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# Heterogeneous Photocatalytic Oxidation an Effective Tool for Wastewater Treatment – A Review

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## 1. Introduction

Heterogeneous photocatalysis has been intensively studied since the discovery of photo-activated water splitting process using titanium dioxide (TiO<sub>2</sub>) as electrode (Fujishima & Honda, 1972) in 1972. Heterogeneous photocatalysis can be defined as a reaction in which a catalytic process is initiated by the action of light.

Fujishima and co. discovered that water can be split into hydrogen and oxygen through this process in 1972. Hence early studies were focused on the production of hydrogen using solar energy as a clean fuel from water (Kawai & Sakata, 1980; Sato & White, 1980). Further studies found that irradiated semiconductor particles could catalyze a lot of interesting and useful reduction-oxidation reactions of organic and inorganic compounds (Fox & Dulay, 1993). Some of the semiconductor particles were found to be able to completely mineralize various organic and inorganic substances which are known as environmental pollutants (Fujishima et al., 2007). Since then, many researches were carried out based on the environmental applications of heterogeneous photocatalysis (Herrmann, 1999; Hoffman et al., 1995; Rajeshwar et al., 2001; Saravanan et al., 2009).

Various studies had been carried out to search for an ideal semiconductor photocatalyst, but titanium dioxide (TiO<sub>2</sub>) remains as a benchmark among other semiconductors. CdS, SnO<sub>2</sub>, WO<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub> etc. were among the semiconductor materials that were being studied but titanium dioxide (TiO<sub>2</sub>) remained an excellent photocatalyst for its high resistance to photocorrosion and desirable band-gap energy (Ye & Ohmori, 2002). It can be used to degrade a variety of organic and inorganic pollutants (Fox & Dulay, 1993; Herrmann et al., 2007). Besides, titanium dioxide (TiO<sub>2</sub>) is easily available in the market, chemically inert and durable (Saravanan et al., 2009) and non-toxic.

In contrast with other conventional methods in environmental cleanup, heterogeneous photocatalysis involved the breakdown of the pollutants from complex molecules into simple and non-hazardous substances. Hence no residue is left and no sludge is produced from the process. Furthermore, no secondary treatment is needed to process the sludge.

Besides, the catalyst remains unchanged throughout the process and thus can be reuse; therefore no consumable chemical is required. All these result in a significant reduction in overall operating cost. In addition, this process can be carried out at extremely low concentrations because the pollutants were strongly adsorbed on the surface of the catalyst, allowing sub part-per-million condition. Summing up all these benefits and advantages, heterogeneous photocatalysis provides a cheap and effective alternative to clean water production and environmental remediation.

In this study, various issues with respect to the attributes of the photocatalyst and the mechanism behind titania-based photocatalysis will be discussed. The following discussion may be relevant to environmental cleanup context, given that the process is subjected to both contaminant reduction and oxidation relying on the tendency of the former to either accept or give up electrons respectively (Rajeshwar & Ibanez, 1995).

### 1.1 Advanced oxidation processes

The phrase *advanced oxidation processes* (AOP) refer specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals (Glaze et al., 1995). It involves two stages of oxidation: (1) the formation of strong oxidants (*e.g.*, hydroxyl radicals) and (2) the reaction of these oxidants with organic contaminants in water (Alnaizy & Akgerman, 2000). In water treatment applications, AOPs usually refer to a specific subset of processes that involve  $O_3$ ,  $H_2O_2$ , and/or UV light. However, often AOPs are also referred to a more general group of processes that also involve semiconductor catalysis, cavitation, E-beam irradiation, and Fenton's reaction (Fox & Dulay, 1993; Legrini et al., 1993). All these processes can produce hydroxyl radicals, which can react with and destroy a wide range of organic contaminants, including phenolics. Although many of the processes noted above have different mechanisms for destroying organic contaminants, in general, the effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals (Fox & Dulay, 1993; Legrini et al., 1993).

### 1.2 Ozonation / UV

The  $O_3$  system is one of the AOP for the destruction of organic compounds in wastewater. Basically, aqueous systems saturated with ozone are irradiated with UV light of 253.7 nm. The extinction coefficient of  $O_3$  at 253.7 nm is 3300 L.mol/cm, much higher than that of  $H_2O_2$  (18.6 L.mol/cm). The decay rate of ozone is about a factor of 1000 higher than that of  $H_2O_2$  (Guittonneau et al., 1991). The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals, which do not act as they recombine producing hydrogen peroxide, as shown in the following Eqns. (1) and (2) (Peyton & Glaze, 1988):



### 1.3 Ultrasonication

Implosion of cavity bubbles in sonicated water containing dissolved gases results in formation of hydrogen and hydroxyl radicals by fragmentation of water molecules. These

radicals in turn combine and generate other oxidative species such as peroxy and super oxide radicals ( $\cdot\text{OH}$ ) as well as hydrogen peroxide; the quantities of each depend on the ambient conditions and the operating parameters. Such  $\cdot\text{OH}$  radicals are used for the degradation of the organic compounds (Kidak & Ince, 2006).

## 1.4 Solar photocatalytic oxidation

In the past years, there have been a number of studies and reviews about this process (Bahnemann, 2004; Fox & Dulay, 1993; Herrmann et al., 2007; Hoffmann et al., 1995; Legrini et al., 1993). Photocatalytic oxidation is based on the use of UV light and a semiconductor. Many catalysts have been tested, although titanium dioxide ( $\text{TiO}_2$ ) in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost (Bahnemann, 2004; Fox & Dulay, 1993; Hoffmann et al., 1995; Legrini et al., 1993).

