

**PHOTOCATALYTICAL REMOVAL OF LEAD IONS FROM
AQUEOUS SOLUTION WITH IMMOBILIZED TiO₂ POWDER
ON CARBON BASED PLASTIC PLATE IN THE PRESENCE OF
CALCIUM OXALATE AND THIOLACTIC ACID.**

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**UNIVERSITI SAINS MALAYSIA
2005**

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by

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List Of Abbreviations

SC	Semiconductor
UV	Ultra Violet
h^+	Hole
eV	Electron Volt
V	Voltage
e^-	Photogenerated Electron
TLA	Thiolactic Acid
vb	Valence Band
cb	Conductance Band
CBPP	Carbon Based Plastic Plate
CP	Coated Plate
DW	Distilled Water
SEM	Scanning Electron Micrograph
TEM	Transmission Electron Microscope
BET	Brunauer, Emmett and Teller (BET)
PET	Polyethylene Terephthalate
C_o	Original Concentration (mg/l)
C	Equilibrium Concentration (mg/l)
Ca _{ox}	Calcium Oxalate
TiO ₂	Titanium Dioxide
nm	Nanometer
μ m	Micrometer
AOT	Advance Oxidation Technologies
GAC	Granular Activated Carbon
TiO ₂ /Ca _{ox} /cPET	Carbon based PET plate coated with immobilized Calcium oxalate followed by immobilized Titanium Dioxide
Ca _{ox} /cPET	Carbon based PET plate coated with immobilized Calcium Oxalate
TiO ₂ /cPET	Carbon based PET plate coated with immobilized Titanium Dioxide

PHOTOCATALYTICAL REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTION WITH IMMOBILIZED TiO₂ POWDER ON CARBON BASED PET PLASTIC PLATE IN THE PRESENCE OF CALCIUM OXALATE AND THIOLACTIC ACID

ABSTRACT

Immobilized calcium oxalate followed by immobilized TiO₂ on a carbon based PET (Polyethylene Terephthalate, PET) plastic plate was fabricated via electrophoretic deposition method. Photocatalytic removal rate of lead ions from aqueous solution was studied using this fabricated plate in the absence and presence of thiolactic acid (TLA). With the weight ratio fixed at 1 : 1 (Ca_{ox} : TiO₂), 100 mg/l of lead could be reduced to more than 98% within 75 minutes of illumination. Results also showed that the rates of the photocatalytic reduction of lead increased with pH. This effect was due to both reduction process and hydroxide precipitation. The removal rate of lead also reduced exponentially with the increasing concentration of lead. Other metal ions namely nickel, zinc, copper and argentums were able to be removed by this system in the following order; Ag⁺>Pb²⁺>Cu²⁺>Ni²⁺>Zn²⁺. The interference of these cations was also studied. Studies revealed the fact that the presence of cations (Ag⁺, Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺ and Hg²⁺) in the presence of Pb, does affect Pb's photocatalytical removal rate. The presence of these cations affected the rate of a Pb's removal in the following order; Zn²⁺ > Cu²⁺ > Cd²⁺ > Hg²⁺ > Ni²⁺ > Ag⁺. Electronegativity and reduction potential were found to be the possible root causes which contribute indirectly to Pb's affected photocatalytical removal rate. Addition of 93 mg/l of TLA (0.1M) was found to be the optimum dosage of TLA. pH, value seemed not to affect the removal rate of lead's in the presence of TLA. It was found to be slightly effective in acid medium. It was also observed, that in the presence of TLA the amount of Ca²⁺ released into the sample solution were 23 % more than the situation where TLA was not used. Studies suggested that the decrease of pH during the first 15 minutes of illumination may be due to the formation of carbonic acid and the formation of CaCO₃ after the period of 15 minutes may have caused the pH of the sample to increase during illumination process. Characterization results suggested that the surface area of an illuminated plate, contain lead deposits on it as the analysis of the area and spot showed the presence of lead. Whereas, on the surface of another illuminated plate where TLA was used in the system during the illumination, the presence of sulfur and lead indicates the possible presence of PbS.

PENYINGKIRAN ION PLUMBUM SECARA FOTO MANGKIN, DARI LARUTAN AKUEUS DENGAN MENGGUNAKAN SATU SISTEM YANG MANGANDUNGI LAPISAN TiO₂ YANG TERIMOBILISASI ATAS SEKEPING PLAT KARBON BERASASKAN PET PLASTIK DENGAN KEHADIRAN KALSIMUM OKSALAT DAN ASID THIOLAKTIK.

