DEVELOPMENT OF BILAYER TiO_2 PHOTOCATALYST SYSTEMS IMMOBILIZED ON STAINLESS STEEL PLATE AND THEIR PHYSICAL AND PHOTOCATALYTIC CHARACTERIZATION

by

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LIST OF ABBREVIATION

AAS	Atomic Absorption Spectroscopy
COD	Chemical Oxygen Demand
g	Gram
mg	Milligram
min	Minute
mL	Milliliter
UV	Ultra Violet
µL	Microlitre
rpm	Rotation per minute
ppm	Parts per million
CBR	Cibacron Brilliant Red
TEM	Tramission Electronic Microscopic
EDX	Energy Dispersion X-Ray
XRD	X-Ray Diffraction
BET	BET surface analysis

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PEMBANGUNAN SISTEM FOTO-PEMANGKINAN TiO_2 DUA LAPISAN YANG DIPEGUN PADA KEPINGAN KELULI DAN PENCIRIAN SIFAT FIZIKAL DAN FOTO-PEMANGKINANNYA

ABSTRAK

Kelemahan utama TiO_2 ialah ia memerlukan cahaya UV di bawah 380 nm yang dianggap berbahaya kepada manusia and mahal dari segi kos untuk mengaktifkan sifat foto-pemangkinannya. Oleh sebab itu, pelbagai teknik telah digunakan untuk megubahkan aktiviti foto-pemangkinan TiO_2. Salah satu kaedah ialah mendopkan atau menggabungkan pelbagai jenis logam oksida, logam sulfida, logam berat and ion logam kepada TiO_2. Sejak kebelakangan ini, penjerap juga digunakan untuk mendop secara sampingan kepada TiO_2. Dalam pengajian ini, lapisan TiO_2 dipegunkan pada permukaan lapisan penjerap NiO dan kitosan yang disokong pada kepingan keluli. Sistem ini dikenali sebagai sistem hibrid fotomangkin dua lapisan. Keberkesanan foto-pemangkinan sistem ini terhadap penyahwarnaan pencerup sibakron merah (CBR), metilena biru (MB) dan bromokresol ungu (BP) di bawah sinaran UV dan cahaya nampak telah dikajikan. Parameter-parameter untuk membina fotomangkin dua lapisan yang telah dioptimisasikan berdasarkan kepada keberkesanan foto-pemangkinannya terhadap penyahwarnaan penjerup CBR dalam pengajian ini ialah suhu pemanasan NiO dan suhu pengeringan kitosan dan jumlah resin fenol formaldehid, TiO_2, NiO dan kitosan. Parameter-parameter lain yang telah dikajikan adalah kesan aditif-aditif tak organic dan kation logam yang terlarutlesap terhadap aktiviti foto-pemangkinan fotomangkin dua lapisan. Penjerap NiO yang telah dipanaskan dalam pelbagai suhu telah dicirikan dengan menggunakan TEM, EDX, XRD dan BET. Fotomangkin dua lapisan TiO_2/NiO boleh menyahwarnakan 90 dan 93.3 % penjerup CBR selepas disinarkan di bawah cahaya UV dan nampak selama satu jam. Ia juga boleh menyahwarnakan 34 % penjerup BP dalam media asid dan 96 % penjerup MB dalam media alkali selepas disinarkan selama satu jam di bawah cahaya nampak. Manakala,

fotomangkin dua lapisan TiO_2/kitosan boleh menyahwarnakan 98 % penjerup BP, 87 % penjerup CBR dan kurang daripada 10 % penjerup MB di bawah sinaran cahaya nampak selama 30 minit. Suhu dan masa pemanasan optimum bagi NiO dan kitosan adalah 400 °C selama 10 jam dan 150 °C selama 5 jam. Jumlah optimum resin fenol formaldehid dalam pengenapan penjerap NiO pada kepingan keluli adalah 0.05 g. Jumlah optimum TiO_2 dan NiO dalam fotomangkin dua lapisan TiO_2/NiO adalah 0.07 g dan 0.2 g. Sementara, jumlah optimum bagi kedua-dua TiO_2 dan kitosan dalam fotomangkin dua lapisan TiO_2/kitosan adalah 0.04 g masing-masing. Aditif-aditif agen pengoksidaan seperti H_2O_2 and $Na_2S_2O_8$ boleh meningkatkan kadar penyahwarnaan larutan penjerup CBR dan BP apabila ia digunakan bersama-sama dengan fotomangkin dua lapisan TiO_2/NiO dan TiO_2/kitosan. Di sebaliknya, adtitif-aditif agen pengoksidaan membantutkan penyahwarnaan MB apabila ia digunakan bersama-sama dengan fotomangkin dua lapisan TiO_2/NiO. Walau bagaimanapun, aditif agen penurunan seperti $NaBH_4$ meningkatkan penyahwarnaan penjerup MB apabila ia digunakan bersama-sama dengan fotomangkin dua lapisan TiO_2/NiO. Fotomangkin dua lapisan melarutlesap 90 dan 35 ppm kation-kation nikel ke dalam larutan pencerup CBR untuk perawatan kali pertama apabila disinarkan di bawah cahaya UV dan nampak. Kation nikel yang terlarutlesap berkurang dalam perawatan seterusnya ke kurang daripada 10 ppm selepas perawatan ketiga untuk kedua-dua sistem sinaran UV dan nampak. Tiada kation ferum (III) yang terlarutlesap ke dalam larutan pencerup di bawah sinaran cahaya nampak. Kation nikel memangkinkan penyahwarnaan larutan pencerup CBR tetapi membantut penyahwarnaan pencerup MB apabila disinarkan di bawah cahaya nampak dengan kehadiran fotomangkin dua lapisan TiO_2/NiO dan pengudaraan. Keputusan-keputusan TEM, XRD, EDX dan BET menunjukkan bahawa NiO yang dipanaskan pada suhu yang lebih tinggi mempunyai size zarah yang lebih besar. Akhirnya, activity foto-pemangkinan TiO_2 boleh ditingkatkan dengan penggandingan NiO dan kitosan sebagai lapisan kedua. Walau bagaimanapun, peningkatan ini kebanyakan untuk pencerup anionic. Kitosan meningkatkan aktiviti

foto-pemangkinan TiO_2 lebih daripada NiO. Ion nikel yang terlarulesap daripada penjerap NiO boleh mempergaruhi aktiviti foto-pemangkinan TiO_2/NiO. Semua agen pengoksidaan meningkatkan penyahwarnaan penjerup anionik tetapi mengurangkan penyahwarnaan pencerup kationik. Kitosan adalah penjerap lebih sesuai dan baik berbanding dengan NiO kerana ia tidak melarutlesapkan sebarang pencemar yang beracun ke dalam larutan yang drawati. Manakala, penjerap NiO membebaskan kation nikel ke dalam larutan yang dirawatkan dan langkah selanjutnya diperlukan untuk memindahkan kation nikel ini.

