually observed. This resulted from a strong inhibition from the inorganic ions on the surface of the TiO₂ semiconductor used. Thus, the presence of these inorganic ions together with their permissible levels on the photocatalytic performance of TiO₂ in water treatment has to be determined to ensure minimal disturbances on the efficient operation of the TiO₂ based treatment process. With such dataa cost-effective fouling prevention with inorganic ions and photocatalyst regeneration strategies can be customized.

A number of studies have been conducted on the effects of different inorganic anions or cations, on both TiO_2 photomineralization and photo-disinfection reactions (Rincón and

Pulgarin, 2004; Habibi et al., 2005; Özkan et al., 2004; Schmelling et al., 1997; Leng et al., 2000; Wong and Chu, 2003; Wang et al., 2004; Chen et al., 1997; Riga et al., 2007; Guillard et al., 2003). It must be emphasized, however, that most of these studies have concentrated on how different inorganic ions affect the rates of photocatalytic reactions with a model surrogate organic compound. The surrogate model organic compound can be biased towards its photocatalytic performance owing to its underlying chemical properties and the main constituent groups that form the compound. For instance, the model compounds with either electronwithdrawing or donating groups will contribute a different degree of interaction to degradation pathways (Herrmann, 1999). Due to the zwitterionic nature of the TiO₂ particles used, it is also possible that the operating pH might have a profound effect on the selective inhibition of inorganic ions on the surface of the TiO_2 particles (Guillard et al., 2003). However, few discussions have been centred on considering how the chemical nature of the model organic used and the operating pH in the photocatalytic reactor on the inhibition of different inorganic ions in photocatalytic water treatment.

To date, the effects of both inorganic cations (i.e. Na⁺, K⁺, Ca^{2+} , Cu^{2+} , Mn^{2+} , Mg^{2+} , Ni^{2+} , Fe^{2+} , Zn^{2+} , Al^{3+}) and inorganic anions (i.e. Cl^{-} , NO_{3}^{-} , HCO_{3}^{-} , ClO_{4}^{-} , SO_{4}^{2-} , HPO_{4}^{2-} , PO_{4}^{3-}) on the photocatalytic water treatment have been investigated (Rincón and Pulgarin, 2004; Habibi et al., 2005; Özkan et al., 2004; Schmelling et al., 1997; Leng et al., 2000; Wong and Chu, 2003; Wang et al., 2004; Chen et al., 1997; Riga et al., 2007; Guillard et al., 2003). A general consensus from these studies concludes that Cu^{2+} , Fe^{2+} , Al^{3+} , Cl^- , PO_4^{3-} at certain levels may decrease photo-mineralization reaction rates while Ca^{2+} , Mg^{2+} , Zn^{2+} may have negligible effects. This is because the Ca^{2+} , Mg^{2+} and Zn^{2+} are at their maximum oxidation states resulting in their inability to inhibit the photocatalysis reaction. The presence of Fe²⁺ can catalyse both the Fenton and photo-Fenton reactions. However Choi et al. (1994) observed that Fe^{2+} fouled the photocatalysts surface by introducing an rusty orange colour change via the formation of Fe(OH)₃, while the PO_4^{3-} in the nominal pH range remains strongly adsorbed onto the TiO₂ surface and further inhibits its photoactivity (Kerzhentsev et al., 1996; Abdullah et al., 1990). Some research groups observed that NO_3^- , SO_4^{2-} , ClO_4^- and HCO_3^- inhibit the surface activity of the photocatalysts, while others suggest no such impact. Both NO₃⁻ and SO₄²⁻ have detrimental effect on the photo-disinfection rate (Habibi et al., 2005). The Cu^{2+} can enhance the photocatalytic activity at its concentration up to 0.1 mM, while further increases in its concentration reduce the reaction rate (Okonomoto et al., 1985). Nitrogen-containing molecules are mineralized into NH_4^+ and mostly NO_3^- . Ammonium ions are relatively stable and their proportion depends mainly on the initial oxidation degree of nitrogen on the irradiation time. Pollutants containing sulfur atoms are mineralized into sulphate ions. While Cl⁻ has no inhibition on the photocatalytic degradation of trichloroethylene at a concentration up to 3.0 mM. On contrary, the addition of oxyanion oxidants such as ClO₂, ClO₃, IO₄, S₂O₈ and BrO₃ increased photoreactivity by scavenging conduction-band electrons and reducing the charge-carrier recombination (Martin et al., 1995). The presence of salts is also known to diminish the

colloidal stability as screening effects become more profound. This was followed the double layer compression and surface charge neutralisation, which increases the mass transfer limitations and reduces surface contacts between the pollutants and catalysts. Other inorganic ions also affect photodegradation rates, where the presence of SO_4^{2-} in a TiO₂ coated glass spiral reactor could double the disappearance rate of the pesticide monocrotophos (Zhu et al., 1995). The Mn²⁺ improved the photoactivity by simultaneously increases the electron–hole pairs and preventing their recombination (Mu et al., 2004).