ABSTRAK

Satu sistem yang khas telah direka bentuk dengan menggunakan pengenaan kalsium oksalat diikuti oleh lapisan TiO₂ yang terimobilisasi di atas satu plat plastic PET (Polietilin Tereftalat, PET) berasaskan karbon melalui kaedah pengenaan elektroforetik. Penyingkiran ion plumbum secara foto mangkin, dari larutan akueus telah dilakukan dengan menggunakan sistem ini dalam keadaan tanpa dan dengan kehadiran Asid Thiolaktik (TLA). Dengan nisbah jisim kalsium oksalat kepada TiO₂ yang terenap atas plat, 1 : 1, sistem telah menyingkirkan ion Pb lebih dari 98% dari larutan akueus dalam 75 minit penyinaran UV. Kadar penyingkiran ion plumbum juga didapati meningkat dengan peningkatan pH larutan. Ini disebabkan oleh proses foto mangkin serta pemendakan hidroksil. Selain itu, kadar penyingkiran ion plumbum juga didapati menurun secara eksponensial dengan kenaikan kepekatan ion plumbum. Sistem ini juga diguna untuk menyingkirkan kation-kation toksik seperti nikel, zink, argentum dan kuprum. Didapati, sistem ini mampu menyingkirkan kation-kation ini dalam urutan berikut; Ag⁺>Pb²⁺>Cu²⁺>Ni²⁺>Zn²⁺. Kajian dilakukan keatas gangguan kehadiran ion-ion toksik seperti Zn²⁺, Cu²⁺, Cd²⁺, Hg²⁺, Ni²⁺ dan Ag⁺ terhadap kadar penyingkiran Pb. Kehadiran kation-kation ini didapati menjejaskan kadar penurunan Pb mengikut urutan berikut ; Zn²⁺ > Cu²⁺ > Cd²⁺ > Hg²⁺ > Ni²⁺ > Ag⁺. Elektronegativiti dan potensi penurunan piawai, adalah antara faktor yang mungkin mendorong turutan penjejasaan kadar penurunan Pb. Dos TLA (0.1M) sebanyak 93 mg/l telah digunakan untuk sistem untuk memperolehi kadar penyingkiran Pb yang optimum. Walaubagaimana pun pada pH larutan sampel yang berbeza, apabila TLA digunakan, didapati kadar penyingkiran ion Pb lebih efektif dalam medium berasid. Juga diperhatikan, dengan kehadiran TLA penyingkiran Ca²⁺ kedalam larutan akueus adalah 23 % lebih dari situasi yang tidak menggunakan TLA. Selain itu, dapat diperhatikan sepanjang penyinaran UV, pengurangan pH dalam masa 15 minit yang pertama mungkin disebabkan oleh pembentukan asid karbonik dan penurunan pH selepas minit ke 15 tersebut mungkin diakibatkan oleh pembentukan CaCO₃ yang semakin meningkat. Kajian morfologi plat yang diaplikasikan dengan kalsium oksalat diikuti oleh lapisan TiO₂, yang telah disinari UV, mendapati kehadiran deposit Pb. Manakala bagi plat yang diaplikasikan dengan kalsium oksalat diikuti oleh lapisan TiO₂, yang telah disinari UV bersama penggunaan TLA, kehadiran sulfur dan plumbum telah dikesan dan ini menunjukkan kemungkinan kehadiran PbS atas plat tersebut.

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 Water Pollution By Heavy Metals

Today water pollution by rapid industrial development has become a major threat facing us in this era. Due to the rapid industrialization growth, organic compounds, toxic metals and various toxic compounds have been released and dispersed into the aquatic system above the limited level (Abayachi, et al., 1985; Abernathy, et al., 1984; Bellanca, et al., 1977; Bower, et al., 1978; Chongkrak, et al., 1982; Hansen, et al., 1990; Gibbs, et al., 1979; Hiromitsu, et al., 1986; Koshima, et al., 1986; Laxen and Harrison, 1993; Okay, et al., 1985; Srikanth, et al., 1993). Water containing dyes, metal ions, non-biodegradable contaminants are released carelessly by irresponsible parties into drains, lakes, rivers and sea beds (Bertin, et al., 1995; Helz, et al., 1975; Henriksen, et al., 1978; Higgins, et al., 1985; Maruyama, et al., 1975; Morrison, et al., 1992; Salanki, et al., 1982; Srivastava, et al., 1989; Tariq, et al., 1996; Yost, et al., 1979)

The mobilization of various toxic metals in our environment can cause excessive exposures which may be hazardous to human health. Metal pollution comes from both natural (erosion of the drainage basin) and anthropogenic sources (Bertin, et al., 1995). Of the various sources of water pollution, one of the most important is from the industrial waste water effluents that enter our aquatic systems. This results in the transformation of places like lakes into sewage lagoons. One of the sources of the heavy metal pollution is leakage from overloaded sewers draining the industrial belt which runs into the rivers or ocean. Some of the industries dump their untreated and partially treated effluent directly into the nearest aquatic system available.

The heavy metal content of aquatic animals originates from two routes of intakes, free ions and simple compounds dissolved in the water. These are taken up directly through the epithelium of the skin, gills and alimentary canal, while others having been accumulated in food organisms, are incorporated by nutrition (Ajmal, et al ., 1996; Brown, 1968). In the past few decades, the presence of heavy metal ions in water and the accumulation in organisms of substances originating from industries have become more and more common. Incorporated metals can influence and thus cause damage to the organisms themselves.

Metal such as mercury, can be concentrated to dangerous levels by microorganisms, fish and plants within the human food chain. They may also be accumulated in stream sediments, only to be released when such deposits are disturbed during periods of high flows. Certain metals maybe transformed by stream microorganisms into much more hazardous metallorganic forms. The actual toxicity of metals to stream life depends on the particular metal present, water hardness, pH, synergistic effects of different metals and on other, as yet undetermined factor (Arokiasamy, et al., 1996; Ajmal, et al., 1996; Brown, 1968)

Industries such as chemicals, pharmaceutical, plating, mining and microelectronics are often discharging water contaminated with toxic organic and inorganic compounds. Pollutants from various industries and agricultural activities are contributing to water contamination which is at unacceptable level all over the world. Despite law and regulations posted on them, discharge of waste water into aquatic system has become a norm. Due to this acts and arising awareness, studies and experiments are being carried out by both, the industrialists and the scientists to provide an efficient method which is cost-

saving, practical and with high stability conditions to overcome this world-wide waste water problem (Baltpruvins, et al., 1997; Benschoten, et al., 1990; Chen, et al., 1997; Clark, et al., 1965 ; Demirci, et al., 1998; Fernandez, et al ., 1995; Huang, 1981; Huang, et al., 1995; Jain, et al., 1997; Jiang, et al., 1998; Johaari and Rohaanin, 1994; Lettermen and Vanderbrook, 1983; Linstedt, et al., 1971; Lin, et al., 1998; Lin and Peng, 1996; Mellah and Chegrouche, 1997; Namasivayam and Ranganathan, 1995 and Rahni and Regube., 1996).