DEVELOPMENT OF BILAYER TiO_2 PHOTOCATALYST SYSTEMS IMMOBILIZED ON STAINLESS STEEL PLATE AND THEIR PHYSICAL AND PHOTOCATALYTIC CHARACTERIZATION

ABSTRACT

The main weakness of TiO_2 is that it needs UV light with wavelengths below 380 nm, which are considered hazardous to human being and expensive in term of cost, to activate its photocatalytic property. Therefore, various techniques had been used to improve the photocatalytic activity of TiO_2. One of the method was doping or combining various types of metal oxides, metal sulfides, noble metal or metal ion with TiO_2. Recently, adsorbent also had been used to co-doped with TiO_2. In this research, TiO_2 layer was immobilized onto the surface of NiO and chitosan adsorbents layer, which were supported onto stainless steel plate. This system was called bilayer photocatalyst hybrid system. Photocatalytic efficiencies of this system to the decolorization of cibacron brilliant red dye (CBR), methylene blue (MB) and bromocresol purple (BP) under UV and visible light illumination had been studied. Parameters of the fabrication of the bilayer photocatalyst that had been optimized based on its photocatalytic efficiency to the decolorization of CBR dye in this research were calcining temperatures of NiO and drying temperatures of chitosan and amount of phenol formaldehyde resin, TiO_2, NiO and chitosan. Other parameters that had been studied were effect of inorganic additives and metal cation leaching on the photocatalytic acitivity of the bilayer photocatalysts. NiO adsorbents that had been calcined at various temperatures were characterized using TEM, EDX, XRD and BET. TiO_2/NiO bilayer photocatalyst could decolorize 90 and 93.3 % of CBR dye after one-hour illumination under UV and visible light. It also could decolorize 34 % of BP dye in acidic medium and 96 % of MB dye in alkaline medium after one-hour illumination under visible light. Whereas, TiO_2/chitosan bilayer photocatalyst could decolorize 98 % of BP, 87 % of CBR and less than 10% of MB dyes under visible light illumination for

30 minutes. Optimum calcining temperature and duration for NiO and chitosan were 400 °C for 10 hours and 150 °C for 5 hours. Optimum amount of phenol formaldehyde resin in the deposition of NiO adsorbent onto stainless steel plate was 0.05 g. Optimum amounts of TiO_2 and NiO in the TiO_2/NiO bilayer photocatalyst were 0.07 g and 0.2 g. While, optimum amounts of both TiO_2 and chitosan in the TiO_2/chitosan bilayer photocatalyst were 0.04 g, respectively. Oxidant additives such as H_2O_2 and $Na_2S_2O_8$ could increase the decolorization rate of CBR and BP dye solution when it was utilized together with TiO_2/NiO and TiO_2/Chitosan bilayer photocatalysts. Contrary, oxidant additives retarded decolorization of MB when it was utilized together with TiO_2/NiO bilayer photocatalyst. However, reductant additive such as $NaBH_4$ increased the decolorization of MB dye when it was utilized together with TiO_2/NiO bilayer photocatalyst. TiO_2/NiO bilayer photocatalyst leached 90 and 35 ppm of nickel cations into the CBR dye solution for the first treatment when illuminating under UV light and visible light. Leached nickel cation reduced in the following treatment to less than 10 ppm after 3rd treatment for both UV and visible light illumination system. There was no iron (III) cation was leached into the dye solution under visible light illumination. Nickel cation did catalyze decolorization of CBR dye solution but retarded the decolorization of MB dye when illuminating under visible light with the presence of TiO_2/NiO bilayer photocatalyst and aeration. Results from TEM, XRD, EDX and BET show that NiO that had been calcined at higher temperature has bigger particle size. Finally, TiO_2 photocatalytic aktiviti could be enhanced by coupling with NiO and chitosan as second layer. However, the enhancement is mostly for anionic dye. Chitosan enhances TiO_2 photocatalytic activity more than NiO. Nickel ion that has leached from the NiO adsorbent does influence the photocatalytic activity of the TiO_2/NiO. All of the oxidants increase the decolorization of anionic dye but decrease the decolorization of cationic dye. Chitosan is more suitable and better adsorbent compared to NiO because it does not release any toxic contaminant into the treated solution. Whereas, NiO adsorbent

releases toxic nickel cation into the treated solution and further step is needed to remove the nickel cation.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.0 Introduction

Water pollution is a major problem in the 21st century, especially in the developing countries. Now, people have realized that water is not an endless resource. Due to the global population growth, the need of clean water also grows. With the rapid development of science and technology, many industries, such as chemical, petrochemical, pharmaceutical and mining need huge amounts of water in their manufacturing processes. Ultrapure water is required in the pharmaceutical, microelectronics and semiconductor industries. Unfortunately, these industries have to discharge water, which is normally contaminated with toxic organic and inorganic compounds. In the recent two decades, water and air are contaminated to an unacceptable level all over the world by the pollutants coming from a variety of industrial and agricultural activities. Meanwhile, governments in most countries nowadays no longer tolerate untreated factory discharges and under the public pressure, regulations have been established to stipulate the level of contamination in the discharged water. Hence, innovative and effective water treatment processes are needed to treat the discharged water effectively in order to maintain the sufficient need of water resources.

The purpose of water purification is to reduce the pollution levels in discharged streams to meet the government regulations and to purify the water to ultrapure levels for industries involving pharmaceuticals, microelectronics and semiconductor. The ideal water treatment process should possess the ability to fully mineralize all the toxic species present in the waste stream without leaving any hazardous residues in the treated water. Besides that, it should be cost effective and economical. However, none of the available treatment technologies has achieved this ideal condition. There are a

number of waste disposal methods, which are currently applied with varying degrees of success. Figure 1.1 shows the various wastewater treatment technologies either currently available or at various stages of development.

Most of the industrial wastes are disposed based on the phase transfer principles processes (Conner, 1990), even though none of them is completely satisfactory. Air stripping is commonly used for removing volatile organic contaminants in wastewater. The process merely transfers the pollutants from the water phase to air phase without destroying them. Another commercialized process for water purification is granular activated carbon adsorption. In this case, the pollutants are transferred from the liquid phase into the solid phase. However, the spent carbon, which contains adsorbed pollutants, must then be disposed again. Because of the above reasons, alternative destructive oxidation processes for water treatment has been given greater attention (Matthews, 1992).

All of the above mentioned treatment methods are non-destructive technologies. Two available destructive technologies currently being used in the water industries are chlorination and ozonation. However, both chlorine and ozone are hazardous strong oxidants, which are not environmental friendly. Furthermore, ozonation has been proven to generate small levels of bromate ions, which are recognized as cancer causing agents (Mills and Hunte, 1997).

Biodegradation is another available destructive technology but its efficiency in degrading industrial waste water is low due to its very slow degradation rates. It is also known to present difficulties during operation at higher concentrations of organic contaminants (Pelizzetti *et al.*, 1990). In addition, active microorganisms that are intended to degrade organic contaminants may at times be killed by the toxicity of the organic contaminants present in the waste water. Therefore maintenance of these

micro-organisms at times can be very expensive. Incineration of organic wastes has been broadly used in developing countries. However, it releases toxic secondary pollutants into the air such as dioxin and furan (Shaub and Tsang, 1983).

In order to deal with the degenerating environment and to solve pollution problems from commercial wastewater discharges, researchers and scientists have been developing new innovative treatment processes. These processes are a new class of technologies that could be used promisingly to treat toxic organics in contaminated water. These new technologies are known as advanced oxidation processes (AOPs), which utilize H_2O_2, O_3, TiO_2, vacuum and UV light. Major AOPs processes are H_2O_2/UV, O_3/UV, H_2O_2/ O_3/UV, TiO_2/UV and VUV (see Figure 1.1).

In H_2O_2/UV, H_2O_2 undergoes homolytic dissociation into two hydroxyl radicals upon illumination by UV light (mainly at 254 nm). These highly reactive hydroxyl radicals will attack and decompose the organic compounds present in the solution. The mechanisms involved are hydrogen abstraction, electrophilic addition and electron transfer. Formation of the hydroxyl radicals in this process sets the limit of its oxidation rate of the contaminants. This is because the organic substrates act as inner filter to the UV light, which illuminates the substrate (Legrini, 1993).

