Water reclamation by Heterogeneous Photocatalysis over TiO$_2$

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19.1 Introduction

The term "photocatalysis" refers to a chemical transformation or the acceleration of a chemical reaction in the presence of light and a photocatalyst (Kisch 1989). The various types of photocatalysts listed in the literature can be classified into three groups (Sakata 1989):
1.   Dye molecules used as homogeneous photocatalysts;
2.   Semiconductors used as heterogeneous photocatalysts (HP); and
3.   A combination of dye and semiconductor species known as dye sensitised photocatalysts.

In HP, reactions occur at an interface of a solid/liquid (for aqueous pollutants) or of a solid/gas (for gaseous pollutants). Photocatalytic reactions are initiated by the absorbance of photons that drive subsequent redox reactions on the irradiated (activated) surface of the photocatalyst. Consequently, the adsorption of pollutants on the photocatalyst is very important for their photodegradation, although photodegradation also can occur at small distances from the irradiated surface, due to the diffusion of reactive species (Kikuchi et al. 1997; Tatsuma et al. 2001). The photocatalyst is involved in the reactions but is not consumed, chemically altered, or transformed. The most popular semiconductor used in HP is TiO$_2$ for being relatively inexpensive, chemically stable, and non-toxic.

The use of HP as a green technology in environmental remediation has been well studied to explore the benefits and tackle the challenges in this field (Chen et al. 2000; Fujishima et al. 2007). The removal of indoor odours by immobilised TiO$_2$ films under weak UV illumination (Ohko et al. 1997), the bactericidal effect of TiO$_2$ under low intensity UV-illumination (Kikuchi et al. 1997), the self-cleaning TiO$_2$ surfaces (Minabe et al. 2000), and the photocatalytic decomposition of endocrine-

disrupter chemicals in water (Ohko et al. 2002) are few examples of using HP in environmental applications.

The growing importance of wastewater reuse and the resulting need to remove recalcitrant pollutants from effluents have impacted the science and engineering of water treatment, to generate significant research interest in this area (Ollis et al. 1989; Herrmann et al. 1993; Gaya and Abdullah 2008; Shon et al. 2008; Lee et al. 2009; Chong et al. 2010; Okour et al. 2010; El Saliby et al. 2011). The widely used conventional biological wastewater treatment technologies have limited ability to remove certain pollutants, such as pharmaceuticals, personal care products, and pesticides from water. Therefore, new treatment methods, chiefly advanced oxidation processes are gaining popularity in solving pollution problems created by such emerging pollutants. The application of HP in water treatment has been considered an effective way to eliminate harmful pollutants either by their complete mineralisation or partial degradation that allows successive biological treatment. The major advantages of HP can be summarised as follows:

1.   Full degradation (mineralisation) of contaminants, even at trace level concentrations;
2.   Formation of toxic or harmful by-products can be avoided;
3.   Minimal production of waste (sludge); and
4.   Possibility to utilise sunlight as energy source.

Hence, the research and development in the field of HP is growing to find improved photocatalysts and systems for various environmental applications. Fundamentals of HP for water treatment using TiO_2, including reactor engineering, the effect of operational parameters, and kinetics and applications of the photocatalytic reactions will be discussed in the following sections.
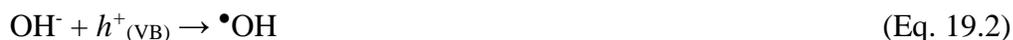

19.2   Fundamentals

The band gap (i.e. the gap between the conduction and valence band) of semiconductors can be simply calculated from the formula: E_G (Band gap in eV) = 1240 / λ (nm), where λ is the excitation wavelength of the semiconductor (Chen et al. 2000). In general, the photocatalytic properties of semiconductors depend on several factors: i) the position of the energetic level; ii) the mobility and mean lifetime of the photogenerated electron and holes; iii) the light absorption coefficient; and iv) the nature of the interface (Augugliaro et al. 2010).

UV irradiation of TiO_2 promotes an electron (e^-) from the valence band to the conduction band, which leaves a positive charge carrier hole (h^+) in the valence band. The e^- and h^+ charges migrate in random directions to the bulk or the surface of the particles. Those elementary charges that reach the surface of the catalyst can react with electron-donor and electron-acceptor species present at the semiconductor/ electrolyte interface. In contrast, those charge carriers that are trapped in the bulk material can only recombine with the release of heat (Linsebigler et al. 1995;

Fujishima et al. 2008). The position of the valence band and conduction band edges, as well as the energetic levels of any redox couples, are essential factors to establish if thermodynamics allow the occurrence of oxidation and/or reduction of the species in solution (Chen et al. 2000).

The adsorption of photons by TiO_2 allows the direct transformation of light quanta into chemical energy (Figure 19.1). After illumination by a UV source the following sequence of events can occur on the surface of TiO_2 (Augugliaro et al. 2010):

$$TiO_2 + hv \rightarrow TiO_2\,(e^-_{(CB)} + h^+_{(VB)}) \qquad \text{(Eq. 19.1)}$$

$$OH^- + h^+_{(VB)} \rightarrow {}^\bullet OH \qquad \text{(Eq. 19.2)}$$

$$O_2 + e^-_{(CB)} \rightarrow {}^\bullet O_2^- \qquad \text{(Eq. 19.3)}$$

$${}^\bullet O_2^- + H^+ \rightarrow {}^\bullet HO_2 \qquad \text{(Eq. 19.4)}$$

$$2\,{}^\bullet HO_2 \rightarrow O_2 + H_2O_2 \qquad \text{(Eq. 19.5)}$$

$$H_2O_2 + {}^\bullet O_2^- \rightarrow OH^- + {}^\bullet OH + O_2 \qquad \text{(Eq. 19.6)}$$