Malaysia has had environment legislation since the early 1920s. However comprehensive legislation and the act to control pollution and enhanced the environment only came into being with the Environment Quality Act in 1974. Table 1.0 shows the safety limits as stipulated in the regulations before disposing them into environment (Legal Research Board, 1999).

1.2 Heterogeneous Photocatalysis

Heterogeneous photocatalysis is an emerging technology valuable for water and air purification and remediation. Fundamental and applied research on this subject has been performed extensively during the last 20 years all over the world, as documented by more than 2000 publications (Litter, et al., 1999). Papers on the field have increased from about 0.7 in the early 80's to more than 23 per month in 1998. Early research in the 70's and 80's was devoted to photovoltaic conversion and energy storage (Litter, et al., 1999).

Table 1.0: Safety Limits Stipulated By The Government (Legal Research Board, 1999)

THIRD SCHEDULE
ENVIRONMENTAL QUALITY ACT 1974
ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS)
REGULATIONS 1979
 (Regulation 8 (1), 8(2), 8(3))
PARAMETER LIMITS OF EFFLUENT OF STANDARDS A AND B.

Parameter	Unit	Standard	
		A	B
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value	-	6.0-9.0	5.5-9.0
(iii) BOD ₅ at 20°C	mg/l	20	50
(iv) COD	mg/l	50	100
(v) Suspended Solid	mg/l	50	100
(vi) Mercury	mg/l	0.005	0.05
(vii) Cadmium	mg/l	0.01	0.02
(viii) Chromium	mg/l	0.05	0.05
hexavalent	mg/l	0.05	0.10
(ix) Arsenic	mg/l	0.05	0.10
(x) Cyanide	mg/l	0.10	0.5
(xi) Lead	mg/l	0.20	1.0
(xii) Chromium; Trivalent	mg/l	0.20	1.0
(xiii) Copper	mg/l	0.20	1.0
(xiv) Manganese	mg/l	0.20	1.0
(xv) Nickel	mg/l	0.20	1.0
(xvi) Tin	mg/l	1.0	1.0
(xvii) Zinc	mg/l	1.0	4.0
(xviii) Boron	mg/l	1.0	5.0
(xix) Iron(Fe)	mg/l	0.001	1.0
(xx) Phenol	mg/l	1.0	2.0
(xxi) Free Chlorine	mg/l	0.50	0.50
(xxii) Sulfide	mg/l	Not Detectable	10.0
(xxiii) Oil and Grease			

Later, synthesis, processing and characterization of new semiconductor materials that were connected to industrial processes became the main interest. Nowadays, the main goal of research and development in the area is the use of the technique for air purification and waste water treatment, forming part of a group of processes known as Advanced Oxidation Technologies (AOTs) as shown in Figure 1.0 (Chen, et al., 2000; Davis, et al., 1999). These methods offer the advantage of destroying pollutants, in contrast to the conventional techniques such as the activated carbon or air stripping that only transfers the contaminants from one phase to another.

1.3 Basic Principle Of Heterogeneous Photocatalysis

The term photocatalysis consist of the combination of photochemistry and catalysis and thus implies that light and catalyst are necessary to bring about or to accelerate a chemical transformation. The catalysts used are semiconductors such as TiO_2 , SnO , ZnO , WO (as shown in Table 1.1 below). They act as catalysts due to their specific electronic structure. A semiconductor (SC) is characterized by an electronic band structures in which the highest occupied energy band, called valence band (vb) and the lowest empty band called the conduction band (cb), are separated by a bandgap.

When a photon of energy higher or equal to the bandgap energy is absorbed by a semiconductor particle, an electron from the vb is promoted to the cb with simultaneous generation of a hole (h^+) in the vb. The e_{cb^-} (electron at the conduction band, cb) and the h_{vb^+} (hole at the valence band) can recombine on the surface or in the bulk of the particle in a few nanoseconds (and the energy dissipated as heat) or can be trapped in surface states where they can