Combination of ozone with UV light is another hydroxyl radical generating process. It can oxidize a great variety of organic compounds in the wastewater. In this process, aqueous systems that have been saturated with ozone, are irradiated with UV light at 254 nm. Oxidation-degradation rates in this process are much higher than the treatments carried out separately with either only ozone or UV light irradiation. The problem with this method is the low ozone solubility in the water and the limitations of the mass transfer in the photoreactor (Khan *et al.*, 1985). Addition of H_2O_2 into the

O_3/UV process could enhance the oxidation-degradation rate via photochemical generation of hydroxyl radicals.

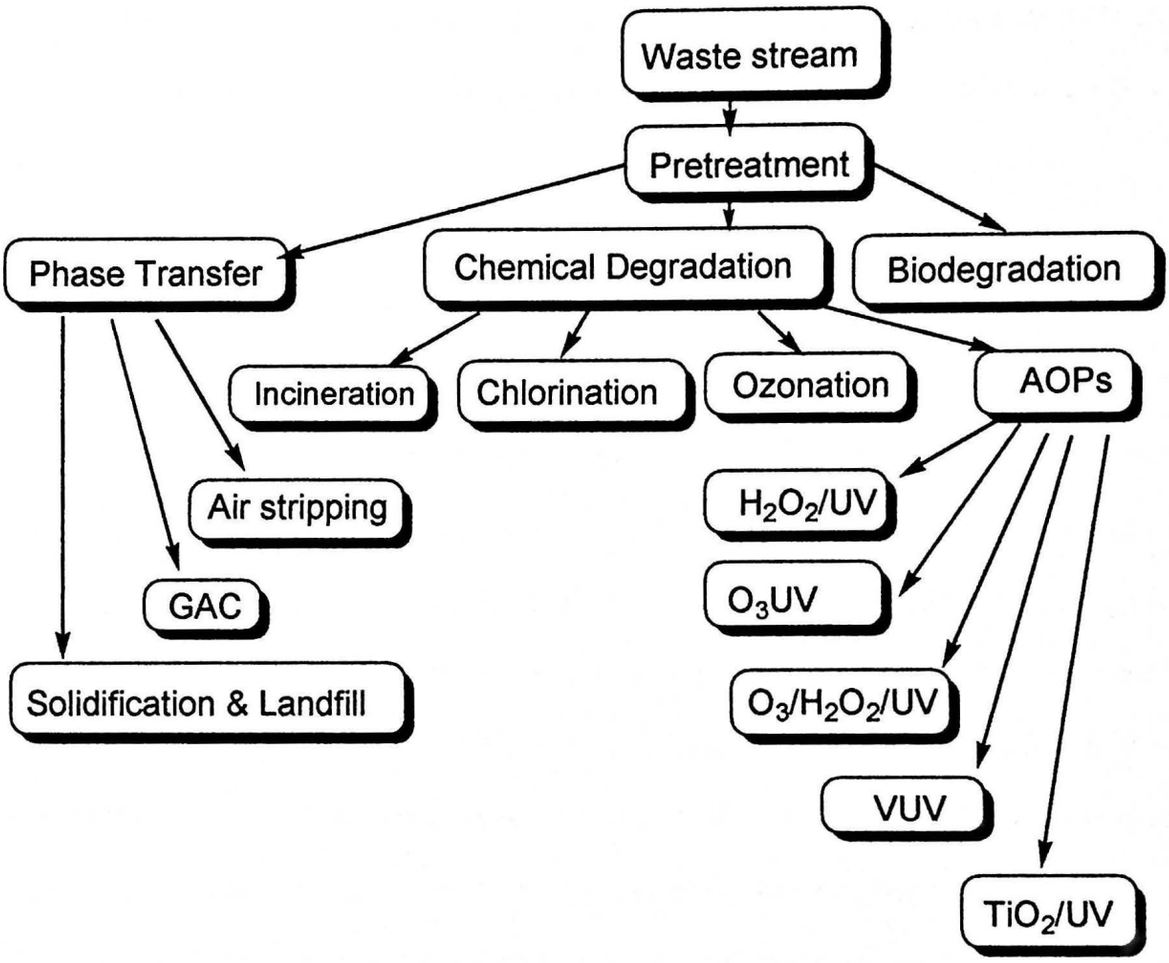

Figure 1.1: Various wastewater treatment technologies in environmental engineering (Chen *et al.*, 2000).

Note: GAC: Granular activated carbon; VUV: Vacuum ultraviolet; AOP: Advantage oxidation processes

The vacuum ultraviolet (VUV) process uses UV-C (wavelength from 100nm to 290nm) to dissociate the H_2O molecules to hydrogen and hydroxyl radicals. The proposed mechanism is shown in equation 1.1:

$$H_2O \xrightarrow{h\upsilon(190\ nm)} 1/2H_2 + OH^{\bullet} \qquad (1.1)$$

The UV-C light is produced from the excimer lamp at wavelength of 190 nm. This process is quite simple and has a distinct advantage whereby no chemicals are needed during the treatment of the wastewater. However, there are only a few research groups having this capability due to the limited availability of the excimer light sources (Legrini, 1993).

The main purpose of AOPs is to produce complete mineralization of organic compounds into carbon dioxide and mineral acids (Schiaello, 1988). Among the AOPs processes, heterogeneous photocatalysis (TiO_2/UV) has received a lot of attention in the last 20 years as an alternative method to treat water containing organic compounds and metal ions. This process is based on the photocatalytic property of the semiconductor to produce hydroxyl radicals under UV light irradiation. This technique has emerged as a feasible alternative to solve environmental problems and to overcome many of the drawbacks that exist in the traditional water treatment technologies. Heterogeneous photocatalysis is different from the other AOPs process because its photocatalyst is reusable and additional oxidants are unnecessary in this process. The main advantages of this technique are:

(i) The oxidation is powerful enough to mineralize almost all-organic pollutants in wastewater and carbon tetrachloride (Choi *et al.*, 1994), which was considered as hydroxyl radical resistant (Ollis, 1985).

(ii) It is considered as a green technology because the ultimate products are CO_2 and H_2O and mineral acids, which are harmless to the environment.

(iii) The oxidant used in this process is atmospheric oxygen and therefore, it is unnecessary to add extra oxidizing agents.

(iv) The catalysts are non-hazardous, chemically stable, reusable and inexpensive.

(v) The catalysts can be activated using low energy UV-A light and therefore, solar illumination can be utilized.

(vi) The process can remove large capacities of the intermediates; therefore, it is commercially comparable to activated carbon adsorption process (Ollis *et al.*, 1989; Miller and Fox, 1993).