Several mechanisms for fouling effects of inorganic ions on TiO₂ photoactivity have been proposed (Burns et al., 1999; Rizzo et al., 2007). These include UV screening, competitive adsorption to surface active sites, competition for photons, surface deposition of precipitates and elemental metals, radical and hole scavenging and direct reaction with the photocatalyst. The NO₃⁻ ion was reported to UV screening the photocatalyst than inhibiting the TiO₂ surface (Burns et al., 1999). The competition for surface active sites involves the constant displacement of hydroxide ions from TiO₂ surface and thus, further reduces the generation of radicals. Quantum yield is reduced as a result of the direct competition of inorganic ions for light photons (lowered number of photons entering the reactor). A similar decrease in photonic efficiency was observed when precipitates were formed and deposited onto the TiO₂ surface, blocking the accessibility of both photons and organic compounds. The ultimate inorganic anions that were determined to scavenge both the hole and radicals include Cl^{-} , HCO_3^{-} , SO_4^{2-} and PO_4^{3-} (Diebold, 2003). A mechanism for Cl⁻ and HCO₃⁻ in inhibiting photocatalysis via hydroxyl radical and holes scavenging was proposed by Matthews and McEnvoy, 1992; Lindner et al., 1995, respectively:

$$Cl^- + OH^{\bullet} \rightarrow Cl^{\bullet} + OH^-$$
 (7.1)

$$\mathrm{Cl}^- + \mathrm{h}^+ \to \mathrm{Cl}^{\bullet}$$
 (7.2)

The Cl⁻ accounted for its inhibitory effect on TiO₂ photocatalysis through a preferential adsorption displacement mechanism over the surface bound OH⁻ ions. This reduces the number of OH⁻ ions available on the TiO₂ surface, and the substituted Cl- further increases the recombination of electron-hole pairs. Among other chlorinated molecules, Cl⁻ ions are readily released in the solution. This effect could be of benefit in a process where photocatalysis is associated with a biological depuration system, which is generally not efficient for chlorinated compounds (Herrmann, 1999). Other ions such as PO₄³⁻ are known to avert adsorption of amino acids over the TiO_2 catalysts, while CO_3^{2-} and other ionic species react with OH radicals to compete with microorganisms and further reduce the efficiency. Thus, the presence of inorganic ions in water subjected to TiO₂ photocatalytic treatment is an important factor in determining its successful implementation.

To resolve TiO_2 photocatalyst fouling issue, preventative or regenerative strategies can be adopted, depending on the nature of the photocatalysts deactivation in the water matrix.

Fouling preventative strategies by means of water pretreatment, complexation and photocatalyst surface modifications can be addressed, while rinsing the TiO₂ surface with different chemical solutions constitutes the regenerative strategies. Water pre-treatment with ion exchange resins is one of a few methods that can be employed to ensure minimal disturbances by inorganic ions. Burns et al. (1999) discussed that the operational cost of water pre-treatment with ion exchange resins can be minimised if the fouling ions were identified and selectively removed. Other preventative strategies such as complexation of fouling agents after"escorting" the ions through the reactor can be utilised, provided that the strong fouling ions are hard to remove from the feed water stream. Modifications of the TiO2 surface to increase the hydrophobicity and adsorption capacity is an upstream preventative way to enhance the rate of photodegradation in the presence of fouling ions. However, this method is unstable and impractical compared to the others, where the modifications are reported to be displaced away with time. As for the regenerative strategies, different types of chemical rinsing were reported to potentially resolubilize surface deposits, precipitates and reduced metals. The fouled ions usually do not form strong surface complexes and can be easily displaced by an ion exchange rinse. Abdullah et al. (1990) reported that TiO₂ fouling with SO_4^{2-} and PO_4^{3-} can be displaced by NaOH, KOH and NaHCO₃, while Cl⁻ can be easily regenerated with water. More complex mixtures of inorganic ions need to be investigated to better mimic real water matrices in photocatalytic water treatment or after investigation of water matrices with one known inorganic ion composition at a time.