Matthews (1990) reported that more than 90% of nitro benzene (NB) mineralization was achieved with  $\text{TiO}_2$  and sunlight. Minero et al. (1994) studied the photocatalytic degradation of NB on  $\text{TiO}_2$  and ZnO and reported complete mineralization with  $\text{TiO}_2$ . Titanium dioxide has become the most studied and used photocatalyst, because it is easily available, chemically robust and durable. It can be used to degrade, *via* photocatalysis, a wide range of organic compounds (Herrmann et al., 2007; Hincapié et al., 2005; Leyva et al., 1998; Robert & Malato, 2002). Photocatalytic degradation of phenolic compounds by employing Degussa P-25® in presence of sunlight has been successfully studied by many researchers (Curcó et al., 1996; Minero et al., 1994).

## 2. Background of photocatalysis

### 2.1 Photocatalytic process

The presence of non-biodegradable and toxic organic compounds in wastewater is one of the major problems in wastewater treatment. Organic compounds like phenol and its derivatives are known for their toxicity and are classified as persistent organic chemicals (POC) which is a major threat to human health. Phenol in particular, which is carcinogenic, is introduced to the water bodies by various means. Industrial manufacturers, normal households, and landfill leachate contribute these organic compounds (Bahnemann, 2004) into the water bodies and makes wastewater treatment more difficult. All these pollutants need to be removed from wastewater before it can be discharged to the environment. Such contaminants may also be found in surface and subsurface water which require treatment to achieve desirable drinking water quality (Lindner et al., 1995). Conventional water treatment process like activated carbon adsorption, membrane filter, ion exchange etc. generate and produce extra waste during the purification system, which will further increase the cost and time. As a result, many studies and researches have been carried out to develop a sustainable and cost-efficient treatment process that can effectively remove or degrade these organic and inorganic chemicals in wastewater (Ahmed et al., 2010; Zeltner et al., 1996) with photocatalysis gaining much attention in the field of contaminant mineralization.

Majority of the natural purification of aqueous systems such as aerated lagoons or ponds, rivers and streams, lakes etc. are caused by the action of sunlight. Organic molecules were breakdown by the action of sunlight to simpler molecules and finally to carbon dioxide and

other mineral compounds. There are many natural accelerators which can be used to accelerate this natural process. The introduction of 'colloidal semiconductor' and catalyst to catalyze distinct redox reactions on semiconductors could boost this sunlight driven natural purification process (Matthews, 1993).

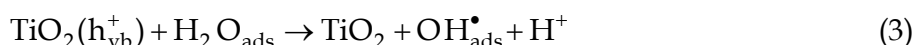
Wastewater treatment using photocatalysis involves the combination of heterogeneous photocatalysis with solar technologies (Zhang et al., 1994). Semiconductor photocatalysis, especially titania-based photocatalysis has been applied to various environmental problems other than water and air purification. Different studies have been carried out from fundamental to practical aspects to improve the process and the properties of the photocatalyst in recent years (Rajeshwar & Ibanez, 1997; Schiavello, 1997; Serpone & Pelizzetti, 1989). Hoffman et al. (1995) reported in that the utilizations of irradiated semiconductors for the degradation of organic pollutants were well documented and have shown positive and encouraging results for various organic pollutants. Various studies have also been carried out from fundamental to practical aspects to improve the process and the properties of the photocatalyst in recent years.

## 2.2 Mechanisms of generating oxidizing species

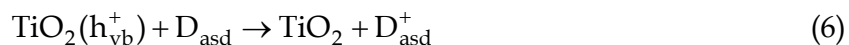
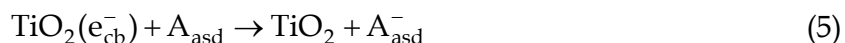
The heterogeneous photocatalysis process is very complex. The oxidizing pathway is not very clear yet. Jean-Marie Herrmann (1999) suggested in that the overall of classic heterogeneous photocatalysis process can be divided into five steps (Herrmann, 1999):-

1. Transfer of reactants to the surface
2. Adsorption of one of the reactants
3. Reactions of the reactants in the adsorbed phase
4. Desorption of the product(s)
5. Diffusion of the product(s) from the surface

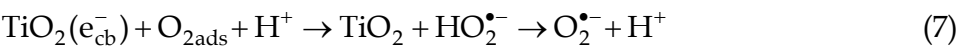
There are two pathways where the OH radicals can be formed. The valence band hole,  $h^+_{vb}$  can either react with the adsorbed water or the surface OH<sup>-</sup> groups on the titanium dioxide (TiO<sub>2</sub>) particle (Ekabi & Serpone, 1988). Equations 3 and 4 show the two reactions.



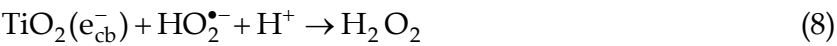
Generally, an acceptor molecules (A) such as O<sub>2</sub> will be adsorbed and react with an electron in the conduction band while a donor molecules (D) such as H<sub>2</sub>O will be adsorbed as well and react with a hole in the valence band. The above reactions are presented in reactions 5 and 6.