Another innovative technology is photoelectrochemistry. This technology has been given a lot of attention because the irradiated TiO_2 electrodes in water could split water into hydrogen and oxygen. This finding was discovered by Fujishima and Honda in 1972 (Fujishima and Honda, 1972). Since that time, researchers also discovered that TiO_2 have the photocatalytic potential to oxidize organic compounds in water to carbon dioxide and mineral acids. The first study involving photocatalysis as a method for water purification was carried out by Pruden and Ollis. (1983). In their study, they discovered that TiO_2 was able to degrade trichloroethylene in water. They also studied the degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of TiO_2, heterogeneous photoassisted catalysis conversion of perchloroethylene, chloroform and carbon tetrachloride (Hsiao *et al.*, 1983), perchloroethylene, dichloroethane, chloroacetic acids and chlorobenzene (Ollis *et al.*, 1984) with illuminated TiO_2 photocatalyst. Since then, a variety of dissolved organic compounds, which could be oxidized to CO_2 by photocatalysis had been studied (Ollis, 1985). Besides oxidation of organic compounds, heterogeneous photocatalysis can also reduce some toxic metal ions such as silver (Hermann *et al.*, 1988), chromium (VI) (Kalil *et al.*, 1998), mercury (Serpone, *et al.*, 1987) and platinum (Angelidids *et al.*, 1998). The oxidation and reduction processes are given in equations 1.2 and 1.3:

$$C_mH_nO_yX_z + (m + sz/2 - kz/4 - y/2)O_2 \xrightarrow[hu]{\text{semiconductor}} mCO_2 + (n-kz)/2\ H_2O + kzH^+ + zXO_s^{-k} \quad (1.2)$$

$$M^{n+} + n/2\ H_2O \xrightarrow[hu]{\text{semiconductor}} M^{o} + nH^{+} + n/4O_2 \qquad (1.3)$$

1.1 Basic principles of heterogeneous photocatalysis

Photocatalysis refers to the combination of photochemistry and catalysis. Both light and catalyst have to be presented together in system in order for the chemical transformation could occur (Kisch, 1989). The catalysts are semiconductors, which can act as catalyst only when they are illuminated with light. This is due to the specific electronic structure characteristic of the catalyst involving an empty conduction band and filled valence band (Boer, 1990). The energy gap between the conduction band and the valence band is relatively small. The energy gap is called bandgap energy and its value usually in the order of a few electronvolts. The electron in the filled valence band can be promoted into the conduction band with a sufficient energy photon. Separation of this charge is an essential step of the photocatalytic reaction. This charge separation process is illustrated in Figure 1.2 and is represented in equation 1.4:

$$TiO_2 \xrightarrow{hv > E_{bg}} e^{-}_{cb} + h^{+}_{vb} \qquad (1.4)$$

The excited electron in the partially filled conduction band and the vacancy in the partially filled valence band can move freely through the semiconductor lattice. The vacancy in the partially filled valence band is referred to as holes and is represented by h^{+}_{vb}. The reactions, which involve the photogenerated electron-hole pairs, are (a) recombination of the electrons and holes with liberation of the absorbed energy in the form of heat, and (b) reaction with electron donor or acceptor substances, which are added into the system to enhance the oxidation and reduction processes respectively.

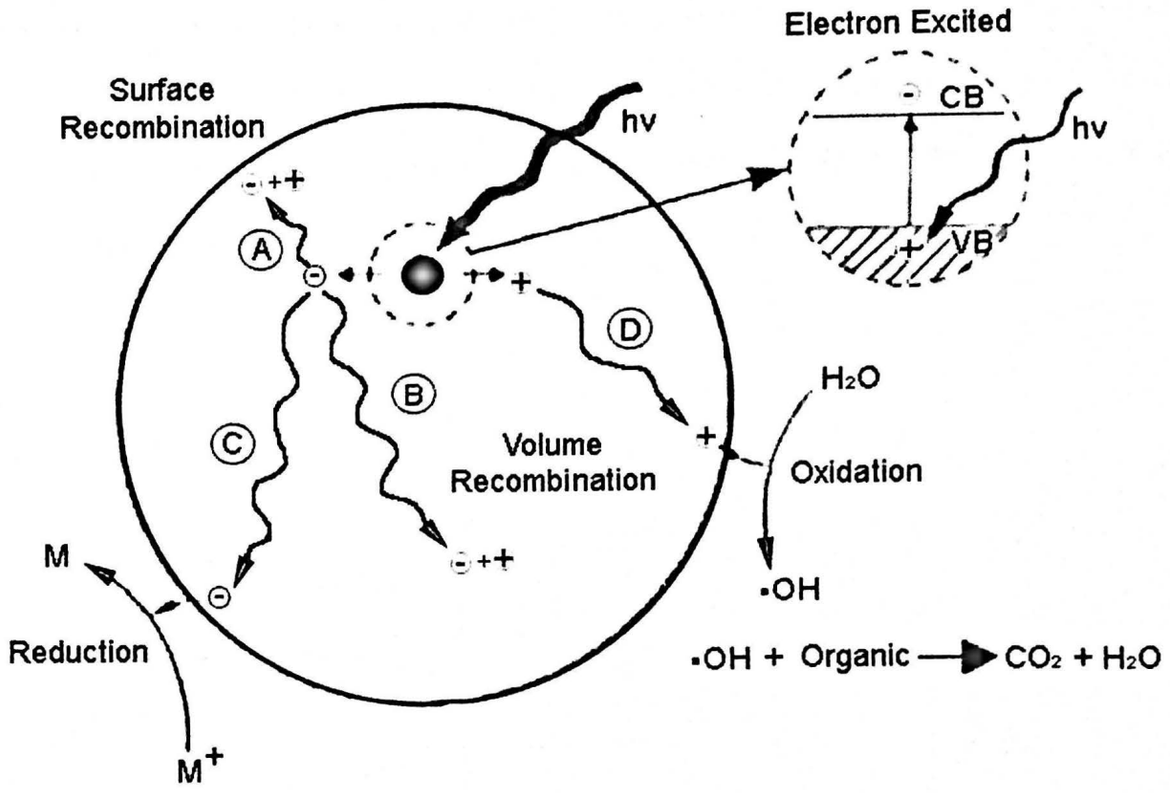

Figure 1.2: Illustration of the generation of electron hole pairs in a spherical semiconductor particle (Boer, 1990)

Valence and conductance band position of various semiconductors and relevant redox couples are illustrated in the Figure 1.3. The reaction pathway of the degradation process is determined by the position of the conduction and valence band of a semiconductor. As an example, MoS_2 with a bandgap of 1.8 eV can thermodynamically photooxidize water but CdSe with a bandgap energy almost similar with MoS_2 is unable to photooxidize water thermodynamically. Instead, CdSe can easily photoreduce water because its conduction band position is higher than MoS_2. In order for a semiconductor particle to act as photocatalyst in the oxidation reaction, the redox potential of the photogenerated valence band hole must be positive enough to generate absorbed hydroxyl radical, which is a powerful oxidant for oxidation of organic pollutants. In the other hand, in order for the semiconductor particle to act as photocatalyst in the reduction reaction, the redox potential of the photogenerated conductance band electron must be negative enough to reduce the adsorbed oxygen

into superoxide or to reduce the adsorbed metal ion into its metallic form. The number of photogenerated electron-hole pairs in the semiconductor particle is dependent on the intensity of the light that is used to irradiate the semiconductor particle and also on the electronic characteristics of the surrounding material or substances that are able to prevent the recombination of the electron-hole pairs