At the solid-liquid interface and on different zones of the same particle, the redox reactions permit the degradation of many organic and inorganic pollutants by means of formation of very reactive radical species generated in the presence of O_2 and H_2O. The role of oxygen is crucial since it i) assists the charge separation in TiO_2 by capturing electrons; ii) participates in reactions as an oxidiser; and iii) also required for the generation of active species such as H_2O_2, ${}^\bullet O_2^-$.
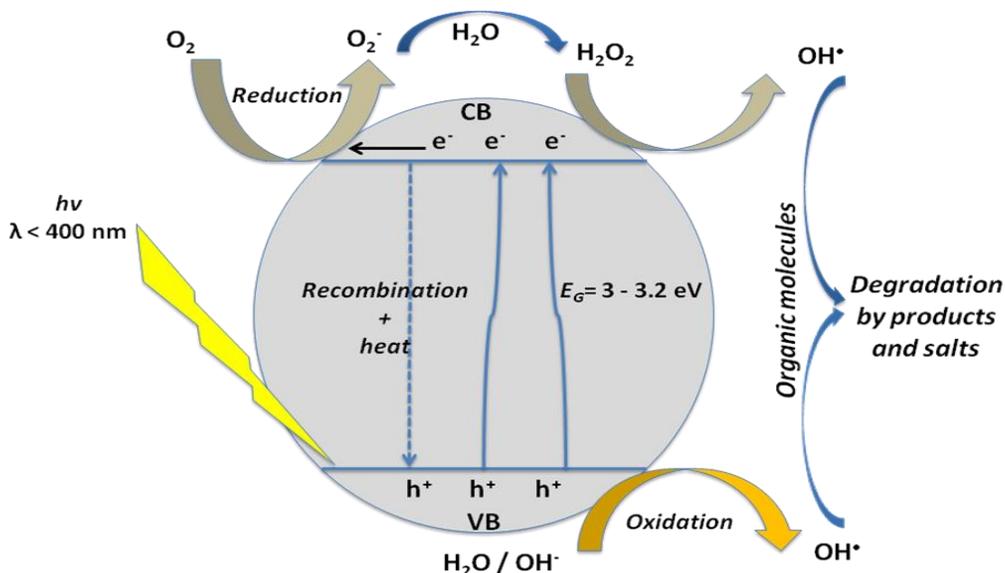

Figure 19.1. A scheme of photo-induced reactions occurring in the bulk and at the surface of a spherical TiO_2 particle

19.3 Photocatalytic Reactors

There are many factors which have to be considered when designing photoreactors for water or wastewater treatment. The geometry of the photoreactor, the photocatalysis mode, and the energy source (UV lamps or solar light) are the main parameters that impact the final design (McCullagh et al. 2011). Based on the geometry, photoreactors could be divided into: i) immersion well; ii) annular; iii) elliptical; iv) multi-lamp; v) film; and vi) fluidised bed classes. According to the photocatalysis mode, photocatalytic reactors are generally classified into: i) slurry photoreactors (Figure 19.2); and ii) fixed-bed photoreactors (Mozia 2010).

For slurry reactors, an aqueous suspension of the photocatalyst is mixed with the polluted stream to ensure maximum contact. Even though the efficiency of these systems is relatively high, the separation of the photocatalysts after treatment for reuse increases process complexity and costs. For fixed-bed photoreactors, the photocatalyst is immobilised on a solid non-reactive support, such as glass or quartz, to avoid the problem of particle separation. Unfortunately, the photocatalytic performance of such systems is typically lacking due to the reduced exposure and activation of photocatalytic surfaces (McCullagh et al. 2011).

The type of energy source affects the feasibility of photocatalytic systems. The traditional use of UV lamps is effective but requires electrical energy, which can negatively affect the cost of the treatment system. In contrast, up to 5% of the solar light spectra is in the UV range that can be used to activate TiO_2. Solar reactors are divided into concentrated and non-concentrated reactors. Various types have been used for heterogeneous photocatalysis, including i) parabolic trough reactor, ii) compound parabolic collecting reactor, iii) double skin sheet reactor, and iv) thin film fixed bed reactor (McCullagh et al. 2011).
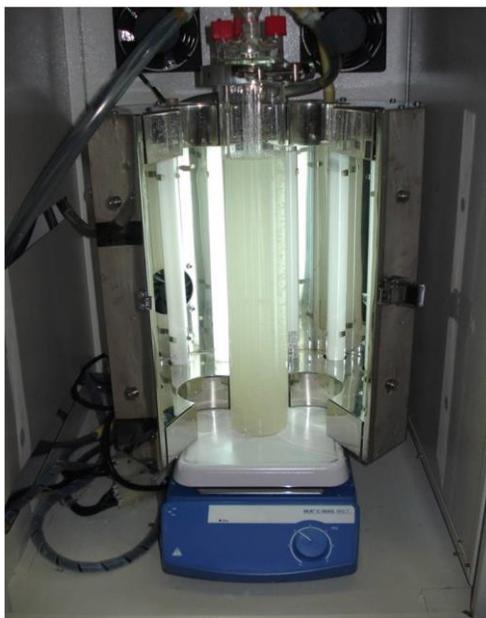

Figure 19.2. A slurry-type annular photoreactor

In the last decade, the photocatalytic degradation of organics was accomplished in hybrid photoreactors such as the photocatalytic membrane reactor (Molinari et al. 2000; Choi et al. 2007; Zhang et al. 2009) and the submerged membrane photocatalysis reactor (Ryu et al. 2005; Fu et al. 2006; Chen et al. 2009). Such hybrid membrane-photocatalytic systems combine the more effective slurry type photoreactors with membrane modules to ensure the effective separation of suspended photocatalysts' particles.

In a recent publication, McCullagh et al. (2011) discussed the latest photoreactor configurations used in environmental remediation. They concluded that the future of photoreactor technology depended on the engineering and design of photoreactors, as well as on the development of more effective photocatalysts, especially in rate-limited systems. For industrial applications, photoreactors need to meet the challenges of capacity, ruggedness, reliability, and ease of operation. In the view of those authors, currently only suspension (slurry) type reactors are capable of (with some limitations) meeting such expectations.

19.4   Operational Parameters

There are several factors (including operational or process parameters) that directly influence the overall photocatalytic process efficiency in a given photoreactor system. The most significant factors include photocatalyst loading, composition and characteristics of the catalyst, contaminant composition and concentration, light intensity, pH of the solution, oxygen supply, and the temperature of reaction. Process engineering parameters such as the type of reactor, retention time, and reactor hydraulics are case-specific and will not be discussed hereafter.