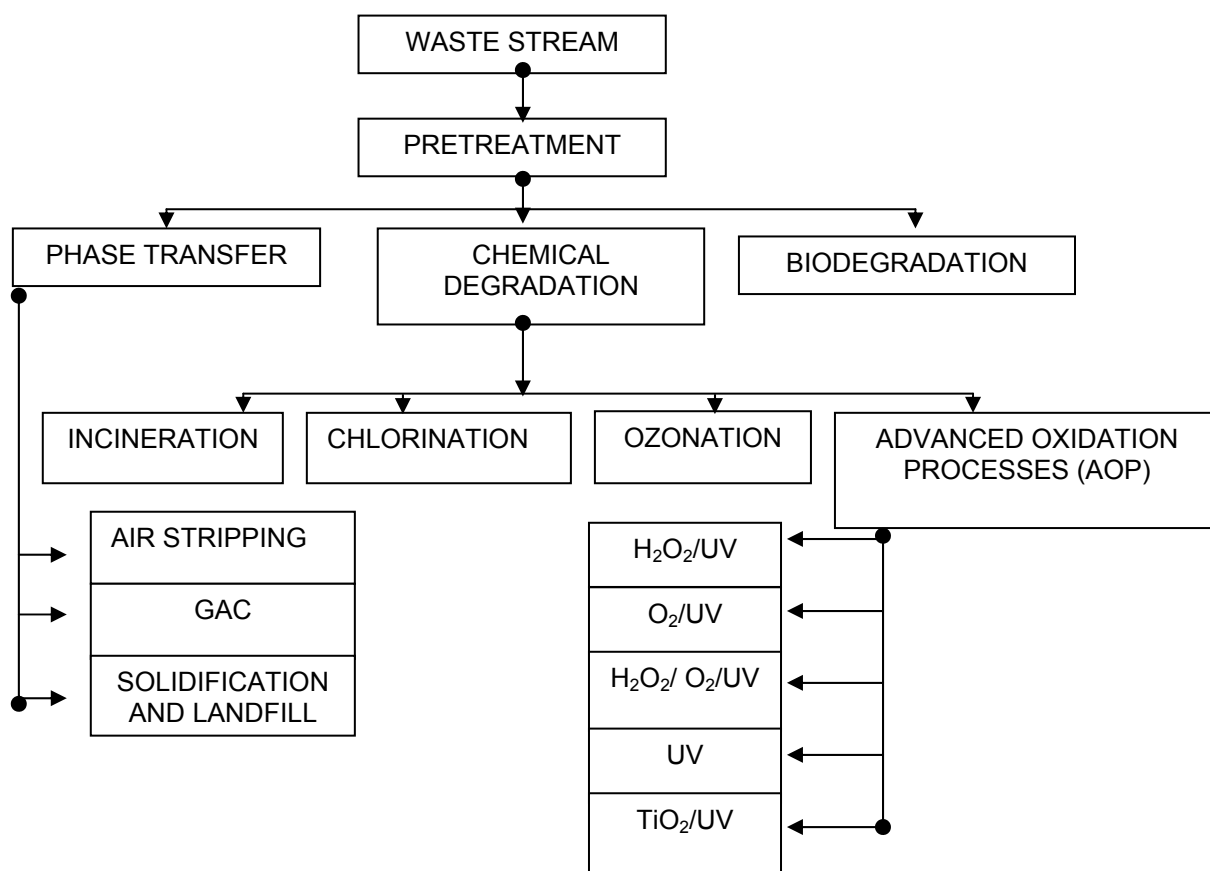


Figure 1.0: Different Waste Water Treatment Technologies In Environmental Engineering (Chen, et al., 2000)

Table 1.1: Bandgap Energies (at pH = 0) And Corresponding Threshold Wavelengths of Various Semiconductors (Chen, et al., 2000)

Semiconductors	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 ₂ O ₃	2.3	539
WO ₃	2.8	443

react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle. Thereby, subsequent anodic and cathodic reactions can be initiated (Serpone, et al., 1997).

The energy level at the bottom of the cb is actually the reduction potential of photoelectrons and the energy level of photoholes, each value reflecting the ability of the system to promote reductions and oxidations. The flatband potential, V_{fb} , locates the energy of both charge carriers at the SC-electrolyte interface, and this depends on the nature of the material and the system equilibria. From a thermodynamic point of view, adsorbed couples can be reduced photocatalytically by cb electrons if they have redox potentials more positive than the V_{fb} of the cb, and can be oxidized by h_{vb+} if they have redox potentials more negative than the V_{fb} of the vb.

The efficiency of a photocatalyst depends on the competition of different interface transfer processes involving electrons and holes and their deactivation by recombination (Fox and. Dulay, 1991; Serpone and Pelizzeti, 1989; Serpone, et al., 1997).

Starting in the late 1960's, researchers have been involved in an unfolding story whose main character is the fascinating material titanium dioxide (TiO_2) (Fujishima, et al., 2000; Yu, et al., 2002;). It all began with photoelectrochemical solar energy conversion and then shifted into the area of environmental photocatalysis (Fujishima, et al., 2000). TiO_2 in particular became the catalyst of choice for a large variety of applications because of its large surface area (7-50m²/g), cheap price, non-toxicity and has redox properties which are favorable both for oxidation for many organic pollutants and for the reduction of a number of metal ions in aqueous solution (Chen, et al.,1998;

Davis, et al.,1999; Horikoshi, et al.,1998; Horikoshi, et al.,1999; Khalil, et al., 1998; Kennedy, et al.,1998; Kobayakawa, et al., 1998; Kolle, et al.,1985; Navio, et al.,1998; Ollis, et al.,1991;Prairie, et al., 1993; Rajh, et al.,1996; Skubal, et al.,2002; Tennakone and Ketipearachchi, U., 1995; Wenhua, et al.,2000; Yu, et al.,2002 ; Zhang, et al., 2001).

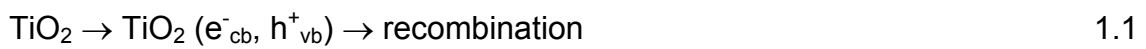
TiO₂ as compared to all other semiconductor photocatalysis, was found to be the most active and is extensively used in both laboratory studies and pilot plants. TiO₂ is cheap, insoluble under most conditions, photostable and non-toxic. Moreover, it is said that sunlight (about 3% of the solar spectrum contains Ultraviolet, UV) can be used as a possible light source for TiO₂ (Chen, et al., 2000).