7.3. Heavy and noble metals

Heavy metals that might be present in trace amount in the wastewater stream are highly toxic in some of their valence states (Kabra et al., 2004). Due to the pliable nature of biological treatment, these intoxicant metals can remain and permeate through the treatment process. To treat such metals, TiO₂ photocatalytic process has been reported to simultaneously convert these metals into non-toxic ionic states and further reduced them into their corresponding elemental form on the TiO₂ surface for metal recovery. Prairie et al. (1994) reported that metals of Ag(I), Cr(IV), Hg(II) and Pt(II) were easily treated with TiO₂ of 0.1 wt% whereas Cd(II), Cu(II) and Ni(II) could not be removed. The extent of such metals conversion and recovery process are highly dependent on the standard reduction potential of the metals for the reduction reactions. It was reported that for an efficient removal of the metals, a positive potential of greater than 0.4 V or the flat band potential of TiO₂ was required (Herrmann, 1999; Kabra et al., 2004). Since the rates of both oxidation (organics) and reduction (metals) on the TiO₂ surface are intrinsically interrelated, the present of sufficient organics in the water matrices were found to facilitate the metal recovery. The redox process for the metal reduction on the TiO₂ surface is given below:

$$Mn^{+} + H_2O \xrightarrow{TiO_2(hv)} M^o + nH^+ + \frac{n}{4}O_2$$
 (7.3)

Herrmann et al. (1988) reported that small crystallites of silver (3 and 8 nm) were initially deposited and began to

agglomerate (few hundreds of nm) when the conversion increased. Since the photosensitive surface was not masked, a relatively large amount of silver was recovered, leaving behind concentration of lower than the detection limits of atomic absorption spectroscopy (≤ 0.01 ppm) in the solution. The effect of various factors on the photoreduction of silver on TiO₂ surface were further investigated (Huang et al., 1996). Angelidis et al. (1998) also reported that even at low concentration of metal ions, the photodeposition of metals on the TiO₂ surface from solution was still effectively performed. However, they noted that the rate of photodeposition was enhanced when Pt-loaded was used instead of unloaded TiO₂ particles. This metal photodeposition property on TiO₂ surface is particularly useful when the water legislation limit on the metal contents becomes more stringent.

8. Life cycle assessment of photocatalytic water treatment processes

In the current development of photocatalytic water/wastewater treatment processes, their possible application for the industry is still being investigated at pilot plant scale. A few pilot plants have been established to obtain feasibility data, such as the treatment efficiency, site area requirements for targeted volume, electrical energy consumption, process emissions and chemical costs. The heterogeneous photocatalysis and photo-Fenton plants located at the INETI (Instituto Nacional de Engenharia, Technologia Industrial e Inovacao, Portugal) and PSA (Plataforma Solar de Almeria, Spain) are two renowned pilot plants that have delivered most of these data for technical analysis. Both plants consist of compound parabolic collectors (4.16 m^2 aperture area) exposed to sunlight, a reservoir tank, a recirculation pump and connecting tubing and are operated in batch mode (Muñoz et al., 2006). Further technical details of these plants can be found in the literature (Gernjak et al., 2006; Lapertot et al., 2006).

In order to assess these photocatalytic processes as emerging technologies for large-scale water/wastewater treatment, a life cycle assessment (LCA) should be evaluated based on the currently available data. LCA is one of the most widely accepted tools that not only consider the environmental impact of the emergent photocatalytic water treatment, but also its technical feasibility and costs. Andreozzi et al. (1999) also pointed out that the potential application of ROS-based oxidation processes entails high costs for energy and reactants consumption. Thus, to consider the feasibility of photocatalytic water treatment on the whole, a comprehensive LCA based on viable technical data should be carried out. Muñoz et al. (2005) carried out a simplified LCA based on small-scale laboratory data of heterogeneous photocatalysis and other AOPs. However, they found that small-scale laboratory data interpretation in their LCA study can lead to inconclusive results.

Using LCA, the environmental burdens from a product, process or activity via materials and energy balances can be defined and reduced as well as the waste discharges, its impacts on the environment and the environmental improvement opportunities over the whole life cycle (Consoli et al., 1993). This holistic LCA approach in decision making over other environmental assessment approaches includes all the burdens and impacts, and focuses on the emissions and wastes generated (Azapagic and Clift, 1999).