19.4.1 Photocatalyst Loading

The increase of TiO_2 loading generally increases the rate of the photocatalytic reaction up to some limit, which is due to the increase in the surface area of the photocatalyst available for adsorption and degradation (Mozia 2010). Since the photocatalytic activity is also dependent on the surface absorption of photons by TiO_2 particles, the further increase of TiO_2 loading above the optimum level leads to light screening (shading effect) that results in a decrease in photoefficiency (Chong et al. 2010). Moreover, increased particle collision and agglomeration at high loadings also results in loss of the active surface area (Kaneco et al. 2004). Therefore, the optimum photocatalyst loading for a particular application only can be established experimentally (Gaya and Abdullah 2008).

19.4.2 Composition and Characteristics of Photocatalysts

While photocatalysis is sometimes described as being non-selective to various pollutants, this is only an appearance and is due to the extreme reactivity of hydroxyl

radicals that readily attack many compounds. However, reaction rates are still strongly dependent on the physicochemical properties of both the photocatalyst (Figure 19.3) and pollutants. Rutile, anatase, mixed photocatalysts (i.e. the industry "standard" Evonik P25), as well as doped photocatalysts show significant differences in photocatalytic performance. The main physical factors affecting photodegradation of certain pollutants are the particle size, surface area, porosity and surface charge. For metal doped TiO_2, the presence of impurities and non-metal compounds also can significantly affect the rate of photocatalytic reaction. Therefore, there is no single "best" photocatalyst that offers a universally high performance for every application.

19.4.3 Concentration of Pollutant

In HP, organic contaminants can be divided into many and various groups according to their chemical compositions, molecular structure, functional groups, solubility, and their pathways of decomposition. In general, the dark adsorption of organics onto TiO_2 surface precedes the photo-oxidation process that occurs during UV irradiation. However, at high pollutant loadings surface saturation may become a 'shading' barrier to the absorption of photons by TiO_2 leading to performance degradation by photocatalyst deactivation (Saquib and Muneer 2003; Arana et al. 2004). The determination of an optimal organic loading for a given photoreactor is essential to ensure effective operational conditions. Palmisano et al. (2007) have reported that organic molecules with electron withdrawing group adsorb better than molecules with electron donating groups. It was also shown that organics with complex molecular formulae (4-chlorophenol, humic acid, etc.) break down to various intermediate products before final mineralisation that have different adsorption affinities toward the photocatalyst than the original pollutant (Palmisano et al. 2007). In contrast, simple compounds such as oxalic acid have been reported to undergo direct mineralisation to CO_2 and H_2O (Bahnemann 2004). Therefore, the degradation of complex material is best monitored by COD/DOC and/or salt concentration measurements, while HPLC and UV-vis spectroscopy (for measuring a single compound concentration) are quite satisfactory for monitoring the degradation of simple compounds to establish the kinetics of the photoreaction.

19.4.4 Effect of pH

The variation of pH has a critical role in the photocatalytic treatment of aqueous organic contaminants. Konstantinou and Albanis (2004) described the effect of pH on the photocatalytic reaction over TiO_2 through: i) changing the ionisation state of TiO_2, ii) modifying the position of the conduction and valence bands, iii) assisting in the agglomeration or dissociation of TiO_2 particles, and iv) interfering in the formation of hydroxyl radicals.

Moreover, the process pH (by definition a measure of hydronium ion mol concentration in water) also directly affects the solubility of pollutants, and particle surface charges. In general, the isoelectric point or the point of zero charge (PZC) of Evonik P25 TiO_2 lies between pH 6 to 7. The increase of pH increases the negative

surface charge, while a decrease will result in more positively charged photocatalyst surface, according to the following reactions (Gaya and Abdullah 2008; Chong et al. 2010):
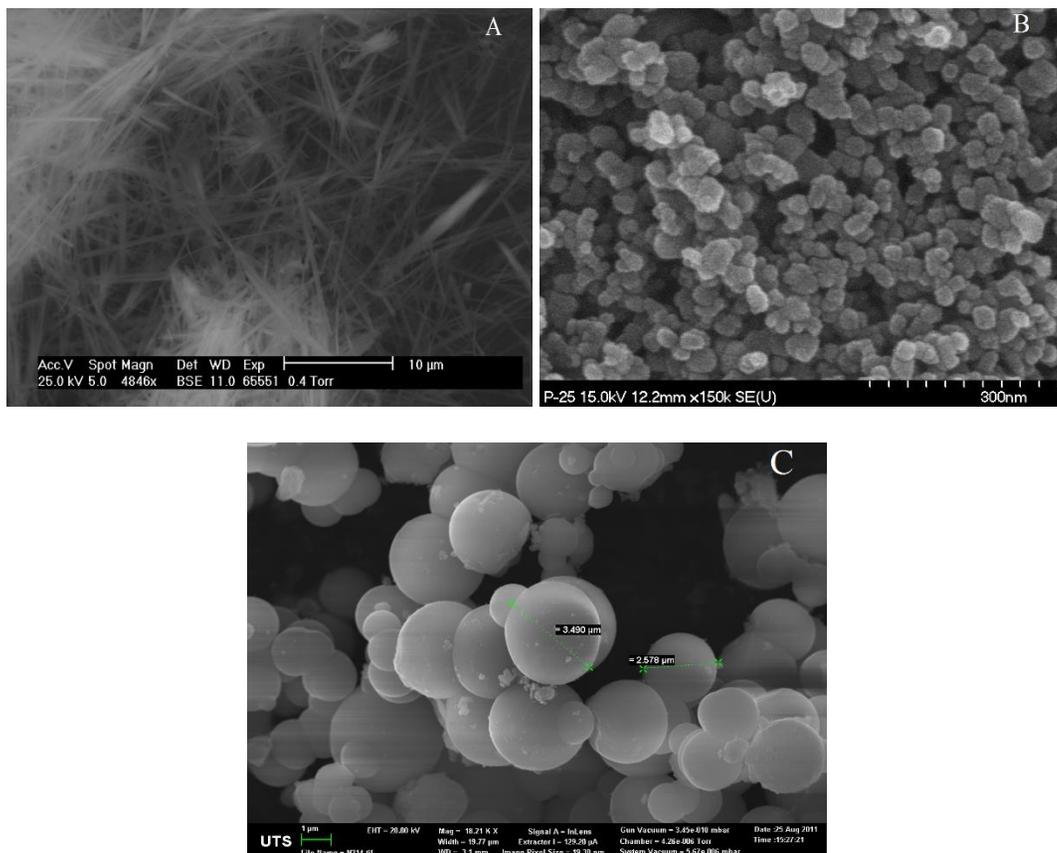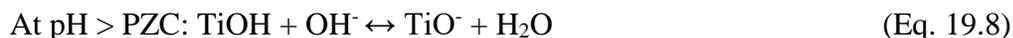
$$At\ pH < PZC: TiOH + H^+ \leftrightarrow TiOH_2^+ \qquad \text{(Eq. 19.7)}$$

$$At\ pH > PZC: TiOH + OH^- \leftrightarrow TiO^- + H_2O \qquad \text{(Eq. 19.8)}$$