TiO₂ exist primarily in two crystallographic forms namely anatase (3.23eV, 384nm) and rutile (3.02eV, 411nm). According to many studies, anatase was found to be in the active form as compared to rutile for photocatalytic reaction. The anatase form has a reasonably well- defined nature, (typically 70:30, anatase to rutile mixture), a non-porous with BET surface area of 55 ±15 m²/g and average particle size of 30 nm. The characteristics provide higher photocatalytic activity than most other readily available samples of TiO₂ (Litter, 2000)

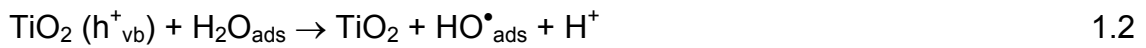
Some authors have also reported that TiO₂ is close to being an ideal photocatalyst in several aspects such as highly stable chemically in aqueous media in a large pH range, photogenerated holes are highly oxidizing and in addition the photogenerated electrons are reducing enough to produce superoxides from dioxygen (Fujishima, et al., 2000).

1.3.1 Mechanism Of TiO₂ Photocatalysis

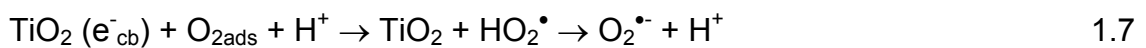
The heterogeneous TiO₂ photocatalytic process is a complex sequence of reactions that can be expressed by the following set of simplified equations shown below. When a photon of energy higher or equal ($h\nu$) to the bandgap energy is absorbed by a semiconductor particle, an electron from the vb is promoted to the cb with simultaneous generation of a hole (h^+) in the vb (equation 1.1)

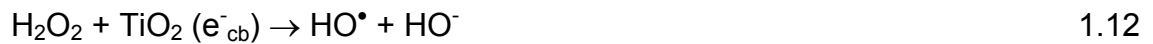


The equations of 1.2 to 1.6, show that the h^+_{vb} and the e^-_{cb} can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle.



Thereby, subsequent anodic and cathodic reactions can be initiated. Oxidative pathway, could be performed by direct hole attack or mediated by HO* radicals, in their free or adsorbed (ads) form as shown in equation 1.7 to 1.12. The oxidative pathway leads, in many cases, to complete mineralization of an organic substrate to CO₂ and H₂O. Generally, A is dissolved O₂, which is transformed into superoxide radical anion (O₂^{•-}) and can lead to the additional formation of HO* (Litter, 2000):





The illustration in Figure 1.1 shows various redox reactions that takes place in a spherical TiO_2 particle when it receives photon energy (Litter, et al., 1999).

1.3.2 Various Usage Of TiO_2 Photocatalyst

Over the past several years, a large number of applications of photocatalytic technology have been examined in various countries. Among them, TiO_2 was used as a self- cleaning material for residential and office buildings such as in exterior tiles, kitchen and bathroom components, plastic surfaces and building stone (Fujishima, et al., 2000).

It has also been used for air- cleaning process as an indoor and outdoor cleaners and purifiers. Here, photocatalyst-equipped air conditioners and interior air cleaners for factories has been applied. TiO_2 has been also used as a purification system for water storage tanks, drainage water and industrial waste (Fujishima, et al., 2000). In hospitals, TiO_2 functions as a self - sterilizing property, when it is used in tiles to cover the floor and walls of the operating rooms, hospital garments and uniforms. TiO_2 was also found to have inhibited tumor growth under the skin of the mice. As the skin was cut and exposed to irradiation the tumor was inhibited (Fujishima, et al., 2000).