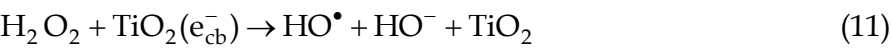
It is widely accepted that O<sub>2</sub> plays an important role in these reactions. Oxygen can trap conduction band electrons to form superoxide ions (O<sub>2</sub><sup>•-</sup>) according to reaction 7. These O<sub>2</sub><sup>•-</sup> can then react with hydrogen ions (H<sup>+</sup>) from the water splitting process to form HO<sub>2</sub><sup>•</sup>.



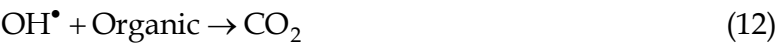
H<sub>2</sub>O<sub>2</sub> could also be formed from the HO<sub>2</sub>•- species by reaction 8.



OH radical (OH•) may be formed from the cleavage of H<sub>2</sub>O<sub>2</sub> via one of the following reactions 9, 10, 11.



The OH radical from reaction 4 is the most important oxidant formed in a photocatalytic process. It is the primary oxidant in the degradation of organic compounds (Ahmed et al., 2010). The degradation reaction is expressed in reaction 12.



2.3 Photocatalytic materials

2.3.1 Photocatalysts

There are many semiconductor materials can be used as a photocatalyst. Semiconductors like TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, ZnS etc. are all suitable materials to initiate a photocatalytic process. Extensive studies and research concludes that an ‘ideal photocatalyst’ should possess the attributes shown in Table 1.

Attributes of an ideal photocatalyst for heterogeneous photocatalysis
<ul style="list-style-type: none"><li>• Stability and sustained photoactivity</li><li>• Biologically and chemically inert, non toxic</li><li>• Low cost</li><li>• Suitability towards visible or near UV light</li><li>• High conversion efficiency and high quantum yield</li><li>• Can be react with wide range of substrate and high adaptability to various environment</li><li>• Good adsorption in solar spectrum</li></ul>

Table 1. Attributes of an ideal photocatalyst for heterogenous photocatalytic process (Bhatkhande et al., 2001)

Titanium dioxide (TiO<sub>2</sub>) has been widely recognized as an excellent photocatalyst. It is known to have superb pigmentary properties, high adsorption in the ultraviolet region, and high stability which allows it to be used in various applications such as electroceramics, glass, and photocatalytic purification of chemical in air and water. Two types of reactors have been developed which are suspension/slurry and thin film/fixed in wastewater



treatment (Chang et al., 2000; Huang et al., 1999; Matthews et al., 1990). The details of these two reactors will be discussed later.

Titanium dioxide ( $\text{TiO}_2$ ) exist as many crystalline forms. The most common forms of crystalline structures are anatase and rutile. Brookite is the most uncommon form due to its instability in terms of the enthalpy of formation. Anatase is the most stable among all the different crystalline forms with  $8\text{--}12\text{kJmol}^{-1}$  (Cotton et al., 1999). It can be converted to rutile when it is heated to approximately  $700^\circ\text{C}$  (Bickley et al., 1991). Anatase is less dense compared to rutile, has a density of  $3900\text{kg/m}^3$  while rutile has a density of  $4260\text{kg/m}^3$ . In the application of photocatalysis, anatase is a more efficient photocatalyst compared to rutile due to its open crystalline structure.

### 2.3.2 Titanium dioxide (Degussa P25)

It was been used extensively in many studies regarding photocatalytic degradation. Photocatalytic degradation studies utilizing Degussa P25 have been well documented due to its chemical stability, readily availability, reproductive ability, and activity as a catalyst for oxidation process (Bekbolet et al., 1998; Bekbolet & Balcioglu, 1996; Saravanan et al., 2009). Vigorous activities and researches are in process to further develop the existing Degussa P25 or synthesizing new materials, which can initiate photocatalysis using solar energy and hence reduce the cost and shortening the total time needed for the degradation. These developments include increasing the effective surface area, increasing the photoactivity, increasing the active sites, enhancing the absorption of photon energy and reducing the band-gap energy.

### 2.4 Photocatalytic reactors

There are many types of reactors have been developed and can be used in photocatalytic studies. These reactors were developed based on the different needs of applications. The selection of these reactors was according to the experiment conditions and applications. Generally the reactors can be briefly categorized into two groups, a suspension/slurry type and a thin film type. A slurry type reactor uses the catalyst in a suspension form whereas a thin film type reactor uses a thin film catalyst. Both types of reactors can be designed to be an immersion well reactor or flat wall reactor. Immersion well reactors were generally used in laboratory scale works for evaluation purposes. It can be run on either batch or continuous mode. The flow of oxidant and the temperature can be easily controlled and monitored. The source of the light can either be single or multiple with or without any reflectors. A suspension form is preferred because it is normally more efficient compared to the thin film reactor. It is because in a suspension type reactor, the catalyst has a higher effective surface area and hence larger surface area in contact with the substrate. This allows a larger amount of photon to hit the surface and results in large adsorption capacity.

Other types of reactors are flat wall and tubular photoreactors. These types of reactors are simple and easy to design. Air can be use as an oxidant option for these reactors. Besides, solar energy can be utilized by these types of reactors. Moreover, reflectors are used in a tubular reactor to concentrate sunlight so that it can enhance the photoreaction.

For the past 20 years, several photocatalytic water treatment reactors have been developed and tested. Different reactors were developed to find the best way of conducting solar

wastewater treatment process. Different principles and technologies were adopted including sunlight concentrating system. Four most frequent used photoreactors will be presented in the following text.

