Photo Catalytic Degradation of Pharmaceutical Drugs using TiO$_2$ Nanoparticles. - A Review

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Abstract—*Pharmaceutical compounds have been detected in the environment and potentially arise from the discharge of excreted and improperly disposed medication from sewage treatment facilities. The presence of these compounds occur in sites as diverse as surface water, drinking water and sewage influent and effluent from water treatment plants. Pharmaceuticals persist in the environment due to their inability to be degraded by natural physical processes such as sunlight photolysis or microbial processes. Pharmaceuticals have been detected in trace concentrations in the natural aquatic environment at concentrations of ng L^{-1} to μg L^{-1}; and this has been a global phenomenon. The observed discharge of pharmaceuticals into the environment from sewage treatment plants suggests many conventional treatment processes are often not effective in reducing their levels in the wastewater stream. To improve the removal efficiencies, novel methods of treating pharmaceutically-rich sewage influent have been developed. Such treatment methods include advanced oxidation processes (AOPs) involving ultraviolet (UV) irradiation alone, combining UV irradiation with hydrogen peroxide to generate hydroxyl (HO·) radicals as an effective oxidising agent and incorporating hydrogen peroxide with Fe^{2+} ions (photo-Fenton) which increases the efficiency of HO· radical generation. More recently, heterogenous photocatalysts such as suspended titanium dioxide (TiO$_2$) have been used to generate HO· radicals. The success of TiO$_2$ as a photocatalyst is dependent on its physicochemical properties as a semiconductor.*

Keywords: *Pharmaceuticals, Photocatalysis, Titanium dioxide, Advanced oxidation process, Waste water treatment, UV.*

Introduction

Pharmaceuticals have been detected in trace concentrations in the natural aquatic environment at concentrations of ng L^{-1} to μg L^{-1} [1-3]; and this has been a global phenomenon [4-5]. The presence of these compounds occur in sites as diverse as surface water [6], drinking water [7] and sewage influent and effluent from water treatment plants [8-10]. Pharmaceuticals persist in the environment due to their inability to be degraded by natural physical processes such as sunlight photolysis or microbial processes [11]. Many compounds that have been detected, such as paracetamol, carbamazepine, diclofenac, and ibuprofen, are entirely synthetic and classed as xenobiotics [12]. As a result, pharmaceuticals detected in natural waters systems must have arisen from their medicinal usage prior to their appearance in urine or faeces. More worrying, their appearance may also be due to unused medications which have been disposed of improperly down the toilet, *via* the sewage system [13] or dumped into rubbish as landfill waste, leading to excessive discharge of leachate into environmental waters [14].

Pharmaceuticals are an important group of emerging contaminants(ECs) and their presence in drinking water has generated significant concerns regarding the risk of estrogenic and other adverse effects on humans and fauna [15]. Approximately 3000 different substances are estimated to be used as pharmaceutical ingredients, including painkillers, antibiotics, antidiabetics, beta blockers, contraceptives, lipid regulators, antidepressants, and impotence drugs. Only a small subset of these ECs has been investigated in environmental studies. The large-scale use of pharmaceuticals has also increased their presence in surface water, groundwater, wastewater and stormwater runoff in urban areas [16-18].

The major concerns in relation to antibiotics, biocides, and pesticides, is the development of bacterial resistance after their release into the environment [19-20] and the detrimental effect on the biodegradation of plant materials, which disrupts the primary food chain in aquatic ecosystems. Biocides are mainly used in bituminous roof sealing membranes and external facades or for grass management and weed control. During rain events, biocides and pesticides are incorporated in surface and groundwater via storm water runoff [21]. These have led to the rapid research & development (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 in-situ generation of highly reactive transitory species (i.e. H_2O_2, OH$^-$, O_2^-, O_3) for mineralization of refractory organic compounds, water pathogens and disinfection by-products [22]. Among these AOPs, heterogeneous photocatalysis employing semiconductor catalysts (TiO$_2$, ZnO, Fe$_2$O$_3$, 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 (TiO_2) has received the greatest interest in R&D of photocatalysis technology. The TiO_2 is the most active photocatalyst under the photon energy of 300 nm< l < 390 nm and remains stable after the repeated catalytic cycles, whereas

Cds or GaP are degraded along to produce toxic products [23]. Other than these, the multi-faceted functional properties of TiO_2 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 TiO_2 surfaces for microbial inactivation and organic mineralization without creating any secondary pollution is well-documented. So far, the application of such TiO_2 catalysts for water treatment is still experiencing a series of technical challenges. The post-separation of the semiconductor TiO_2 catalyst after water treatment remains as the major obstacle towards the practicality as an industrial process. The fine particle size of the TiO_2, 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.