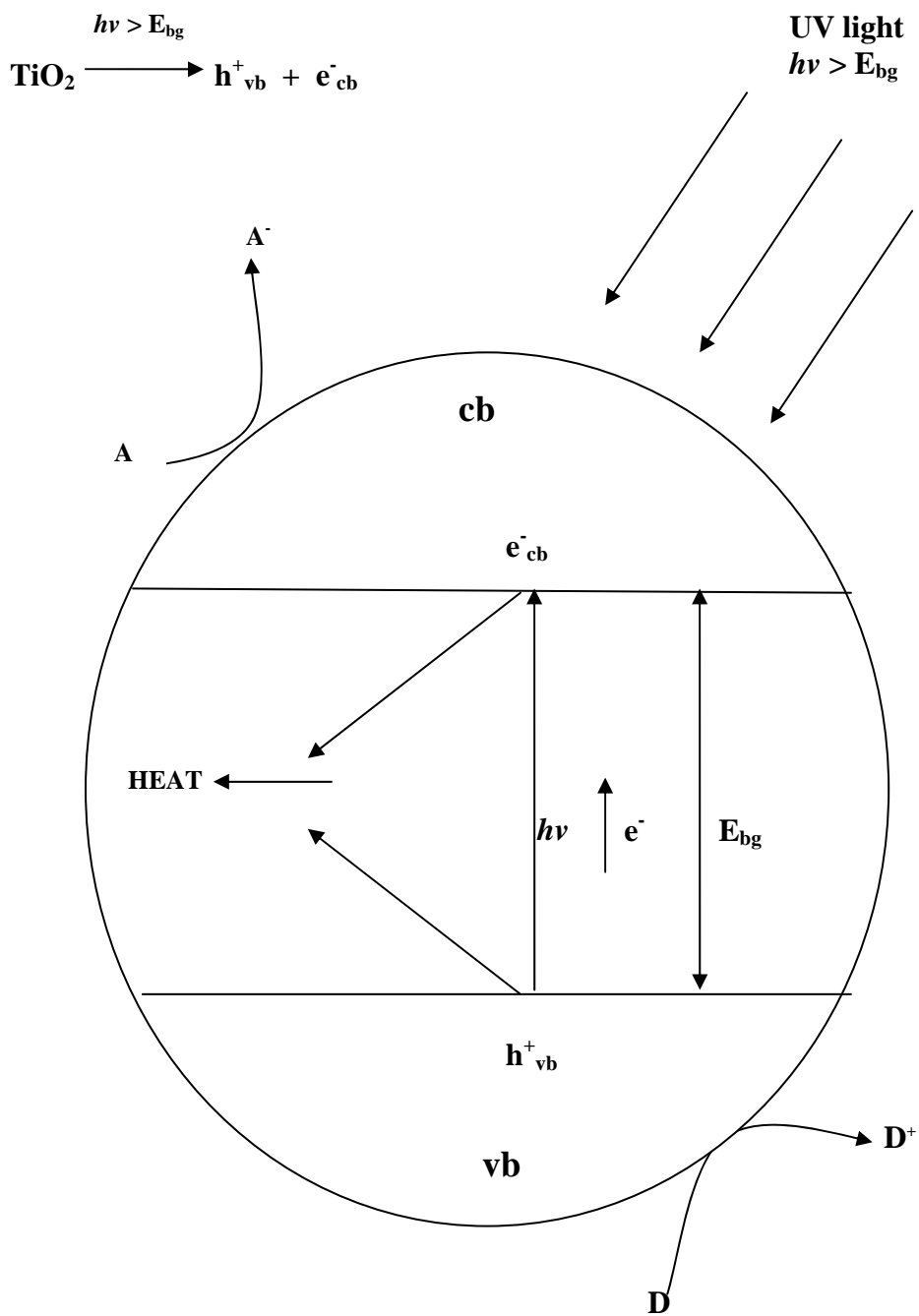


Figure 1.1: Schematic Illustration Of Generation Of Electron Hole Pairs In Spherical TiO_2 Semiconductor Particle Together With Some Of The Consecutive Redox Reactions That Take Place (Litter, et al., 1999)

Besides the above area, TiO_2 is also well known in organic and inorganic waste treatment. According to Otto Horvath and Hgyi (Horvath, et al., 2001), toxic metals such as Hg(II) , Bi(III) and Cu(II) could be reduced by intermediates generated by hole oxidation of added organics. This was carried out in aqueous system containing ethanol as a sacrificial electron donor.

In another study, photo mineralization of the constituent pyrimidine and purine bases in nucleic acid by UV illuminated TiO_2 particulates in an aqueous suspension were carried out (Horikoshi, et al., 1999). It was found that the photo mineralization of carbon atoms in the bases was faster in all cases than conversion of the nitrogen atoms. The three major mechanistic steps in the overall of these bases were;

- (i) Adsorption of the bases to the positively charge TiO_2 photocatalyst surface through the atoms bearing the greater negative charge.
- (ii) Hydroxyl radical attack at ring atoms possessing the greater electron densities
- (iii) Conversion of the carbons and nitrogen to carbon dioxide and to ammonia, nitrate ions and nitrogen respectively.

1.4 Immobilization Of TiO_2

Titanium dioxide photocatalysis has been demonstrated to be a promising method for the pollutant treatment mainly due to its capability of, removing metal ions and complete mineralization or at least partly destroying a variety of organic pollutants. However, much attention in this area was focused on the use of slurry system, about which the need to separate the spent fine catalysts particles and to keep the semiconductor suspended is usually necessary. According to several literature reports, the use of suspension requires recycling

of the ultra fine catalyst from the treated liquid and this can post inconvenience besides being a time consuming and expensive process. In addition, the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved organic species (Whenhua, et al., 2000 and Chen, et al., 2001).

Recently, studies have been carried out to minimize these problems by immobilizing TiO₂ on various materials such as glass and stainless steel. These studies on several different methods for the immobilization of TiO₂ on solid support substrates have been investigated by other workers and these are listed in Table 1.2. The various techniques used in these studies show serious attempts by researchers to find an ideal substitute to the widely used suspension method.

1.4.1 Electrophoretic Method (EPD)

The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found application in the past 40 years mainly in traditional ceramic technology (Gani, 1994). EPD (Electrophoretic Deposition) is achieved via motion of charged particles dispersed in a liquid towards an electrode under an applied electric field. Deposit formation on the electrode is achieved via particle coagulation. EPD is essentially a two-step process. In the first step, charged particles suspended in a liquid migrate towards an electrode under the effect of an electric field (electrophoresis). In the second step, the particles deposit on the electrode forming a relatively dense and homogeneous compact or film.