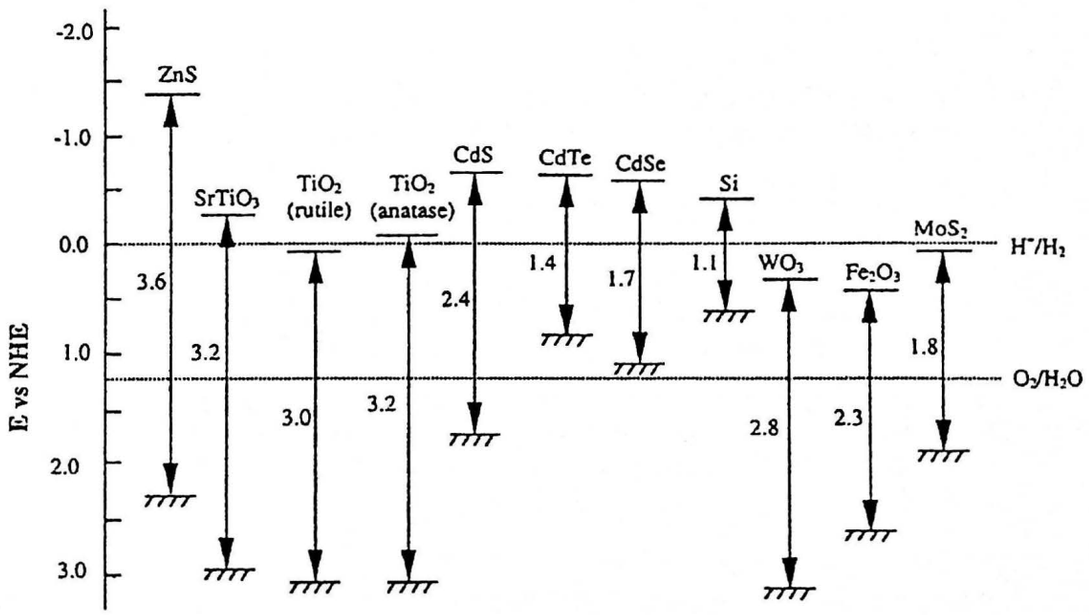

Figure 1.3: Valence and conductance band positions of semiconductors at pH = 0 (Suppan, 1994).

Hence, photocatalytic technology is different from other water treatment methods because it involves both oxidation and reduction reactions. Reduction reactions are mainly used to remove dissolved metal ions whereas the oxidation reactions are used to mineralize the dissolved toxic organic compounds. The oxidation and reduction processes must occur simultaneously in order for the overall photocatalytic activity to be sustained. In the photocatalytic process, organic compounds and water molecules act as reductants whereas oxygen and metal ion act as oxidants. Both oxidation and reduction kinetics are interdependent and either one can be a rate-controlling step to the whole process.

Semiconductor materials, which are commercially available and able to act as photocatalysts are TiO_2 (Augugliaro *et al.*, 1991), ZnO (Barbeni *et al.*, 1985), CdS, ZnS (Al-Sayyed *et al.*, 1991), Fe_2O_3 and WO_3 (Beknolet *et al.*, 1996). However, not all of them are suitable for catalyzing oxidation and reduction reactions for a wide range of organic compounds and inorganic compounds. Table 1.1 shows the photocatalytic semiconductors, which are commonly used in water treatment process.

Table 1.1: Bandgap energies of various semiconductors at pH = 0 and its corresponding threshold wavelength (Rajeshwar and Ibanez, 1997)

Semiconductor	Bandgap (eV)	Wavelength (nm)
TiO_2	3.0-3.2	413-388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe_2O_3	2.3	539
WO_3	2.8	443

The threshold wavelength could be calculated using the following equation:

$$\lambda_{bg}\ (nm) = 1240/E_{bg}\ (eV) \qquad (1.5)$$

However, threshold wavelengths, which are shown in the Table 1.1, may be altered when the semiconductor surface is in contact with the electrolyte solution (Finklea, 1993). Lower bandgap energy semiconductors are preferred for photocatalytic activity when solar energy is used for the activation. However, low bandgap semiconductors such as CDS and CdSe are unstable (Mills and Morris, 1993) and its ions are easily leached into the water.

An ideal photocatalyst must have high activity, ability to be activated with visible or near UV light energy, stable when irradiated under light, reusable, chemically and

biologically inert and inexpensive. Among the semiconductor photocatalysts, which have been tested in laboratory studies, TiO_2 is the most popular and is extensively used in both laboratory studies and pilot plants (Hermann *et al.*, 1983). Moreover, sunlight that contains about 3% of UV-A ($\lambda \leq 388nm$) can be used as light source to activate TiO_2 (Turchi *et al.*, 1993).

Titanium dioxide exists in two crystalline forms i.e. anatase and rutile. In most studies, anatase has been proven to oxidize acid/acetate mixtures (Krautler and Nard, 1978), phenols (Sclafani and Hermann, 1996), cyclohexane and 2-propanol (Sclafani and Hermann, 1996) and was always more effective than the rutile form. Anatase form has a well-defined nature, is non porous with BET surface area of 554±15 m^2/g and has an average particle size of 30 nm (Chen *et al.*, 2000). Its photocatalytic activity is higher than most other available crystalline forms of TiO_2.

1.2 Mechanism of the Photocatalytic Reaction

Although the overall reactions of the photocatalytic semiconductor are oxidation and reduction, the main steps that cause both oxidation and reduction are still not well understood. The photocatalytic process is a four-phase system, which consists of electronic phase, liquid, solid and gas phases. The electronic phase is the UV light source. It relates to the excitation of the electron in the valence band into the conduction band. The liquid phase is the wastewater, solid phase is the catalyst and the gas phase is the oxygen that is contained in the water. When a semiconductor particle is illuminated by light that has higher energy than the semiconductor bandgap energy, E_{bg}, electrons, which occupy the valence band, will be excited to the conduction band. Subsequently, a hole is generated in the valence band and the free electrons are produced in the conduction band (Equation 1.4). This reaction is the first essential step of the photocatalytic reaction. Since the catalyst is always in contact with the liquid solution, transfer of the charge would occur until it has achieved an

electrostatic equilibrium. In metals, excessive charge is confined on the surface. However, in the semiconductor, the excessive charge would be distributed in a region, which is called space-charge region. Existence of this region is due to the expansion of this region from the surface to the bulk of the semiconductor. This region plays a very important role in the photocatalytic process. Due to the presence of the surface charge region, the photo-excited electron can be separated from the hole and migrate ($k^{e^-}_{diff}$, $k^{h^+}_{diff}$) to the particle surface. This would produce a potential gradient between the bulk solid and its external surface. This potential gradient is caused by the depletion of the conduction band electrons in the space charge-region (Bard, 1979). Electro-neutrality of the surface can only be formed when the electrons and holes have equal arrival rates at the steady state condition (Childs and Ollis, 1981). Equations 1.6 and 1.7 represent the electron-hole pairs migration.

$$e^-_{cb} \xrightarrow{k^{e^-}_{diff}} e^-_{tr} \qquad (1.6)$$

$$h^+_{vb} \xrightarrow{k^{h^+}_{diff}} h^+_{tr} \qquad (1.7)$$

The fate and the dynamics of the photogenerated electron-hole pairs are very important in the degradation processes. Commonly, photogenerated electrons and holes have two basic destinies. The first one is the recombination of the photo-excited electron with the holes and the input energy is released as heat. This may happen during their transportation to the particle surface (Equation 1.6). Besides that, they may react with the electron acceptor and electron donor, which accumulate on the particle surface after they have migrated to the catalyst surface. Consequently, they initiate the reduction and oxidation processes, which are represented by equations (1.9) and (1.10)

$$e^-_{cb} + h^+_{vb} \xrightarrow{k_{rec}} \text{heat} \quad (1.8)$$

$$A + e^-_{tr} \xrightarrow{k_{red}} A^{\bullet -} \quad (1.9)$$

$$D + h^+_{tr} \xrightarrow{k_{ox}} D^{+\bullet} \quad (1.10)$$

Where, A is the electron acceptor and D is the electron donor.