Mechanism of TiO_2 photocatalysis

The fundamentals of photophysics and photochemistry underlying the heterogeneous photocatalysis employing the semiconductor TiO_2 catalyst have been intensively reported in many literatures [24]. 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 (hν) of greater than or equal to the bandgap energy of TiO_2 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. The mechanism of the electron- hole pair formation when the TiO_2 particle is irradiated with adequate

hν is depicted in Fig. 1. The light wavelength for such photon energy usually corresponds to l < 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 that occur at the photon activated surface are as follows:
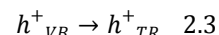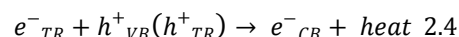
Photoexcitation:
$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad 2.1$$
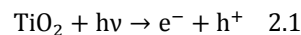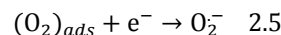
Charge-carrier trapping of e^-:
$$e^-_{CB} \rightarrow e^-_{TR} \quad 2.2$$
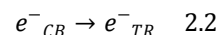
Charge-carrier trapping of h^+:
$$h^+_{VB} \rightarrow h^+_{TR} \quad 2.3$$

Electron-hole recombination:
$$e^-_{TR} + h^+_{VB}(h^+_{TR}) \rightarrow e^-_{CB} + heat \quad 2.4$$

Photoexcited e^- scavenging:
$$(O_2)_{ads} + e^- \rightarrow O_2^- \quad 2.5$$

Oxidation of hydroxyls:
$$OH^- + h^+ \rightarrow OH^{\cdot} \quad 2.6$$

Photodegradation by $OH^{\cdot}$:
$$R - H + OH^{\cdot} \rightarrow R' + H_2O \quad 2.7$$

Direct photoholes:
$$R + h^+ \rightarrow R^{+\cdot} \rightarrow Intermediate(s),$$
$$Final\ Degradation\ Products \quad 2.8$$
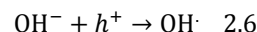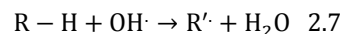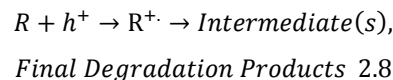
Protonation of superoxides:
$$O_2^- + OH^{\cdot} \rightarrow HOO^{\cdot} \quad 2.9$$

Co-scavenging of e^-:
$$HOO^{\cdot} + e^- \rightarrow HO_2^- \quad 2.10$$
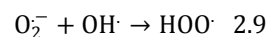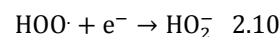
Formation of H_2O_2:
$$HOO^- + H^+ \rightarrow H_2O_2 \quad 2.11$$
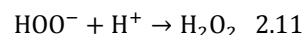
For heterogeneous photocatalysis, the liquid phase organic compounds are degraded to its corresponding intermediates and further mineralized to carbon dioxide and water, if the irradiation time is extended (Eq. 2.12)
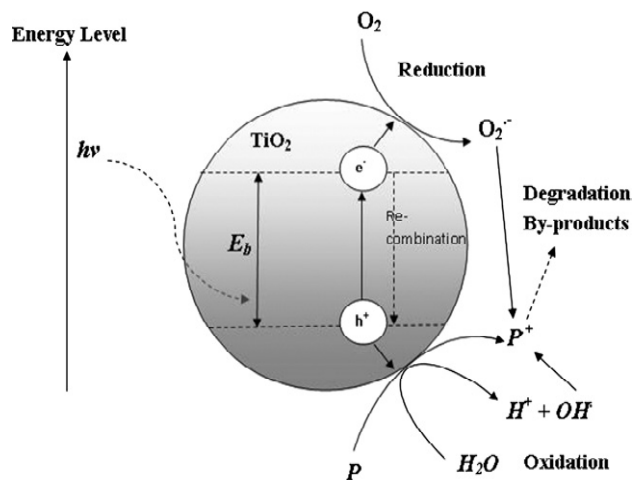
$$Organic\ contaminants \xrightarrow{TiO_2/h\nu} Intermediate(s)$$
$$\rightarrow CO_2 + H_2O \quad 2.12$$
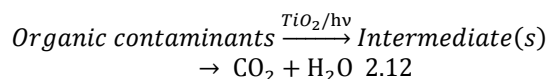
Fig. 1 Mechanism of Electron hole pair formation in TiO$_2$