#### 2.4.1 Parabolic through reactor (PTR)

A parabolic through reactor adopted the principle of parabolic through solar concentrating system' to concentrate the sunlight on the focal point using Dewar tube. The schematic presentation is given in Fig. 1. The PTR concentrates the parallel (direct) rays of the photocatalytically active ultra-violet part of the solar spectrum and can be characterized as a typical plug flow reactor. Borosilicate glass tube which positioned along the focal line was filled with contaminant with titanium dioxide ( $\text{TiO}_2$ ) in suspension with a flowrate ranges between  $250\text{--}3500\text{Lh}^{-1}$ . This type of reactor had been selected as the first solar detoxification loops in Albuquerque and California in USA and Almeria in Spain (Bahnemann, 2004). Several research groups from the European continent have tested the PTR which installed at the Plataforma Solar de Almeria (PSA) in Spain for solar wastewater purification in the early 1990s (Bahnemann, 2004).

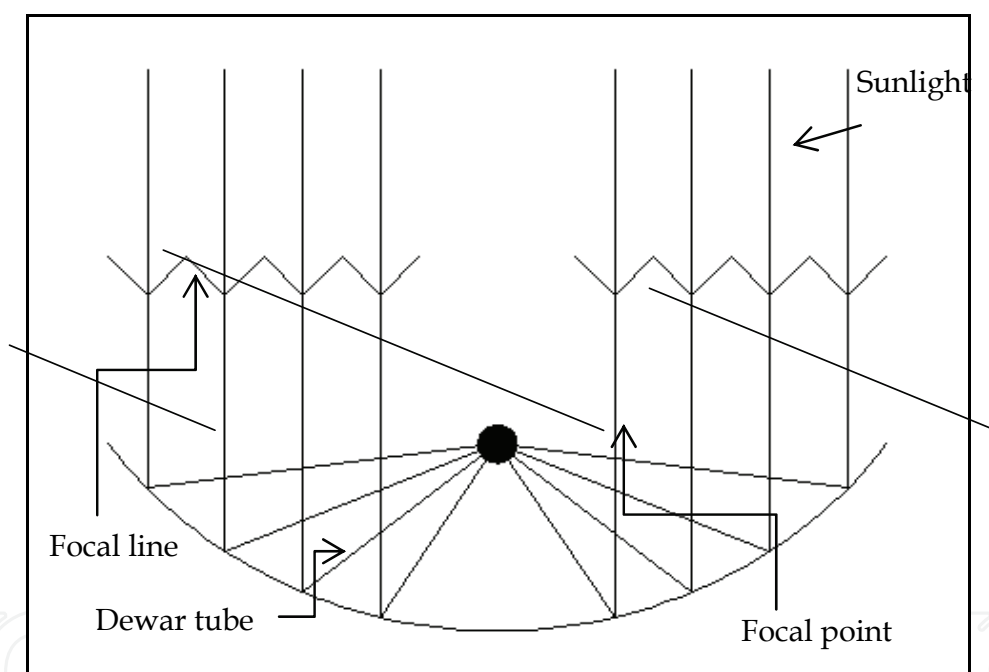


Fig. 1. A schematic view of a parabolic through solar concentrator

#### 2.4.2 Thin film fixed bed reactor (TFFBR)

Thin film fixed bed reactor (TFFBR) is one of the very first solar reactor which does not utilize a solar concentrating system. It implies that the TFFBR can utilize the diffuse as well as the direct portion of the solar UV-A illumination for the photocatalytic process. A TFFBR installed at PSA is depicted in Fig. 2 (Bockelmann et al., 1995; Goslich et al., 1997; Hilgendorff et al., 1993). The most important aspect in the TFFBR is the slopping plate coated with photocatalyst like Degussa P25 (Bockelmann, 1993) and rinsed with contaminated water in a very thin film ( $\sim 100\mu\text{m}$ ). The flowrate was controlled by a cassette peristaltic pump and ranges from  $1\text{--}6.5\text{Lh}^{-1}$  (Bockelmann et al., 1995).





Fig. 2. A TFFBR installed at the PSA in Spain (Bockelmann et al., 1995)

The TFFBR was tested during its operation at the PSA. The efficiency of the performance of the TFFBR was found to be higher than that of the PTR during several test campaigns utilizing both model pollutants dissolved in pure water and real wastewater samples collected from a variety of industrial companies (Bahnemann, 2004).

**2.4.3 Compound parabolic collecting reactor (CPCR)**

The compound parabolic collecting reactor (CPCR) is a through reactor without any solar concentrating properties. The major difference between the PTR and CPCR is the shape of their reflecting mirrors. The reflector of a PTR has a parabolic profile and the pipe is