Table 1.2: Different Techniques of Immobilization

Immobilization Method For TiO ₂	Objective Of Work	References
1. Impregnation of pumice stone pellets with commercially available TiO ₂	For the photocatalytic degradation of 3-nitrobenzenesulfonic acid (3-NBSA), Acid Orange-7 (AO-7, a dye) and real wastewaters	Venkata Subba Rao K., A. Rachel, M. Subrahmanyam and Boule, P.
2. Coating on soda lime glass (2.5 cm×20 cm) by dipping process	Photocatalytic degradation of methyl tertiary butyl ether (MTBE) vapor	Sang Eun Park, Hyunku Joo and Joon Wun Kang.
3. TiO ₂ was immobilized on stainless steel tellerette packings	Objective of the work was to examine this new type of immobilized photocatalyst packing to determine its potential	Mehrab Mehrvar, William Anderson, A. and Murray Moo-Young.
4. TiO ₂ powder was immobilized on solid support substrates (stainless steel, titanium alloy, titanium metal, and tin oxide coated glass) using electrophoretic coating and spray coating	For the degradation of phenol in aqueous solution	Byrne, J. A., Eggins B., R., Brown, N. M. D., McKinney, B. and Rouse, M. Pages 25-36
5. Impregnation of TiO ₂ on pumice stone or volvic lava	Photochemical study of 4,4'-dinitrostilbene-2,2'-disulfonate (DSD) degradation	Anita Rachel, Bernadette Lavédrine, Jean-Pierre Aguer and
6. TiO ₂ powders were electrophoretically immobilized onto titanium foil	The photocatalytic removal of bacterial pollutants from drinking water	Dunlop, P. S. M., Byrne, J. A., Manga, N. and. Eggins B., R.
7. Two formed of Titanium catalyst : sol-gel and thermal film	To observe the fate of <i>Cryptosporidium</i> oocysts using these techniques	Curtis, T. P.; Walker, G.; Dowling, B. M. and Christensen P. A.

8. A reactor consist of a fiberglass sheet impregnated with TiO ₂ catalyst	To study the degradation of microcystin toxins	Gordon, S.; Shephard, Sonja Stockenström, David de Villiers, Willem J. Engelbrecht and Gabriël F. S.
9. Nanocrystalline photocatalyst TiO ₂ is immobilized on glass	In aid of solar decontamination of organic pollutants in water	Kumara, G. R. R. A., ; Sultanbawa, F. M., ; Perera, V. P. S., ; Kottegoda, I. R. M. and Tennakone, K.
10. TiO ₂ -epoxidized natural rubber on Al plate via electrophoretic deposition	Fabrication of the plate and degradation of phenol	Nawi, M. A., ; Lim, C., K., ; Tanaka, K., and Jab, M., S.

In general, EPD can be applied to any solid that is available in the form of a fine powder (<30 μm) or a colloidal suspension (Boccaccini and Zhitomirsky, 2002). Indeed, examples of EPD of any material class can be found, including metals, polymers, carbides, oxides, nitrides and glasses (Gani, 1994; Sarkar and Nicholson, 1996; Van der Biest and Vandeperre 1999). Major difficulties are linked to the selection of adequate solvents and additives, in particular regarding the chemical compatibility of the components of the binder–dispersant–solvent system (Boccaccini and Zhitomirsky, 2002).

A recent paper by Nawi, et al. (2003) demonstrates immobilization of TiO_2 onto Al plate by EPD technique. The deposition was enhanced by addition of epoxidized natural rubber (ENR). As an evaluation study of the technique's effectiveness, the immobilized TiO_2 was further tested for the degradation of phenol. ENR addition into the immobilizing solution was found to have improved the adhesiveness and robustness of the deposit and also significantly enhanced the immobilization process.

1.5 Photocatalytical Removal Of Metal-Waste

Kobayashi et al., (1983), searched for a suitable reaction system for a simultaneous photo deposition of lead oxide and palladium, and of ruthenium dioxide and platinum, onto TiO_2 . The results obtained in this study gave not only direct evidence of effective sites for heterogeneous reactions but also suggestions for the usefulness of the simultaneous photo deposition as means for modification of semiconductor surfaces to attach special functions such as electro-catalytic activity and high stability against decomposition in aqueous solutions.

Skubal and his co-workers, investigated the use of TiO₂ nanoparticles to remove aqueous cadmium from simulated wastewater was carried out. Nanosized colloids of anatase TiO₂ were synthesized through the controlled hydrolysis of TiCl₄ and their surfaces modified with TLA (Thiolactic Acid). Colloids were introduced into 65 ppm cadmium-laden water and were subsequently illuminated with 253.7 nm light. Upon illumination, greater than 90% of cadmium was removed by both adsorption and reduction processes onto the TLA-modified TiO₂. These removal and reduction process were catalytic in nature (Skubal et al, 2002).

Mercury (II) (Hg²⁺) a frequent component of industrial waste waters is remarkably toxic at concentrations above 0.05 mg/l and cannot be biologically or chemically degraded. However TiO₂ was able to reduce it to safer state. Hg²⁺ reduction, leading to Hg deposition on bare TiO₂ was made possible by a reductive system consisting of a layer of calcium oxalate coated on paper, followed by a layer of TiO₂. This system was also able to remove Ag to a lesser extent from solutions under solar irradiation. The deposited metal was determined and confirmed using x-ray diffractometry (Tennakone, et al., 1997).

Chen et al (Chen, et al., 1997) used x-ray absorption spectroscopies to monitor photoreduction reaction products of Hg²⁺ onto TiO₂ nanoparticle surfaces after UV illumination. The XANES (X-ray Absorption Near Edge Structure) and the FT-XAFS (Fourier Transform – X-ray Absorption Fine Structure) spectra of adsorbed Hg²⁺ in the presence of methanol after illumination indicated that almost all of the Hg²⁺ was reduced to metal state. When TiO₂ was modified by adsorption of Thiolactic acid (TLA), less than 50% photoreduction took place, showing that this adsorber hindered Hg

photoreduction. This was reported to be different from the case of Cu^{2+} for which adsorbed TLA enhances the photoreduction. The photoreduction techniques appear to be most promising since the mercury ions were reduced to elemental mercury which can be safely recovered or removed (Khalil, et al., 2002; Serpone, et al., 1987).