Reaction in equation (1.8) is mainly caused by the low efficiencies of photocatalytic processes and according to Alfano *et al.* (1997), the recombination (k_{rec}) of the electrons and holes occurs mainly in the bulk of the catalyst particle. The possibility of this recombination can be prevented if the separated mobile species are trapped by surface adsorbates or other sites. If the surface adsorbates possess a redox potential, which is appropriate for a thermodynamically allowed reaction, the photogenerated hole that has reached the surface may have high probability to react with the surface adsorbates. Hence, a hole can oxidize (k_{ox}) the adsorbed electron donor by abstracting the electron from it while the mobile free electron in the conduction band can reduce (k_{red}) the adsorbed acceptor by transferring the electron to it. After the electron donor has been oxidized, it would become a cation radical and the electron acceptor, which has received electron from the conduction band, would become anion radical. These radical ions can take part in several reaction pathways. The first pathway is reacting chemically with themselves or other adsorbates. The second is combining by back electron transfer to form an excited state of one of the reactants or to waste the excitation energy by the non-radiative pathway. The third is diffusing from the semiconductor surface and reacting chemically with other species in the bulk solution. If the rate of the formation of cation radical is almost similar to the rate of the back electron transfer, any molecule with an oxidation potential less positive than the semiconductor valence band edge would be oxidized through a photoinduced

process. This is because under these conditions, interfacial electron transfer at the illuminated interface is thermodynamically possible. Similarly, the reduction, which is induced by photons, can also occur to any molecule possessing a reduction potential, which is less negative than the conduction band edge (Fox. and Dulay, 1993).

TiO_2 surface is readily hydroxylated when it is in contact with water. Water and dissociated water molecules are bonded to the TiO_2 surface. The hydroxylated surface coverage of 7 – 10 OH^-/nm^2 at room temperature had been reported by Morishige *et al.* (1985) and Suda and Morimoto (1987). Turchi and Ollis (1990), Jaeger and Bard (1979) and Fox and Chen (1981) had experimentally observed the reactions of the trapped holes with absorbed solvent molecules (H_2O and OH^-). They concluded that hydroxyl radicals were produced when the holes that migrated to the semiconductor surface abstracted electron from the water molecule or hydroxyl ion. Equations (1.11) and (1.12) are used to represent these reactions;

$$h^+_{tr} + H_2O \xrightarrow{k_{ox}} OH^{\bullet}_{ads} + H^+ \qquad (1.11)$$

$$h^+_{tr} + OH^- \xrightarrow{k_{ox}} OH^{\bullet}_{ads} \qquad (1.12)$$

Where, ads means adsorption.

Besides that, these holes can also abstract electron from the adsorbed organic substrates RX according to equation 1.13:

$$h^+_{tr} + RX_{ads} \longrightarrow RX^{+\bullet}_{ads} \qquad (1.13)$$

Due to the high concentration of adsorbed H_2O and OH^- on the catalyst particle surface, the reactions, which are more important in the oxidative processes, are equations (1.11) and (1.12). Manthews (1984) had studied the oxidation process in

water-free aerated organic solvents and discovered that only partial oxidation can be achieved. However, complete mineralization of numerous organic compounds in aqueous solutions has been reported by Al-Ekabi *et al.* (1989), Matthews, (1990), and Low *et al.*, (1991). Acccording to Low *et al.,* (1991), the nitrate and ammonium ions were formed in titanium dioxide mediated photocatalytic degradation of organic compounds containing nitrogen atoms. This proved that organic compounds have been totally mineralized to carbon dioxide, water, mineral acid and ion. Based on the above reports, it is obvious that direct reaction between the organic compounds and the valence band holes (Equation 1.13) is insignificant (Wang *et al.*, 1992). Therefore, in order for the organic compounds to be completely destroyed, the presence of water and hydroxyl groups are necessary. Photogenerated electrons must also react in order for it not to accumulate in the catalyst particles. Accumulation of the photogenerated electrons on TiO_2 particles had been reported by Wang *et al.* (1992) when TiO_2 was used to oxidize 1.6M aqueous methanol.

The hole consumption rate must be equal to the electron consumption rate when the photoassisted reaction is at the steady state. Therefore, electron scavengers or acceptors, which are used to trap the excess electrons, must be present in the photocatalytic process. The most common electron acceptor, which is available at little or no cost is oxygen. The reactions between oxygen and the electron at the surface of semiconductor had been discussed by Okamoto *et al.* (1985a), Krautler and Nard (1978), Matthews (1984) and Al-Ekabi and Serpone (1988). The reactions are represented in equations (1.14) and (1.20) are as follows:

$$e^-_{tr} + O_{2\cdot ads} \longrightarrow O^{-\bullet}_{2\cdot ads} \quad (1.14)$$

$$H^+ + O^{-\bullet}_{2\cdot ads} \longrightarrow HO^{\bullet}_2 \quad (1.15)$$

$$2HO^{\bullet}_2 \longrightarrow H_2O_2 + O_2 \quad (1.16)$$

$$HO^{\bullet}_2 + O^{-\bullet}_{2\cdot ads} \longrightarrow O_2 + HO_2^- \quad (1.17)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad (1.18)$$

$$H_2O_2 \longrightarrow H_2 + O_2 \quad (1.19)$$

$$H_2O_2 + HO^{\bullet}_2 \longrightarrow OH^{\bullet} + H_2O + O_2 \quad (1.20)$$

Jaeger and Bard (1979) had verified the formation of these species using electron spin resonance measurements. Formation of H_2O_2 in the degradation of phenol in TiO_2 suspensions by aerating the solution with O_2 and He, respectively also has been confirmed by Auguliaro *et al.* (1990). Species, which are generated from equations (1.14) to (1.20), are present either at the interface or in the solution and can take part in the complex degradation scheme and will finally leads to the final mineralization of organic species. Through this complex degradation scheme, one hydroxyl radical is generated from three electrons. In the other half-cell reaction, one hole produces one hydroxyl radical (Equations 1.10 and 1.11). Therefore, most of the hydroxyl radicals are generated through hole reactions (Okamoto *et al.*, 1985b).

More hydroxyl radicals would be produced when the hydrogen peroxide formed from the reactions (1.16) and (1.19) decompose further through the following equations as depicted in equations (1.21) to (1.23):

$$H_2O_2 \xrightarrow{h\upsilon} 2OH^{\bullet} \quad (1.21)$$

$$H_2O_2 + O_2^{-\bullet} \longrightarrow OH^{\bullet} + OH^{-} + O_2 \quad (1.22)$$

$$H_2O_2 + e^{-}_{tr} \longrightarrow OH^{\bullet} + OH^{-} \quad (1.23)$$

Studies by Tanaka *et al.* (1989b), Wei *et al.* (1990) and Martyanov *et al.* (1997) showed that addition of hydrogen peroxide would improve the photocatalytic process. The improvement of the process would most probably be due to the reactions from equations (1.21) to (1.23). Turchi and Ollis. (1990), Bard (1979) and Matthews (1984) had proposed that the highly reactive hydroxyl radicals, which are formed from the above equations, are the primary oxidizing species in the photocatalytic processes and the rate determining reaction step may be the formation of hydroxyl radicals. This proposal is supported by the following facts:

(a) Organic compounds cannot be completely mineralized in the water-free organic solvents (Matthews, 1984).

(b) Concentration of the steady-state hydroxyl radicals in the UV-irradiated titanium dioxide aqueous solution could go to as high as 10^{-9} M (Ireland and Valinieks, 1992). This amount is much higher than those in the processes of ozonation, direct photolysis of H_2O_2 and radiolysis (i.e., $< 10^{-12}$ M)

(c) The intermediates, which are detected during the photocatalytic degradation of aromatic mostly, have hydroxylated structures. These had been reported by Turchi and ollis (1990), Okamoto *et al.* (1985a) and Augugliaro *et al.* (1988). The intermediates, which are produced in this reaction, are consistent with those found when the similar aromatics compounds are reacted with a known source of hydroxyl radicals (Cox, *et al.*, 1980).