Muñoz et al. (2006) carried out a LCA based on the two pilot plants of INETI and PSA, which treated 1 m³ of methyphenylglycerine (MPG) to destroy non-biodegradable and toxic compounds to a level that met the quality of aquatic ecosystems with both homogeneous photo-Fenton and heterogeneous photocatalysis. Other technically rationale assumptions were also made to facilitate the estimation of energy and materials consumed and produced. Nine impact categories of the possible large-scale photocatalytic water treatment process were included in the analysis, namely; global warming potential, ozone depletion potential, human toxicity potential, fresh-water aquatic toxicity potential, photochemical oxidant formation potential, acidification potential, eutrophication potential, non-renewable energy consumption and land use.

Fig. 11 shows the LCA results for possible large-scale water application using photocatalytic technology. The LCA results showed that the retrofitting of heterogeneous photocatalysis process to the existing biological wastewater treatment can lower eutrophication potential, but require higher site area requirement and electricity consumption. These technical constraints are a direct result from the requirement for a large land area and the raw materials to build the parabolic collector infrastructure and high power needed to pump the wastewater through the system. However, the results from the impact categories cannot be compared directly to each other as they were expressed in different measurement units. From the engineering point of view, these constraints mainly arise from the low photoactivity of the catalyst used under solar irradiation. Further materials engineering solutions and studies should be carried out to resolve such technical issues to permit the scale-up of the technology to a commercially viable process.

9. Future challenges and prospects

Semiconductor photocatalytic technology using either UV light or solar has become more prominent owing to its advantages of the use of vast additive chemicals or disinfectants and its mineralization aspects. These are particularly important, as recalcitrant organics are mineralized rather than being transformed to another phase. Coupled with the ambient operation of the process, all these make photocatalytic water treatment technology a viable alternative for commercialisation in the near future. Different water contaminants, ranging from hazardous contaminants of pesticides, herbicides and detergents to pathogens, viruses, coliforms and sporesare effectively removedby this photocatalytic process.



Fig. 11 - Life cycle impact assessment results for the alternatives under study (Muñoz et al., 2006).

The applicability of the heterogeneous photocatalytic technology for water treatment is constrained by several key technical issues that need to be further investigated. The first consideration would be whether the photocatalytic process is a pre-treatment step or a stand-alone system. The nonselective reactivity on the non-biodegradable water soluble pollutants means the photocatalytic process can be used effectively as a pre-treatment step to enhance biodegradation of recalcitrant organic pollutants prior to biological water treatment. In such a way, the residence time and reaction volume for the biological treatment could be significantly reduced. If the photocatalytic process is used as a stand-alone treatment system, the residence time required might be prolonged for total bacterial inactivation or mineralization. As discussed, this is hindered by the slow kinetics, low photoefficiency and a need for continuous (without interruption) illumination to achieve the required total organic carbon removal or microbial inactivation. For the stand-alone system, the site area requirement might be proportionally from any increased reaction volume required.

In order to promote the feasibility of photocatalytic water treatment technology in the near future, several key technical constraints ranging from catalyst development to reactor design and process optimization have to be addressed. These include (i) catalyst improvement for a high photo-efficiency that can utilize wider solar spectra; (ii) catalyst immobilization strategy to provide a cost-effective solid-liquid separation; (iii) improvement in the photocatalytic operation for wider pH range and to minimize the addition of oxidant additives; (iv) new integrated or coupling system for enhanced photomineralization or photo-disinfection kinetics and (v) effective design of photocatalytic reactor system or parabolic solar collector for higher utilization of solar energy to reduce the electricity costs. Currently, the utilization of solar energy is limited by the photo-efficiency of the TiO₂ catalyst bandgap to only 5% of the solar spectrum. The need for continuous illumination for efficient inactivation of pathogens has diverted solar utilization to artificial UV lampdriven process. In addition, the low efficacy design of current solar collecting technology (0.04% capture of original solar photons) has encouraged the developmental progress of photocatalytic technology in water treatment industry. Further pilot plant investigations with different reactor configurations are needed to ensure that the photocatalytic water technology is well-established and presents vast techno-economic data for any LCA study. Finally, a largescale photocatalytic treatment process with high efficacy, solar-driven and low site area requirements can be realized in the short future with rapid evaluation of different possible pilot plant configurations.

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