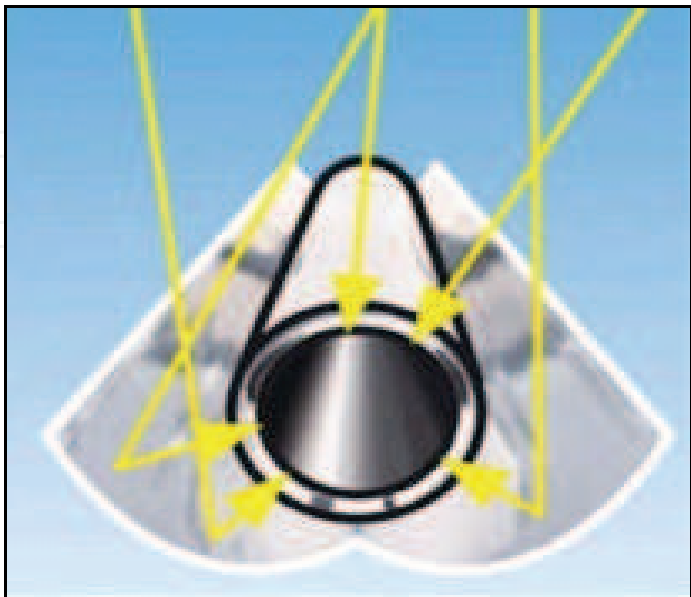


Fig. 3. Schematic view of the reflector of a CPCR

positioned along the focal line. Subsequently only parallel light which enters the parabolic through can be concentrated on the pipe. The reflector of a CPCR generally made up of two half circle profiles side by side. The focal line is situated just above the connections of the two circles. Thus light entering from almost any angle can be reflected to the focal line of the CPCR. Fig. 3 shows the schematic view of the reflector of a CPCR.

#### 2.4.4 Double skin sheet reactor (DSSR)

The double skin sheet reactor is a new kind of reactor which does not have a light concentrating properties. It is a flat and transparent structured box made of PLEXIGLAS® (Van Well et al., 1997). PLEXIGLAS® is a trademark of a commercialized Poly(methyl methacrylate) (PMMA) which is a transparent thermoplastic. The inner structure of the DSSR is depicted in Fig. 4. The suspension of the model pollutant and the photocatalyst is allowed to flow through these channels. The DSSR can use both the diffuse and direct portion of the sunlight.

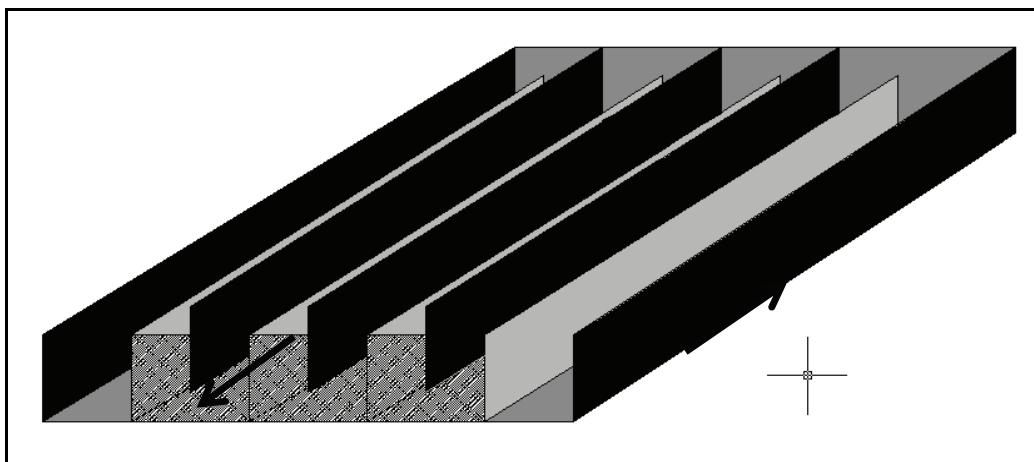


Fig. 4. A schematic view of the inner structure of a DSSR

#### 2.5 Synthesis and doping method

Many studies had been carried out to alter the characteristics of the titanium dioxide ( $\text{TiO}_2$ ) in order to improve the practical and commercial values of titanium dioxide ( $\text{TiO}_2$ ) as a photocatalyst. For most of the cases, doping was carried out to improve the photocatalytic activity, the absorption of visible region of the solar spectrum, and to impart separable property.

Ao et al. (2009) reported the degradation of a dye (Red X-3B) under sunlight using N-doped titania-coated g- $\text{Fe}_2\text{O}_3$  magnetic activated carbon (NT-MAC). The titanium dioxide ( $\text{TiO}_2$ ) was doped with nitrogen to improve the visible light absorption while the g- $\text{Fe}_2\text{O}_3$  magnetic activated carbon was coated to impart the magnetic properties. The preparations were carried out under low temperature and ambient pressure. It is reported that the photocatalytic of the NT-MAC was approximately three times than that of Degussa P25. The separation can be done easily using an external magnetic field. Furthermore, the prepared NT-MAC can be recycled and reused without any mass losing and the degradation of the X-3B remains higher than 85% after six cycles (Ao et al., 2009).

Han et al. (2009) studied the degradation of organic dyes using various modified titanium dioxide ( $\text{TiO}_2$ ) photocatalysts. The modifications include doping with metals (noble metals, transition metals, lanthanide metals, alkaline and alkaline earth metals, cadmium sulphide etc.) and non-metals (nitrogen, fluorine, sulphur, carbon etc.). The purposes of these modifications and doping were to improve photocatalytic efficiency, complete degradation of organic dyes, improve visible light absorption, improve stability and reproducibility, and to improve recycle and reuse abilities of titanium dioxide ( $\text{TiO}_2$ ). The modified titanium dioxide ( $\text{TiO}_2$ ) showed considerably improved photocatalytic activity. For example, a complete degradation of Rhodamine (RB) in 105 minutes was observed using silver doped indium (III) oxide-coated  $\text{TiO}_2$  ( $\text{Ag}/\text{In}_2\text{O}_3\text{-TiO}_2$ ) as photocatalyst in 2008. It is more efficient than degradation using Degussa P25 which is 85.9% (Han et al., 2009).