Figure 19.3. Photocatalysts with different physicochemical characteristics. **(A)** H-titanate nanofibres; **(B)** TiO$_2$ nanoparticles; **(C)** nitrogen doped peroxotitanate micropsheres

Therefore, the adsorption of charged molecules or species onto TiO$_2$ is strongly influenced by the pH of the aqueous medium. Negatively charged contaminants are better adsorbed at lower pH (pH < PZC), while positively charged contaminants are better adsorbed at higher pH (pH > PZC) by electrostatic interaction.

Surface charge neutralisation (pH = PZC) promoted to the formation of larger particle clusters and easier sedimentation (Chong et al. 2010). However, the aggregation of particles also may be detrimental by reducing the photocatalytic efficiency through the reduction of the exposed surface area, and the shading effect. The size of agglomerates was found to be highly dependent on the pH difference relative to the PZC (Malato et al. 2009).

The reaction between a hydroxide ion and a positive hole generates a hydroxyl radical (Eq. 19.2). This reaction is favoured under alkaline conditions since there is more OH^- available at the TiO_2 surface. The reaction between H^+ ions and e^- also generates reactive radical species (Eq. 19.4), and under acidic conditions, the positive holes might be the major oxidation species (Konstantinou and Albanis 2004). Moreover, hydroxyl radicals also can form through Eq. 19.6. Therefore, it can be seen that the process pH has multiple effects on the photocatalytic reactions; and thus, it is essential to determine the optimal process pH for specific applications.

19.4.5 Light Intensity

The excitation of TiO_2 surface by a radiant photonic flux ($\lambda < 400$ nm) occurs at very low light intensity. Fujishima et al. (2000) indicated that few photons of energy (as low as 1 $\mu W/cm^2$) are sufficient for the initiation of the photocatalytic reaction. However, the increase in light intensity is essential to ensure that the photocatalyst surface is being appropriately irradiated. The photocatalytic activity of TiO_2 is related to the incident light intensity, and the relationship can be summarised as follows (Ollis et al. 1991; Qamar et al. 2006: Mozia 2010): i) at low light intensities (0-20 mW/cm^2) the photocatalytic reaction rate is proportional to the radiant flux; ii) at intermediate light intensities (approx. 25 mW/cm^2) the effect is proportional to the square root of radiant flux; and iii) at high light intensities the activity becomes constant.

The increase of reaction rate at low irradiation intensities is due to the formation of electron-hole pairs, with a negligible recombination rate. Above a certain radiant flux, the rate of recombination becomes significant that affects the photocatalytic reaction rate. At very high radiant flux intensities, the saturated surface coverage results in mass transfer limitations (adsorption and desorption), coupled with another limiting step of the electron transfer from the photocatalyst to the oxygen (Doll and Frimmel 2005).

19.4.6 Dissolved Oxygen

The role of oxygen in the photocatalytic reaction was presented in Equations 19.3 and 19.6 that describe the pertinent reactions occurring on TiO_2 surface. Dissolved oxygen (DO) has a primary role in the formation of reactive species and the stabilisation of intermediates. It was also reported that DO induced the cleavage mechanism for aromatic rings that are present in many organic pollutants (Chong et al. 2010). Previous work found that the concentration of DO can be a limiting factor that sometimes significantly hinders the photo-mineralisation process (Wang and Hong 2000). However, increased photocatalytic activity also can occur in the absence of oxygen, due to the reduced absorption of UV photon by dissolved oxygen molecules at $\lambda < 254$ nm. The DO molecules act as an inner filter and reduce the effective photonic flux on the surface of the photocatalyst (Shirayama et al. 2001).

19.4.7 Temperature

The photocatalytic decomposition of organics usually can proceed without a need for increasing the ambient water temperature. However, an increase in degradation rates was observed with an increase in the temperature range between 20 °C and 80 °C (Malato et al. 2009). Operating the photocatalytic process at low temperatures (near 0 °C) hindered the desorption of the final product from the photocatalyst surface, which caused an increase in the apparent activation energy. In contrast, temperatures above 80 °C disfavoured the adsorption of pollutants and also enhanced the recombination of charge carriers, which were considered the main limiting steps (Gaya and Abdullah 2008; Mozia 2010; Chong et al. 2010).

19.5   Optimisation Methodology

The optimisation of photoreactor systems is usually undertaken by the conventional one-parameter-at-a-time approach. In other words, the optimisation is achieved by varying one parameter while all the others are kept constant. After determining the optimal condition for a given variable, based on the decomposition rate of a target pollutant, other parameters are subsequently tested until all parameters have been optimised. This method is widely accepted and has been used to optimise many operating systems. However, the limitation of this procedure is that the interaction of parameters at different levels cannot be tested. The multivariable optimisation approach is becoming increasingly popular because the optimisation process is more effective, and the interaction among different parameters can be interpreted using the analysis of variance, statistical regression, and response surface analysis (Chong et al. 2010).

19.6   Process Efficiency

The optimisation of a photocatalytic process for a specific reaction (single contaminant) is crucial for the determination of a sound photoreactor/operation parameter configuration. The process efficiency of the system should be assessed based on a standardised method to allow comparisons between different processes. The quantum yield "Φ" (Φ = rate of reaction / adsorption rate of radiation) was suggested to evaluate the process efficiency in photocatalytic processes (Calvert and Pitts 1966). However, it's very difficult to determine Φ by experimental investigation in many photocatalytic reactors. This is mainly due to the refraction, scattering, transmission and adsorption of light by the suspended particles (Chen et al. 2000).