Hydroxyl radicals are very reactive species. This is because it has an unpaired electron, which is highly unstable. It reacts rapidly and non-selectively with the organic

compounds through an oxidation pathway. It is able to oxidize almost all organic pollutants in the wastewater by abstracting the hydrogen from the organic compounds. This is due to its high oxidation potential (Table 1.2). The oxidation of organic compounds by the reactive hydroxyl radicals may take place either in the bulk solution or on the catalyst surface. Turchi and Ollis (1990) had proposed four different reaction pathways based on the reaction of the hydroxyl radicals with the organic compounds in the photocatalytic degradation process. These four reaction pathways are shown in equations (1.24) to (1.27) as follows:

(a) Reaction of the adsorbed hydroxyl radicals with the adsorbed organic species.

$$OH^{\bullet}_{ads} + R_{ads} \longrightarrow R^{\bullet}_{ads} \qquad (1.24)$$

(b) Reaction of the non-bound hydroxyl radicals with the adsorbed organic species

$$OH^{\bullet} + R_{ads} \longrightarrow R_{ads} \qquad (1.25)$$

(c) Reaction of the adsorbed hydroxyl radicals with a free organic species arriving at the catalyst surface

$$OH^{\bullet}_{ads} + R_F \longrightarrow R^{\bullet}_F \qquad (1.26)$$

(d) Reaction occurs between two free species in the bulk solution.

$$OH^{\bullet} + R_F \longrightarrow R^{\bullet}_F \qquad (1.27)$$

Based on the different reaction pathways, four kinetic models had been developed, which had similar degradation rate forms and were consistent to the reported initial data and temporal degradation data. However, Fox (1993) reported that surface-bound hydroxyl radicals are more stable compared to those in the bulk solution when pulse radiolysis and time-resolved diffusion reflectance was used to measure the

hydroxyl radicals concentration in the photocatalytic process. Minero *et al.* (1992) had obtained similar results indicating that the degradation process occurs at the surface or within a few monolayers around the photocatalytic particles. All of these results show that the main reaction of the photocatalytic degradation process occurs on the surface of the catalyst.

Peroxy radicals in equations (1.24) to (1.27) are added to the oxygen molecules and initiate thermal (chain) reactions leading to the formation of CO_2, H_2O and mineral acid according to equation (1.28):

$$R^{\bullet}_{ads} + O_2 \rightarrow RO^{\bullet}_2 \rightarrow \rightarrow CO_2 + H_2O + \text{Mineral acid} \qquad (1.28)$$

Table 1.2: oxidation potentials of some oxidants (Legrini, *et al.*, 1993)

Species	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.8
atomic oxygen	2.42
ozone	2.07
hydrogen peroxide	1.78
perhydroxyl raidcal	1.7
permanganate	1.68
hypobromous acid	1.59
chlorine dioxide	1.57
hypochlorous acid	1.49
hypoiodous acid	1.45
chlorine	1.36
bromine	1.09
iodine	0.54

Superoxide and /or perhydroxyl radicals, which are formed from the reduction of the oxygen by the catalyst during photocatalytic oxidation of organic compounds, eventually form hydroxyl radicals that enter into the oxidation cycle (Mills and Hunte, 1997). Besides oxygen, any dissolved metal ions can consume electrons and complete the redox cycle as long as the reduction potential of the metal ions are more positive than the conduction of the photocatalyst. After the metal ions have been reduced, the

reduced form of metal usually deposits on the catalyst surface, which may or may not be easily removed (Foster *et al.*, 1993). The positions of the valence and conduction bands of anatase TiO_2 photocatalyst in contact with an aqueous electrolyte solution at different pH and reduction potentials of some of the environmentally fretful metal ions were shown in the Figure 1.4. The position of both conduction and valence bands of anatase TiO_2 are pH dependent. The positions of these bands may shift to more cathodic potentials when the pH of the electrolyte of the solution is increased (Chen *et al.*, 2000). However, reduction potentials of all metal ions except Cr (VI), which are shown in Figure 1.4 are not dependent on pH. Therefore, these would mean that the metal ions are more favorable to be photo-reduced with increasing of pH.

Based on the information in Figure 1.4, Cd^{2+}, Fe^{2+} and Cr^{3+} cannot be photo-reduced by TiO_2 because their reduction potentials are more negative than that of photo-excited electrons in the TiO_2. However, Au^{3+}, Cr^{6+}, Hg^{2+} (including $HgCl_2$, $HgCl_4^{2-}$), Ag^+, Hg_2^{2+}, Fe^{3+}, Cu^+ and Cu^{2+} can be reduced thermodynamically. Among the above metal ions, Fe^{3+} and Cr^{6+} could not be reduced to iron and chromium metals respectively but they could be reduced to Fe^{2+} and Cr^{3+}. For Pb^{2+} and Ni^{2+}, due to their low driving force, it is also unlikely to be reduced under most conditions. Moreover, concentration of the particular metal ion may alter its redox reduction potential. Besides, according to Figure 1.4, oxygen is expected to be reduced preferentially compared to most ions if it is present in the solution. That is the reason why nitrogen gas is used to purge the reaction system in most studies. The purging is to eliminate the oxygen gas and to increase the photo-reduction efficiency of the metal ions.