Narayana et al. (2011) studied the photocatalytic decolourization of basic green dye using pure and ferum (Fe) and cobalt (Co) doped titanium dioxide ( $\text{TiO}_2$ ) under sunlight irradiation. The purpose of doping was to improve the visible light absorption of the photocatalyst. The doped titanium dioxide ( $\text{TiO}_2$ ) was prepared using sol-gel method. The Fe-doped titanium dioxide ( $\text{TiO}_2$ ) showed the highest photoactivity among the other two with a 98% degradation of dye under sunlight illumination. Hence, doped titanium dioxide ( $\text{TiO}_2$ ) can have very high commercial value in wastewater treatment since it utilizes only sunlight, which is a natural resource for reaction activation (Narayana et al., 2011).

Wang et al. (2010) doped titanium dioxide ( $\text{TiO}_2$ ) with tin (Sn) and nitrogen (N) intended to improve the visible light absorption of titanium dioxide ( $\text{TiO}_2$ ) photocatalyst. The doping was successfully carried out via simple sol-gel method. Pure  $\text{TiO}_2$ , N-doped  $\text{TiO}_2$ , Sn-doped  $\text{TiO}_2$ , and co-doped N/Sn- $\text{TiO}_2$  were tested separately to compare their characteristics. N/Sn- $\text{TiO}_2$  recorded the highest absorption in the visible region of solar spectrum. Besides, N/Sn- $\text{TiO}_2$  also recorded the highest visible-light activity among the other three by using 4-chlorophenol (4-CP) in water under visible light illumination. Surprisingly, N/Sn- $\text{TiO}_2$  also had the highest photoactivity under UV irradiation. This implies that the co-doping of two foreign ions is more efficient in improving photoactivity of titanium dioxide ( $\text{TiO}_2$ ) compared to doping of one ion (Wang et al., 2010).

A simple sol-gel method to prepare titania-coated magnetic porous silica (TMS) photocatalyst was reported by Wang et al. (2010). The TMS was then employed in the degradation of red X-3B dye under UV and visible light irradiation to determine its photocatalytic activity. The same was done using commercialized titanium dioxide ( $\text{TiO}_2$ ), Degussa P25 for comparison purpose. They recorded that the TMS had considerably higher photoactivity compared to that of Degussa P25, under either UV or visible light illumination. The TMS can be separated by applying external magnetic and thus can be reused without any mass loss. Hence, TMS can be a suitable photocatalyst for practical water purification system due to its high photocatalytic activity and separability (Wang et al., 2010).

## 2.6 Applications of photocatalysis on water and wastewater treatment

Since the discovery of water splitting phenomenon via photocatalysis by Fujishima and Honda in 1972, the research and development of the heterogeneous photocatalytic process has never been stop and has been growing rapidly (Linsebigler et al., 1995). Though early studies and researches were focused on the energy production i.e. the production of clean

fuel using hydrogen, heterogeneous photocatalysis has taken a new step since its breakthrough in the environmental remediation field. Today, this technique has been implemented in various applications, from water and air treatment to health applications.

### 2.6.1 Degradation of organics

The degradation of organics perhaps is the most important applications of photocatalysis. The degradations of organic compounds such as alcohols, carboxylic acids, phenolic derivatives or chlorinated aromatics into non-hazardous and harmless products or residues such as carbon dioxide, water or other minerals had been well documented (Bhatkande et al., 2001; Chen & Ray, 2001; Michael et al., 1995; Mills et al., 1993; Pirkanniemi & Sillanpaa, 2002). Joanna et al. (2000) reported that oily water can also be treated effectively by photocatalysis. Herbicides and pesticides like 2, 4, 5, trichlorophenoxyacetic acid, 2, 4, 5, trichlorophenol, s-triazine herbicides and DDT which generally considered as hazardous pollutants can also be completely mineralized (Olis et al., 1991).

### 2.6.2 Elimination of inorganics

Other than the organic chemical compounds mentioned above, a variety of inorganic compounds are sensitive to photochemical conversion on the catalyst surfaces. Inorganics such as chlorate and bromate (Mills et al., 1996), azide, halide ions, nitric oxide (NO), palladium (Pd) and rhodium (Rh) species, and sulphur species can be broken down (Michael et al., 1995). Metal salts like silver nitrate ( $\text{AgNO}_3$ ), mercury (II) chloride ( $\text{HgCl}_2$ ) and organometallic materials can be eliminated from water (Bhatkande et al., 2001), as well as cyanide ( $\text{CN}^-$ ), thiocyanate ( $\text{SCN}^-$ ), ammonia ( $\text{NH}_3$ ), nitrates ( $\text{NO}_3^-$ ) and nitrites ( $\text{NO}_2^-$ ) (Blake, 2001).

### 2.6.3 Elimination of natural organic matter

Humic substances (HS) can be generally defined as a class of naturally existing biogenic heterogeneous organic substances that can be further classified as being yellow-brown and having high molecular weights (MacCarthy, 2001). HS can also be defined as the fraction of filtered water that adsorb on XAD-8 resin (a non-ionic polymeric adsorbent) at pH 2 (Obernosterer & Herndl, 2000). They are the major components of the dissolved organic carbon (DOC) pool in surface water (marine waters and fresh waters) and sub-surface or ground waters. They are often said to be a main factor that lead to yellowish-brown colour in the water bodies (Schmitt-Kopplin, 1998). The concentration of the HS differs from place to place; seawater normally contains 2-3mg/L of HS. According to Gaffney et al. (1996), their physical properties like size and their chemical properties like the structure and the number and position of the functional group differ, relying on the origin and the age of the substance (Gaffney et al., 1996).