A relative photonic efficiency "ζ_r" (ζ_r = initial disappearance rate of substrate / initial disappearance rate of phenol) has been proposed to overcome the difficulties encountered by the measurement of Φ (Serpone et al. 1997). The method consisted of measuring the initial disappearance reaction rate of phenol using Evonik P25 as a "standard" photocatalyst, and then measuring the initial disappearance rate of the

target substrate under identical experimental conditions. The ζ_r can be used to calculate the quantum yield of the substrate ($\Phi_{substrate}$) relatively to the quantum yield of phenol on Evonik P25 (Φ_{phenol}) by $\Phi_{substrate} = \zeta_r \, \Phi_{phenol}$. The relative photonic efficiency allows the comparison of results of studies performed in different laboratories. Nevertheless, experimental conditions must be identical, besides that the initial rate does not consider the formation of intermediate compounds, and how those might affect the degradation of their parental products. It follows that the evaluation of photocatalytic processes using a universal reference or indicator is still not possible, since many factors and parameters have interrelated influences on the reaction rate.

19.7 Kinetics of the Photocatalytic Reaction

The kinetics of mineralisation in heterogeneous photocatalysis is often described in the literature with the Langmuir-Hinshelwood (L-H) model. Although this model was originally proposed for gaseous–solid reactions (Satterfield 1970) it also can describe solid–liquid reactions (Ollis 1985). In the L-M model the r rate of reaction is proportional to the θ fraction of surface covered by the substrate (pollutant):

$$r = -\frac{dC}{dt} = k\Theta \qquad\qquad (\text{Eq. 19.9})$$

Θ is obtained from Langmuir's equation

$$\Theta = \frac{K \cdot C}{1 + K \cdot C} \qquad\qquad (\text{Eq. 19.10})$$

Hence

$$r = k \cdot \frac{K \cdot C}{1 + K \cdot C} \qquad\qquad (\text{Eq. 19.11})$$

with k = reaction rate; K = constant of adsorption equilibrium; and C = substrate concentration at t time. The integration of Eq. 19.11 between zero and t times yields

$$\ln\left(\frac{C_0}{C_t}\right) + K \cdot (C_0 - C_t) = k \cdot K \cdot t \qquad\qquad (\text{Eq. 19.12})$$

with C_0 and C_t = substrate concentration at zero and t irradiation times, respectively. Solving Eq. 19.12 for k requires the knowledge of K. For that, the θ surface coverage fraction can also be expressed from the number of adsorbed molecules at a given final (equilibrium) concentration as

$$\Theta = \frac{n_{ads}}{n_0} = \frac{K \cdot C}{1 + K \cdot C} \qquad\qquad (\text{Eq. 19.13})$$

that can be re-arranged as

$$\frac{1}{n_{ads}} = \frac{1}{n_0} + \frac{1}{n_0 K} \cdot \frac{1}{C}$$ (Eq. 19.14)

with n_{ads} and n_0 = covered and total number of available adsorption sites, respectively. Noting that Eq. 19.14 is linear, both K and n_0 can be determined from plotting $1/n_{ads}$ versus $1/C$. It also can be seen from Eq. 19.11 that the reaction will be of zero order for relatively high substrate concentrations (and/or K values) (KC >> 1), and of first order for relatively low substrate concentrations and/or K values (KC << 1).

In the photocatalytic degradation of Methylene Blue, a widely used model pollutant, Herrmann (1999) reported zero and first order reactions for 5 mmol and 1 mmol initial concentrations, respectively. For the latter case, which is typical in most applications of photocatalysis, the denominator in Eq. 19.11 approaches 1 (one), and thus

$$r = k \cdot \Theta = k \cdot K \cdot C = k_a \cdot C$$ (Eq. 19.15)

with k_a apparent (pseudo) rate constant. The integral form of Eq. 19.15 is

$$C_t = C_0 \cdot e^{-k_a \cdot t}$$ (Eq. 19.16)

The linearised form of Eq. 19.16 is often used to obtain the k_a apparent reaction rate. However, data linearisation also transforms the random (Gaussian) distribution of the error term, which is contrary to the fundamental assumption of random errors used in the derivation of linear regression. Therefore, it is advisable to obtain reaction rates from Eq. 19.17 using nonlinear regression/fitting techniques that are provided by many modern statistical software packages.

$$\ln\left(\frac{C_0}{C_t}\right) = k_a \cdot t$$ (Eq. 19.17)

It is also emphasised that both the k reaction rate constant used in the L-M model and the k_a apparent reaction rate constant used in the first order model are lumped (bulk) parameters. Those parameters take into account a number of factors, such as hydraulic conditions and photonic conditions. It follows that the obtained rate values are only valid for the given experimental conditions, cannot be used for the up-scaling of equipment, nor to compare catalyst performances reported elsewhere. Their utility is in quantifying and comparing relative performances when assessing the effects of various experimental factors.

19.8 Applications in Water Treatment

Nowadays, most water remediation technologies generate a significant amount of wastewater that requires costly retreatment or discharge to evaporation ponds, rivers and oceans. Therefore, the development of zero-wastewater discharge technologies will help alleviate these problems. TiO_2 photocatalysis is considered a viable alternative to conventional water treatment systems with the added benefit of

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being a clean and environmentally friendly technology. Moreover, it can be used to degrade recalcitrant pollutants that are normally difficult to treat using conventional water treatment. HP applications in water treatment are numerous and embrace organic pollutants degradation, heavy metal removal, bacteria deactivation and nitrate reduction.

19.8.1 Degradation of Organic Pollutants

Organic pollutants are diverse and complex organic molecules that occur in natural waters, rainwater, and storm water as well as in wastewater. The majority of these organic pollutants could be immobilised, separated and removed from water using conventional methods such as flocculation, bioreactors and membrane filtration. However, some classified as recalcitrant micro-pollutants (antibiotics, toxins, PPCPs, dyes and herbicides, etc.) are difficult to separate, filter and resist biological wastewater treatment processes. The degradation of these pollutants could be achieved by heterogeneous photocatalysis using TiO_2, few examples are shown in Table 19.1.