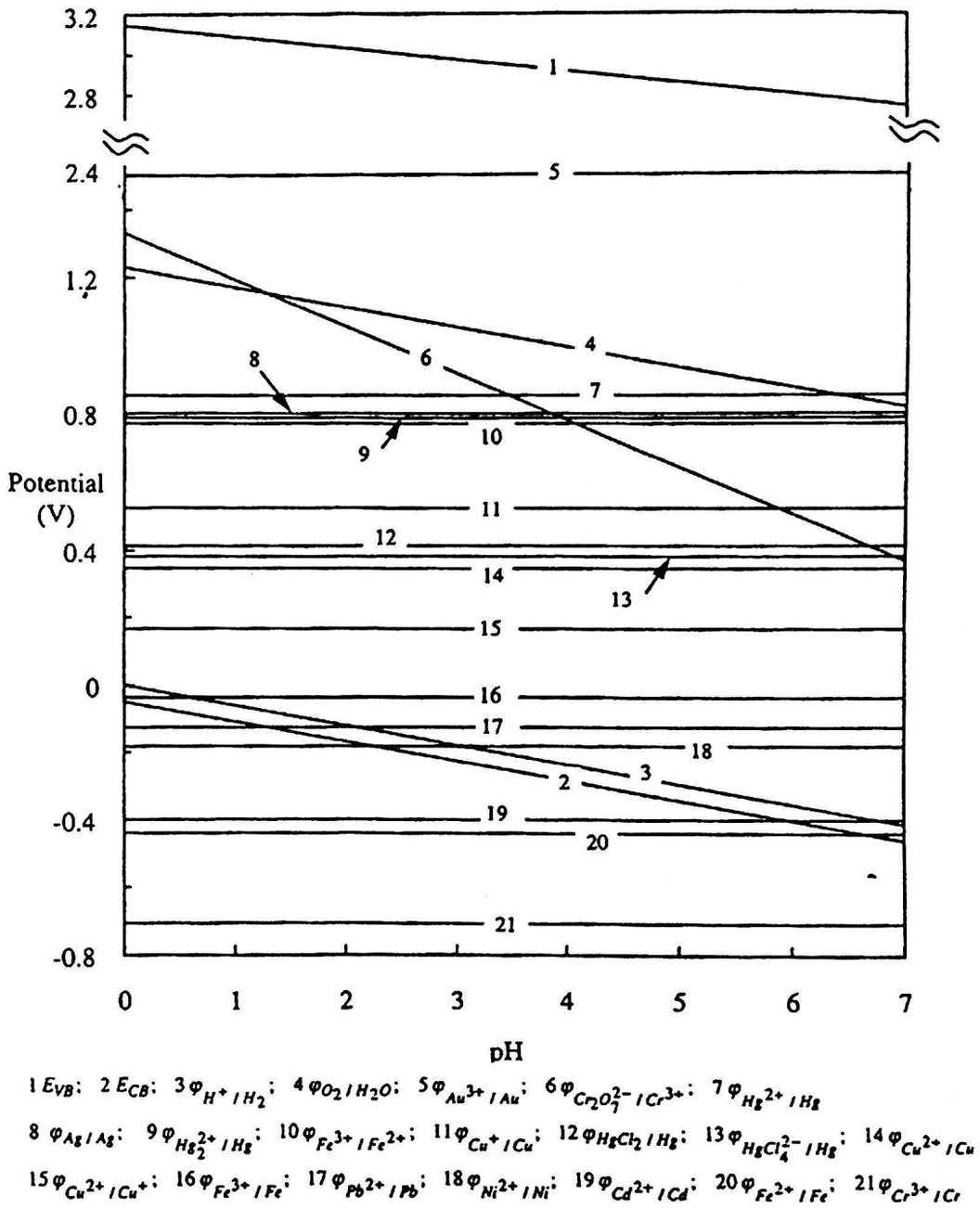

Figure 1.4: Positions of valence and conduction bands of TiO_2 (anatase) and the reduction potentials of metallic ions of interest at different pH (Chen *et al.*, 2000).

1.3 Role of adsorption in photocatalytic degradation

The role of adsorption in photocatalytic degradation is very important in order to determine the rate of the whole degradation process. This is because when the targeted organic contaminant to be degraded moves slowly toward the photocatalyst surface, less organic contaminant would be degraded within a certain period of time, no matter how good the photocatalytic potential that is possessed by the photocatalyst.

Therefore, adsorption of the organic contaminant by the photocatalyst is the determining step that has to be taken into account in order for the whole degradation process could be optimized. Organic contaminants that adsorb faster onto the photocatalyst surface can increase the degradation rate. However, organic contaminants, such as dyes that adsorb too fast onto the photocatalyst surface will show a very promising decolorizing treatment during the first run but quite poor performance in the following treatment. This is due to the excessive organic contaminants that is adsorbed onto the photocatalyst surface and prevent the light from reaching it. Once the photocatalyst does not receive the light energy to excite its electron from the valence band to conduction band, there would be no generation of holes and the usual photocatalytic mechanisms would not proceed on the photocatalyst surface.

Concerning the effect of adsorption during the photocatalytic degradation of pollutants, Bekkouche *et al.*, (2004) had studied the adsorption of phenol on titanium dioxide (TiO_2) in suspension form. The experiment was carried out by mixing the phenol solution with the suspended titanium dioxide mixture and the system's temperature was maintained at 25 °C. Sample was collected at regular intervals by syringe and filtered before measuring it using UV-vis spectrophotometer. The equilibrium of adsorption was reached after one hour of stirring. The conclusion that had been drawn was that phenol was weakly adsorbed onto titanium dioxide. The type of adsorption between the phenol and titanium dioxide is chemisorption and it is represented well by the Langmuir model. The optimum pH range for this adsorption was between 5 and 6. This study also showed that there was an advantage to operate the adsorption at great velocity of agitation by ultrasonic drives and also at natural pH. Ultrasonic agitation increased the quantity of phenol adsorbed by 5 %. This mode of agitation reduces the phenomenon of agglomeration of titanium dioxide particles and therefore increases the interfacial area of the catalyst.

The kinetics of photocatalytic degradation of four different model organic compounds namely formic acid (FA), oxalic acid (OA), 4-chlorophenol (4-CP) and the herbicide monuron (3-(4-chlorophenyl)-1,1-dimethylurea) in a self-constructed batch-mode plate photoreactor with a thin flow of contaminated aqueous solution circulating over an illuminated particulate layer of P25 TiO_2 (Degussa) had been studied by Kry´sa *et al.*, (2006). Both OA and FA were found to be adsorbed on TiO_2 surface. Their mineralization, induced by direct transfer of photogenerated holes, proceeded in a single step, without observable intermediates, following approximately zero order kinetics. Numerical simulations were performed using a newly proposed kinetic model based on the photostationary state assumption. The model allowed an explanation of the order of the observed reaction as well as independent comparison between competitive adsorption of organic compounds and oxygen on the photocatalyst surface thus yielding a better fit for the case of competing 4-CP and monuron. These two organic compounds were not adsorbed by the photocatalyst under the conditions used and were degraded through the action of photogenerated hydroxyl radicals. Most important, it was concluded that their degradation proceeded with lower photoefficiency than for the adsorbed compounds (FA and OA). The mineralization of both 4-CP and monuron followed zero order kinetics and their degradation was close to first order. The different rates of reaction orders were consistently explained using the photostationary state approach. In this study, organic contaminants that were adsorbed onto the TiO_2 were degraded faster than the one that was not adsorbed by TiO_2. This is because the adsorption of the organic contaminants onto the TiO_2 particulate surface is the rate determining step within the degradation mechanism and therefore it affects the kinetics of the degradation process.

Shona *et al.*, (2005) had studied the effects of chemical coupling of flocculation and adsorption with photocatalysis in treating persistent organic pollutants in

wastewater. The experiment was carried out in suspension form and the results showed that initial reverse reaction occurred when titanium dioxide alone was used as a catalyst in the treatment. The results also showed that powdered activated carbon adsorption followed by photocatalysis were ineffective in alleviating reverse reaction. However, when powdered activated carbon and titanium dioxide catalyst were added simultaneously in the wastewater, the reverse reaction was eliminated thoroughly.

Inumaru *et al.*, (2004) had prepared n-Octyl-grafted TiO_2 (C_8-TiO_2) as a model of a photocatalyst with high molecular adsorption selectivity. Photocatalytic activity of the model photocatalyst was investigated. They found out that the catalyst was highly active in the presence of concentrated phenol (1000ppm) and 4-nonylphenol (2ppm) and it decomposed both chemicals in 180 minutes, while pristine TiO_2 (P-25) under the same conditions showed much lower activity. The high C_8-TiO_2 activity was ascribed to the molecular selective adsorption of the organic molecules on the alkyl-grafted hydrophobic surface. Infrared spectra showed that the grafted alkyl groups were gradually decomposed under photoirradiation. The model catalyst demonstrated that molecular selective adsorption is important for removal of low-concentration contaminants in the presence of other, more concentrated compounds.

Franch *et al.*, (2005) had studied the role of Fe (III) on the TiO_2 -assisted photocatalytic degradation of maleic acid. The study on the kinetics of the removal of organic matter, as well as the identification of all the stable mineralization intermediates, demonstrated that the presence of Fe (III), adsorbed onto the TiO_2 surface, rendered a more efficient process through a cleaner mineralization pathway compared to bare TiO_2. Furthermore, the behaviour of the system did not depend on the iron source. On the other hand, the influence of Fe (III) on the interaction of maleic acid with TiO_2 in the solid phase was studied using ATR–FTIR technique. In the TiO_2 + UV assays, maleic, acrylic, malonic, oxalic, acetic and formic acids have been