HS are known to have the ability to change the behaviour of certain pollutants considerably, such as trace metal speciation and toxicity, (Bekbolet & Balcioglu, 1996; Shin et al., 1996), solubilisation and adsorption of hydrophobic contaminants (Chiou et al., 1986; Tanaka et al., 1997) and aqueous photochemistry (Fukushima et al., 2000). HS can act as substrates for bacterial growth, hinder the bacterial degradation of impurities (colours), interact with heavy metals such as Fe, Mn and Pb and thus making them difficult to remove, help to



transport the metals into the environment and also contribute to pipe corruptions (Motheo & Pinhedo, 2000). Besides, HS can also act as a source of methyl groups and hence react with hypochlorite ions which are being used as biocide in water treatment plants to produce disinfectant by-products. Examples of these by-products are trihalomethanes, haloacetic acids, other chlorinated compounds and nitriles. Some of these by-products are suspected to be carcinogenic. Till date, more than 150 products have been recognized as the products of the reaction between HS and chlorine.

The advance oxidation process has been implemented to decrease the organic matter in water including the HS. Its major advantage is that the advance oxidation process does not produce any toxic by-products or residues which required further treatment or disposal. Till date, the degradation of HS using photocatalytic process has not been studied well. The very first study based on this was carried out by Bekbolet in 1996, who studies the effectiveness of photocatalytic treatment on the degradation of model humic substances or humic acid (Bekbolet & Ozkosemen, 1996).

Bekbolet and Ozkosemen studied about the degradation via photocatalytic process using humic acid as a model pollutant. Through the experiment, they found out that after one hour of illumination in the presence of 1.0g of Degussa P25, 40% of the TOC and 75% of the colour (400nm) were removed (Bekbolet & Ozkosemen, 1996). Bekbolet and co. again studied the removal of colour caused by humic acid in the presence of common inorganic ions (e.g. chloride, nitrate, phosphate and sulphate ions) at pH 6.8, and they found some removal (Bekbolet et al., 1998). In other researches where humic acid was used as an additional matrix for the degradation of some organic pollutants, a 80% removal of commercialized humic acid was recorded by using irradiation in the presence of Degussa P25 (Minero et al., 1997). Another similar study showed a reduction around 50% of the concentration of humic acid in just 12 minutes using suspension of Degussa P25 irradiated by a mercury lamp (Eggins et al., 1997).

#### 2.6.4 Removing trace metals

Trace metals especially mercury (Hg), lead (Pb), chromium (Cr) and many others are considered extremely hazardous to human being. The presence of these metals in water bodies should be removed. Photocatalysis can be used to remove heavy metals like mercury (Hg), chromium (Cr), lead (Pb), cadmium (Cd), arsenic (As), nickel (Ni), and copper (Cu) (Blake, 2001; Olis et al., 1991). Other than that, the photochemical ability of the photocatalysis enables it to recover costly metals from industrial waste discharge such as gold (Au), platinum (Pt) and silver (Ag) (Olis et al., 1991).

#### 2.6.5 Water disinfections

Photocatalysis can be used in water disinfections because it can kill or destroy various bacteria and viruses. In 1997, a study by Mills and LeHunte reported that *Streptococcus mutans*, *streptococcus natuss*, *streptococcus cricetus*, *escherichia coli*, *scaccharomycescerevisisas*, *lactobacillus acidophilus*, poliovirus 1 were destructed effectively using heterogeneous photocatalysis (Mills & LeHunte, 1997). With algae blooming in fresh water supplies becoming more and more common, the subsequent possibility of cyanobacterial microcystin pollution of portable water caused by *Microcystin* toxins. In 2002, Shephard et al. reported

that Microcystin toxins can be degraded on immobilized titanium dioxide ( $\text{TiO}_2$ ) photocatalyst (Shephard et al., 2002). Matsunaga and Tomoda in 1985 first reported on photocatalytic disinfection. They found that in the presence of high concentrations of microorganisms, disinfection process was effective and more efficient. Similarly, Belapurkar et al., 2006 prepared high surface area  $\text{TiO}_2$  by hydrothermal method using titanium isopropoxide. They applied for disinfection of water and found to be effective when 1 L of water was photolysed by solar light in a plastic tray containing  $\text{TiO}_2$  photocatalyst coated on a stainless plate. Their study also proved that the technique can be used for disinfection of ~20 L water daily using solar light. Finally concluded that the photocatalytic technique using solar light, a viable, simple and easy-to-use device for disinfection of drinking water on liter scale (Belapurkar et al., 2006).

### 2.6.6 Seawater treatment

Lately, the decomposition of humic substances in artificial seawater (highly saline water) and natural seawater were studied by Al-Rasheed and Cardin (Al-Rasheed & Cardin, 2003). Although the decompositions were found to be slower compared with a fresh water media usually employ by other researches, no toxic or hazardous by-products were found throughout the decomposition process.