Fluoroquinolone antibiotics such as moxifloxacin are increasingly used to treat microbial infections in humans and animals. As a result, antibiotic residues and by-products have been constantly detected in most of wastewater effluents across Europe (Speltini et al. 2010). The photocatalytic degradation of moxifloxacin in a batch slurry photoreactor over P25-TiO_2 resulted in fourteen degradation products (Van Doorslaer et al. 2013). However, the most important finding was that no residual antibacterial activity could be observed after 12 min of degradation time. Accordingly, effluent pre-treatment by heterogeneous photocatalysis was recommended to reduce the antibacterial activity of moxifloxacin in wastewater effluents.
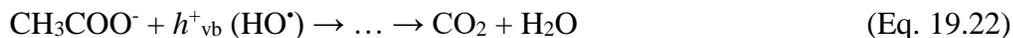
Other micro-pollutants such as herbicides are easily transported from the site of application to surrounding ecosystems including rivers and groundwater. This is mainly due to their high solubility, persistence in the environment and long half-life dissipation. For instance, clomazone herbicide has a half-life ranging from 24–82 days which permit its mobilisation to the groundwater (Abramovic et al. 2013). Contaminated groundwater was efficiently treated with a suspension of P25-TiO_2 under different light sources (Table 1). A UV/TiO_2 treatment system eliminated clomazone from water with an optimum loading of TiO_2 equal to 0.5 mg/ml at the pH 10.3.

19.8.2 Heavy Metal Removal

Heterogeneous photocatalysis has been also used for the reduction of aqueous heavy metals, their immobilisation and removal. To achieve successful photoreduction, the bottom level of the conduction band of the photocatalyst should be more negative than the reduction potential of the heavy metal (Litter 2009). In this way, heavy metals are reduced to less toxic forms, precipitated/immobilised than

filtered using membrane. The conventional chemical reduction processes involve the use of large quantities of expensive reducing agents such as $FeSO_4$, $FeCl_2$, $NaHSO_3$ or SO_2, which creates secondary pollution (Barrera-Diaz et al. 2012). Photocatalytic reduction of heavy metals is a promising technology to clean heavy metal contaminated waters and wastewaters.

Mercury(II) is a frequent component of industrial wastewaters and is found in pesticides, fungicides, herbicides, insecticides and bactericides. The photocatalytic transformation of Hg(II) metal ion was achieved to species of lower toxicity and easier to separate from the aqueous phase (De la Fourniere et al. 2007). $P25\text{-}TiO_2$ photocatalysed the reduction in a recirculating photoreactor set up under UV light irradiation. The absence of oxygen favoured Hg(II) removal at pH 11, where HgO was formed together with Hg(0). Photoreduction reactions were also proposed for two different phenylmercury salts (PMA ($C_6H_5HgCH_3CO_2$) and PMC (C_6H_5HgCl)) used as mercury source:

$$C_6H_5Hg^+ \, (Cl^- \text{ or } CH3COO^-) + (HO^{\bullet}) + H^+ \rightarrow C_6H_5OH + Hg^{2+} \, (Cl^- \text{ or } CH_3COO^-) \text{ (Eq. 19.18)}$$

$$Hg^{2+} + e^-_{cb} \rightarrow Hg(I) \qquad \text{(Eq. 19.19)}$$

$$Hg(I) + e^-_{cb} \rightarrow Hg(0) \qquad \text{(Eq. 19.20)}$$

$$C_6H_5OH + h^+_{vb} \, (HO^{\bullet}) \rightarrow \ldots \rightarrow CO_2 + H_2O \qquad \text{(Eq. 19.21)}$$

$$CH_3COO^- + h^+_{vb} \, (HO^{\bullet}) \rightarrow \ldots \rightarrow CO_2 + H_2O \qquad \text{(Eq. 19.22)}$$

Later on, Lopez-Munoz et al. (2011) studied the influence of pH and the addition of methanol, formic acid and oxalic acid as sacrificial additives on the extent of Hg(II) photocatalytic reduction. The photoreaction was carried out using $P25\text{-}TiO_2$ in a cylindrical Pyrex batch reactor illuminated by 150W medium pressure mercury lamp (Heraeus TQ-150). It was found that the addition of organic additives enhanced the photocatalytic reduction to Hg(0) in acidic medium while no effect was observed at high solution pH (10).

The photoreduction of Cr(VI), a common toxic pollutant of wastewater, to Cr(III) was achieved by a new class of visible-light active titania photocatalyst (Zhang et al. 2013). The photocatalyst was synthesised by a one-step low-temperature solvothermal route using HNO_3 as a nitrogen precursor to acquire visible activity. Cr(VI) aqueous solutions were exposed to both visible and UV light and treated with different types of TiO_2 photocatalysts. It was shown that the new photocatalyst performed better than others for the reduction of Cr(VI) to Cr(III) in water under both UV and visible light ($\lambda > 420$ nm) irradiation. The conversion of Cr(VI) into more environmentally benign oxidation states was also investigated by Gherbi et al. (2013) using $CuAl_2O_4/TiO_2$ hetero-junction photocatalyst (spinel-titania bi-functional system). The photoreduction was carried out at 25°C in a double walled sealed tank reactor with infrared cut-off filter and a 200 W tungsten lamp. Results revealed that the chromate reduction rate increased as light flux increased, and it was also enhanced by the presence of salicylic acid in a solution which favoured the separation of (e^-/h+) pairs.

Table 19.1. Few recalcitrant micro-pollutant photocatalytic degradation systems over TiO_2

Photocatalysts	Organic pollutants	Photocatalytic systems	Irradiation sources	References
•$dTiO_2$ anatase •20-MWCNT-TiO_2 •Commercial anatase	Ketoprofen	Batch slurry photoreactor	Heraeus TQ 150 medium-pressure Hg-vapor lamp and TNN 15/32 low-pressure Hg-vapor lamp	Martinez et al. (2013)
P25-TiO_2	2,4-dichlorophenol	Recirculating slurry photoreactor	Xenon lamp (PHILIPS XOP-15-OF, 1500 W)	Bayarri et al. (2013)
P25-TiO_2	Moxifloxacin	Batch slurry photoreactor	UV-A pen ray (300-440 nm with main peak at 365 nm)	Van Doorslaer et al. (2013)
P25-TiO_2	[D-Leu]-Microcystin-LR	Flat plate glass reactor coated with TiO_2	Natural solar light	Vilela et al. (2012)
P25-TiO_2	3-chloropyridine	•Batch slurry photoreactor •Compound parabolic collector solar photoreactor	•UV Spotlight Source Lightningcure TM L8022 •Natural solar light	Ortega-Liebana et al. (2012)
Commercial TiO_2 (Riedel-de Haen, Germany)	Perfluoro-carboxylic acids	Batch slurry photoreactor	Low-pressure mercury UV-lamp (16W, 254 nm, Phillips)	Panchangam et al. (2009)
P25-TiO_2	Clomazone	Batch slurry photoreactor	•Natural solar light •125 W high-pressure mercury lamp (Philips, HPL-N) •50 W halogen lamp (Philips) and a 400 nm cut-off filter	Abramovic et al. (2013)
Hybrid BiOBR-TiO_2	Rhodamine B	Batch slurry photoreactor	300 W Xe lamp with a 400 nm cut-off filter	Wei et al. (2013)