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 TiO$_2$ surface bounded and do not recombine immediately after photon excitation. 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 (HO$_2^-$) and subsequently H2O2 as shown in (Eqs. 2.9 and 2.10) respectively. The HO$_2^-$ 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. 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^-_{TR} are good redundant (+0.5 to +1.5 V against NHE), depending on the type of catalysts and oxidation conditions.

The overall photocatalysis reaction can be divided into five independent steps:

1. Mass transfer of the organic contaminant(s) in the liquid phase to the TiO$_2$ 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

4. Desorption of the intermediate(s) from the TiO$_2$ surface.

5. Mass transfer of the intermediate(s) from the interface region to the bulk fluid.

Photocatalyst modification and doping

As TiO$_2$ 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 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, dyed sensitizers, noble metals or metal ions incorporation, transition metals and non-metals doping [25-27].

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. The presence of electron acceptors could scavenge the excited electrons and altogether prevent the recombination of electronehole pairs. Recent studies shown that modified TiO$_2$ catalysts have an enhanced photoactivity under solar irradiation [28].

Similarly, noble metals (e.g. Ag, Ni, Cu, Pt, Rh, and Pd) with Fermi level lower than TiO$_2$ catalyst have also been deposited on the TiO$_2$ surface for enhanced charge separation. 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 TiO$_2$ is incorporated into the TiO2 crystal lattice [29]. Such incorporation introduces impurity in the bandgap of TiO2 and thus, reduces the photonic energy requirements. More recently, the use of non-metal dopants (e.g. N, C, F, S and etc.) can improve the photoactivity and feasibility of TiO$_2$ catalysts for industrial application. 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.

Conclusion

Photocatalytic degradation processes can degrade these contaminants without necessarily adding complex chemicals. This is a much green and less complex route than many other options, if energy onsumption can be reduced. Different water contaminants, ranging from hazardous contaminants of pesticides, herbicides and detergents to pathogens, viruses, coliforms and sporesare effectively removedby this photocatalytic process.

The literature suggests that TiO_2 assisted degradation systems may be potentially feasible wastewater treatment processes for the degradation of pharamceuticals, given that some studies have reported on the complete mineralization of particular pharmaceuticals. In addition, much of the current literature concerning the photocatalytic degradation of pharmaceuticals use undoped TiO_2 materials such as Aeroxide P25. While it has been observed that the use of doped TiO_2 materials has enhanced the photodegradation of various organic contaminants such as dyes and pesticides, little is known about the photocatalytic behaviour of these materials in the degradation of pharmaceutical compounds.

In order to promote the feasibility of photocatalytic watertreatment 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

- Catalyst improvement for a high photo-efficiency that can utilize wider solar spectra;

- Catalyst immobilization strategy to provide a cost-effective solideliquid separation;

- Improvement in the photocatalytic operation for wider pH range and to minimize the addition of oxidant additives;

- New integrated or coupling system for enhanced photomineralization or photo-disinfection kinetics and

- Effective design of photocatalytic reactor system or parabolic solar collector for higher utilization of solar energy to reduce the electricity costs.

Water regulatory agencies need to be informed of the proper treatment technique to adopt while treating tainted wastewater. This will contribute in no small measure to the quality of drinking water.

Biosensors need to be further developed for rapid detection of specific contaminants. In order to have a natural ecosystem that is completely free of pharmaceuticals and endocrine-disrupting compounds, there is a need to introduce green

chemistry in the production and development of numerous drugs, medical, and personal care products that are affordable and do not persist in the environment. A regulatory framework based on the precautionary principle should be implemented to screen all compounds for their ecotoxicity prior to approval for use.

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