The degradation of some crude oil components (dodecane and toluene) via photocatalysis using seawater media was carried out in 1997 (Minero et al., 1997). No chlorinated compounds were found over the course of irradiation. 100% degradation was recorded after just few hours of illumination. Ziolli and Jardim reported in 2002 that seawater-soluble crude oil fractions can be decomposed under the irradiation of nanoparticles of titania using artificial light (Ziolli & Jardim, 2002).

## 2.7 Current and future scope

The number of new publications regarding photocatalysis for water and wastewater treatment has been increasing significantly since the last decade.

The photocatalytic oxidation of towards water treatment has caught up most of the attention. Recently, the attention started to shift onto the oxidation of volatile organic or inorganic compounds present in ground water for an efficient treatment. Photocatalytic reduction organic compounds and metal-containing ions and researches on cell destroying and disinfection by irradiated titania has also caught up some attention (Zaleska, 2008).

Subsequently, titania-based photocatalysts has been commercialized in various fields firstly in Japan, followed by the United States and then China. This commercialization of  $\text{TiO}_2$ -based photocatalysts products was started during the mid 90s in Japan. Among commercialisation the purification equipment (e.g. air purifiers, air conditioners, portable water purification system, purification system for pools) and household equipment is more promising achievements in field of water treatment. (Zaleska, 2008).

Though a number of commercial  $\text{TiO}_2$  is available in market they lag in low sensitivity of photocatalyst towards visible light, which cannot take up the visible spectrum (largest part) in the solar radiation for waste treatment. Hence scientific community is eager to increase the sensitivity of photocatalyst to visible light so that sunlight could be used for excitation for a sustainable waste treatment.



In the present scenario, the major difficulty regarding the doped  $\text{TiO}_2$  photocatalyst is the possible loss of photoactivity due to recycling of photocatalyst and long-term storage. It is believed that the efficiency of the metal-doped  $\text{TiO}_2$  under visible light wholly depends on the synthesizing and doping method adopted. In some cases, such doped photocatalysts showed zero activity under visible light or considerably lower activity in the ultraviolet spectral range compared to the non-doped  $\text{TiO}_2$  because of high carrier recombination rates through the metal ion levels. The problem is that the non-metal-doped  $\text{TiO}_2$  catalyst has very low photoactivity under visible light compared to that under UV light (Zaleska, 2008).  $\text{TiO}_2$  with visible light absorption can be employed to purify and disinfect the water and make it more suitable for consumption. Beside these limitations the major edge of the photocatalytic oxidation process over other process is because it's an only green and sustainable process towards waste treatment.

### 3. Conclusion

Strictly speaking, contaminant treatment can be defined as the complete degradation or mineralization of the contaminants. However, the photocatalytic degradation is suitable for treating hazardous organic pollutants. Generally, biological treatment is the most economical treatment option and the most compatible with the environment when feasible. Though the feasibility of adopting the photocatalytic oxidation is much explored they are not adopted practically, due to the problem of surplus power needed for generation of UV radiation. But in the present years ferrite doped titanium dioxide ( $\text{TiO}_2$ ) addresses this issue and, it also enhances the reusability of the catalyst. Hence it could be an ideal treatment to transform the bio-persistent compounds for an effective treatment system with sustainability. They also address the green technology, by utilizing sunlight as their source of excitation. This could be further eliminates or reduces the production of sludge's, a secondary pollutant. In near future the practise of biological methods could be replaced by the heterogeneous oxidation process. Such replacement will lead pathway to a green technology for the sustainable development.

### 4. Acknowledgement

The authors are grateful to IPPP, Department of Civil Engineering and Faculty of Engineering University of Malaya for their grant (RG091/10SUS) and moral support respectively.

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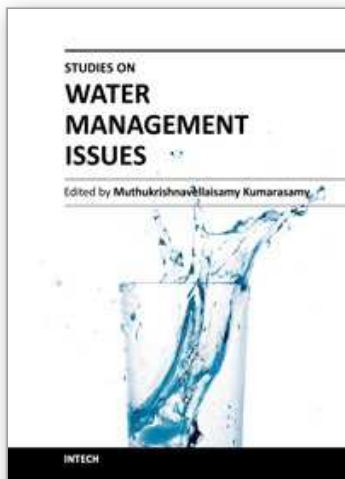
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### **Studies on Water Management Issues**

Edited by Dr. Muthukrishnavellaisamy Kumarasamy

ISBN 978-953-307-961-5

Hard cover, 274 pages

**Publisher** InTech

**Published online** 18, January, 2012

**Published in print edition** January, 2012

This book shares knowledge gained through water management related research. It describes a broad range of approaches and technologies, of which have been developed and used by researchers for managing water resource problems. This multidisciplinary book covers water management issues under surface water management, groundwater management, water quality management, and water resource planning management subtopics. The main objective of this book is to enable a better understanding of these perspectives relating to water management practices. This book is expected to be useful to researchers, policy-makers, and non-governmental organizations working on water related projects in countries worldwide.

#### **How to reference**

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Cheng Chee Kaan, Azrina Abd Aziz, Shaliza Ibrahim, Manickam Matheswaran and Pichiah Saravanan (2012). Heterogeneous Photocatalytic Oxidation an Effective Tool for Wastewater Treatment – A Review, Studies on Water Management Issues, Dr. Muthukrishnavellaisamy Kumarasamy (Ed.), ISBN: 978-953-307-961-5, InTech, Available from: <http://www.intechopen.com/books/studies-on-water-management-issues/heterogeneous-photocatalytic-oxidation-an-effective-tool-for-wastewater-treatment-a-review>

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