A new generation of titanate materials has been also developed as effective adsorbent of toxic heavy metals. A family of peroxo-titanate was synthesised for the optimal sorption of strontium and actinide (Nyman and Hobbs 2006). The new

materials were better adsorbent than the conventional sodium titanate materials and exhibited improved performance in highly alkaline and high-ionic-strength solutions. Also, the adsorption of As(III) was carried out using TiO_2 nanofibers with different phases such as amorphous, anatase, mixed anatase-rutile and rutile (Vu et al. 2013). The highest adsorption capacity was recorded for the amorphous nanofibers and was attributed to their high surface area and porous volume.

19.8.3 Bacteria Deactivation

The deactivation of pathogenic microorganisms over TiO_2 has been investigated as a means to treat contaminated water (Table 19.2), and the deactivation process could be summarised in the following:

- Adhesion of bacteria to the photocatalyst (immobilised or slurry type);
- Generation of hydroxyl radicals on TiO_2 during irradiation; and
- Deactivation of bacteria by creating irreversible damage (through hydroxyl radicals attack) to the cell wall leading to dissociation of the microorganism.

Pablos et al. (2013) reported that the bacterial adhesion onto immobilised TiO_2 was mainly due to hydrophobicity (under electrostatically favourable conditions) and aquatic chemistry (under unfavourable conditions). Two bacterial strains with differences in their membrane structure (*Escherichia coli* and *Enterococcus faecalis*) were studied. It was found that bacterial adhesion was not due to differences between both bacteria. In contrast, the configuration of the catalyst and the composition of the suspension (affecting electrostatic forces) affected the extent of bacterial adhesion. The highest level of adhesion was recorded in solutions containing organic matter in combination with divalent ions such as Ca^{2+} which can bridge between bacteria and catalyst or bacteria and organic matter. The bivalent cations neutralise the repulsion forces between similarly charged surfaces of bacteria and TiO_2 leading to more effective deactivation.

The deactivation of bacteria is not considered complete before the point of irreversible damage (Wang et al. 2013; Xiong and Hu 2013). Microorganisms are complex, compared to organic molecules by having complex structures and capability of repairing and re-growing after damages are done. A residual disinfecting effect was reached using a UVA/LED/TiO_2 photocatalytic system that treats antibiotic-resistant bacterium (*E. coli* ATCC 700891). The system significantly inactivated the bacterium at higher light intensities, and residual disinfecting effect could kill almost all bacteria after 90 min UV periodic illumination within the following 240 min dark period (Xiong and Hu 2013). In a different setup, the inactivation of gram-negative bacteria was complete after 120 min of UVA irradiation over TiO_2 and reached 99.9% for *Escherichia coli* and 99% for *Pseudomonas aeruginosa*. Under similar conditions, the inactivation efficiency against bacteria by nano-TiO_2 varied, and it was attributed to a higher self-defence property or self-repair ability of *P. aeruginosa* than *E. coli* (Wang et al. 2013).

Table 19.2. Inactivation of bacteria in aqueous photocatalytic systems

Bacteria	Photocatalyst	Irradiation source	Inactivation^/time*	References
Escherichia coli O157:H7	TiO$_2$ ceramic TiO$_2$ coated carbon nanotubes	Fluorescent light (30 mW/ cm^2)	• 5 x 10^{-2} min^{-1} • 2.23 x 10^{-2} min^{-1}	Oza et al. (2013)
• *Escherichia coli* • *Pseudomonas aeruginosa*	TiO$_2$ nanoparticles	Philips TL 8 W, black light lamp	• 99.9 % / 120 min • 99 % / 120 min	Wang et al. (2013)
Escherichia coli ATCC 700891	Immobilised TiO$_2$	UVA/LED lamp 3 W	100 % / 90 min light 240 min dark cycle	Xiong and Hu (2013)
• *Salmonella typhimurium* • *Listeria monocytogenes*	P25-TiO$_2$	Philips LEA-180B, 8 W, black light lamp	• 100% /180 min • <100% /180 min	Long et al. (2014)
• *Escherichia coli* ATCC 10536 (Gram-negative) • *Lactobacillus rhamnosus* S25 (Gram-positive)	TiO$_2$ xerogels	Halogen lamp (50W)	• 100% / 48 h • 100% / 24 h	Tasseroul et al. (2013)
Bacillus amyloliquifacience NCIM 2829	N-doped TiO$_2$ mesoporous thin films	Tungsten lamp 30 mW/m^2	100 % / 3 h	Soni et al. (2013)
• *Enterococcus faecalis* MTCC 439 • *Klebsiella pneumoniae* MTCC 4030	Reactive plasma processed nanocrystalline TiO$_2$	UVA lamp (365 nm, 125 W)	• 95 % / 60 min • 60 % / 60 min	Vijay et al. (2013)

^ (%) percentage or rate constant in min^{-1}

* Minutes or hours

19.8.4 Nitrate Reduction

The overuse of fertilisers worldwide had a negative impact on groundwater quality. Water contamination with nitrate has been recorded due to runoff and leaching of nitrogen fertilisers into water aquifers. In addition, the discharge of untreated industrial wastewater into natural waters has played a significant role in algae blooming which threatened the health and sustainability of aquatic fauna. In water, nitrate (NO^{3-}) is considered a potentially hazardous material that is converted to nitrite by microbes which causes harmful effects on the human body, such as liver damage, cancers and blue baby syndrome (Garron et al. 2005).

The photocatalytic reduction systems designed for nitrate reduction are not different from the systems used for organic, bacteria and heavy metal removal.

Therefore, the concurrent treatment of various contaminants is always possible which significantly reduce the installation and operation costs.

The catalytic reduction of nitrate is well investigated using metallic doped titania such as Pd-Cu/TiO$_2$ (Bae et al. 2013; Kim et al. 2013), Pd-Cu/titania nanotubes (Chen et al. 2013) and Pd-Cu/(Mg-Nb)-TiO$_2$ (Bou-Orm et al. 2013). However, the photoreduction of nitrate over TiO$_2$ was also reported using organic acids as a hole scavenger (Kominami et al. 2001; Li et al. 2010; Yang et al. 2013). Kominami et al. (2001) examined the photocatalytic reduction of nitrate ion (NO$^-_3$) in an aqueous suspension of metal-loaded TiO$_2$ in the presence of oxalic acid (OA) as a hole scavenger. The photoreduction increased with the following order of loaded metals, (Pt, Pd, Co) < (Ni, Au) < (Ag, Cu). It was concluded that TiO$_2$ powder loaded with Cu showed both high nitrate reduction and OA consumption. Li et al. (2010) used benzene as a hole scavenger and Pt-Cu/TiO$_2$ photocatalyst in his nitrate photoreduction investigations. N$_2$ was the final product of the photocatalytic nitrate reduction over the bimetallic photocatalyst. N$_2$ production was strongly dependent on TiO$_2$ calcination temperature, the Pt/Cu ratio and the metal loading amount. A 300 °C calcination temperature, a Pt loading amount of 5 wt.% and the Pt/Cu ratio of 4/1 were reported as optimums. Recently, the photoreduction of nitrate in synthetic and real brines was carried out in the presence of formic acid and TiO$_2$ (Evonik P90) (Yang et al. 2013). This system converted most of the reduced nitrate to volatile N species and a small portion to ammonium.

19.9   Combined Processes: HP + Chemical/Physical Treatment

Coupling HP systems with other technologies in order to increase the efficiency of water treatment processes has been described (Table 19.3). Augugliaro et al. (2006) reviewed the combination of heterogeneous photocatalysis with chemical and physical operations. Operations were divided into two different categories based on the type of activities coupled:

- Processes that affect the photocatalytic mechanism thus improving the efficiency of the photocatalytic process such as ultrasonic irradiation, photo-Fenton reaction, ozonation and electrochemical treatment; and

- Processes that do not affect the photocatalytic mechanisms but improve the efficiency of the overall process such as biological treatment, membrane reactor, membrane photoreactor, or physical adsorption.

Combining different operations with HP provides an excellent way to achieve better quality product water than single process treatment systems. In conventional systems, the main drawback of water chlorination in drinking water treatment plants is the formation trihalomethanes precursors, which are considered carcinogenic compounds. An Activated Carbon Bed (ACB), an Ozonation Reactor (OR) and a Submerged Membrane Photocatalytic Reactor (SMPR) with TiO$_2$/UV were compared in terms of reduction efficiency of trihalomethanes precursors after chlorination (Reguerro et al. 2013). OR showed low removal percentages of 40−50% while SMPR

and ACB were more efficient technologies achieving 87% and 86%, respectively. The SMPR process can run continuously with a minor loss of efficiency and with almost no-waste products and doesn't need frequent regeneration. Bai et al. (2013) studied the performance of a concurrent photocatalytic membrane water purification system using hierarchical 3D dendritic TiO_2 nanospheres built with ultra-long 1D nanoribbon/wires. Hierarchical TiO_2 nanoribbon/wire spheres showed better photodegradation of acid orange 7 and Rhodamine B pollutants and less ability to fouling the membrane compared to TiO_2-P25 under the same conditions. The porous functional layer that was formed on the membrane surface resulted in high water flux, in comparison to the dense layer formed by TiO_2-P25. This strategy has mitigated the disadvantages usually encountered when using nanoparticles in hybrid photocatalytic-membrane treatment systems for water purification.

The degradation of diclofenac sodium using combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis was investigated (Bagal and Gogate 2014). The efficiency of the system was dependent on the cavitational effects (intense turbulence with liquid circulation currents) which created local hot spots resulting in generation of hydroxyl radicals. Hydroxyl radicals were then expected to intensify the efficacy of the heterogeneous photocatalysis operation. Intense turbulences were formed by a slit venturi (cavitating device) in the hydrodynamic cavitation reactor which was described in details by Bagal and Gogate (2014). Different operating parameters and photocatalytic systems were tested. Under optimised conditions, a hydrodynamic cavitation in conjunction with UV/TiO_2/H_2O_2 was reported for high degradation of diclofenac sodium (95% removal) with 76% reduction in total organic carbon.

Table 19.3. A list of recently combined photocatalysis/physical chemical operations for water treatment

HP combined processes	Target pollutant(s)	References
Hydrodynamic cavitation	Diclofenac sodium	Bagal and Gogate (2014)
Photo-Fenton reaction	3-chloropyridine	Ortega-Liebana et al. (2012)
	Oxalic acid	Quici et al. (2005)
Dielectric Plasma discharge	Toluene	Ban et al. (2006)
Ozonation	Benzenesulfonate	Zsilák et al. (2014)
HP process intensification with static mixer	Phenol, Cr(VI) and acid orange 7	Li et al. (2011)
Photocatalytic membrane reactor	Trihalomethanes	Reguero et al. (2013)
	Synthetic wastewater	Erdei et al. (2008)
	Benzene	Molinari et al. (2009)
Non-woven membrane filtration	4-chlorophenol	Horng et al. (2009)

19.10   Conclusions and Future Prospects

Heterogeneous photocatalysis processes that decompose aqueous contaminants are highly dependent on the reaction conditions and the setup of photocatalytic reactors. The adoption of a "standardised" reactor system only allows the partial comparison of different classes and types of photocatalysts, since the "quantum yield" itself depends on the experimental conditions used. Therefore, the evaluation and assessment of photocatalytic treatment systems requires substantial experimental work.

Visible-light responsive photocatalysts promise a more effective utilisation of solar energy, and thus stimulate significant research. Doping and co-doping of titania is a practical approach to obtain improved visible-light active photocatalysts. However, many of the reported doping processes require expensive equipment and/or complicated procedures that are expensive, and often unfeasible for industrial-scale production. The research and production of engineered nanomaterials that are both highly photoactive and easily separated from water are of great interest for water purification and pollution control.

19.11   References

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