Large amount of silver at concentrations up to 6000 mg/l are normally found in effluents from photographic processes and waste water from silver jewelers (Huang, et al., 1996). The toxic effects of silver are not completely understood, but it is known as an effective bactericide which can have adverse effect on the biological system (Huang, et al., 1996). Hada et al (1982) and Clark et al (1965) have reported the study and ability of silver depositions on TiO_2 surface after the UV and infrared (IR) irradiation respectively. Hada and his co-researches, using TiO_2 powders and TiO_2 single crystals, interpreted the deposition by the transfer of cb electrons to adsorbed Ag^+ as opposed to a previous simpler scheme, Stern-Volmer behavior (Hada, et al., 1982). As for Clark and Vondjidis, concerning the nature of the deposits, the earlier IR studies gave evidences of metallic silver after UV irradiation (Clark, et al., 1965).

Huang et al (Huang, et al., 1996) reported the removal of silver in photographic processing waste by TiO_2 photocatalysis using UV or solar light. Silver was reduced to metal state, whereas thiosulfate, the predominant chemical in spent fixer, plays a complicated role as a hole scavenger and as a silver stabilizer. The metallic silver was separated from TiO_2 by sonication.

Titanium dioxide aqueous suspension was used to remove and concentrate Cu (II) ions in aqueous solutions through a cyclic process of photo deposition, separation and oxidation. Illuminated, nitrogen-purged solutions

containing copper sulfate, excess sodium sulfate, excess sodium formate (pH 3.6) and titanium dioxide formed a purple Cu-TiO₂ species. Cu (II) concentrations were reduced from 51 µg/ml to less than 0.018 µg/ml (Foster, 1993).

1.6 Lead

Lead is a naturally occurring metal. People have used lead for its useful properties such as low melting point, pliability and resistance to corrosion. Although lead is a useful metal, it is a known toxin and can produce harmful effects if not handled properly. Because of its widespread use, many jobs or occupation can expose people to lead.

Effluents from industrial processes represent important point sources of metal pollution. In the case of lead, the principal discharges occur at metal plating, photographic material, dyeing processes, explosive manufacturing, base metal mines, lead smelters and battery manufacturers (Watson, et al., 1973; Slapik, et al., 1982; Groffman, et al., 1992; Chen, et al., 2001; Moore, et al., 1990). Currently, 4×10^9 kg of lead are mined and disposed each year by global industrial activities. Lead contamination in the environment has long been recognized as a serious health problem in the United States (Groffman, et al., 1992).

Health studies done in Poland for duration of 2 years have linked elevated levels of lead in the environment with retardation and learning disabilities in children (Groffman, et al., 1992). Lead poisoning usually is first noticed as weakness, insomnia, constipation, blood changes, nerve and kidney damage and death in extreme exposures (Chen, et al., 2001; U.S. Department Of Transportation, 2000; Zhang, et al., 1998). According to Godwin, lead

poisoning is one of the most common pediatric health problems (Godwin, 2001). Lead poisoning can afflict both children and adults, but the greatest concern is for children, whom can tend to develop permanent mental and neurological problem. It was learnt that lead, which acts as a cumulative poison, is an enzyme inhibitor. Once mobile in the environment in ionic form, it finds its way through drinking water, food and air. Limit values of lead in drinking water and surface water intended for drinking as set by EU (European Union), USEPA and WHO (World Health Organization) are 10, 50 and 10 $\mu\text{g/l}$ respectively (Bhattacharjee, et al., 2003). Realizing the toxicity and the danger imposed by the presence of lead, various methods, such activated carbon, activated sludge, organic ligands, coagulants, precipitants, zeolites and many more have been carried out in many studies in order to remove lead from various sources (Baltpruvins, et al.,1996; Benjamin, et al., 1981; Cherry, et al.,1982; Groffman, et al., 1992; Hannah, et al.,1977; Kadirvelu, et al., 2000; Leentvaar, et al., 1978; Linstedt, et al., 1971; Namasivayam, et al., 1998; Nilsson, et al., 1971; Rowley, et al.,1984; Slapik, et al., 1982; Stephenson, et al., 1996; Zhang, et al., 1998). Among them, one of the most advanced and widely researched on currently is the photocatalysis method. Its usage on lead removal has been an on-going study. Various literatures have reported on the use of photocatalysis to remove lead (Chen, et al.,2001; Horvath, et al.,2001; Lawless, et al.,1990 ; Tanaka, et al.,1986; Tennakone, et al.,1997 ; Vohra, et al.,2000).

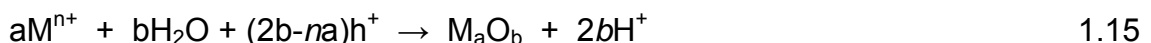
According to Otto Horvath and Hgyi (Horvath, et al., 2001), Pb (II), could be reduced by intermediates generated by hole oxidation of added organics. This was carried out in aqueous system containing ethanol as a sacrificial electron donor.

Pb^{2+} reduction, leading to metallic lead deposition which is not possible on bare TiO_2 was made possible by a reductive system consisting of a layer of calcium oxalate coated on paper, followed by a layer of TiO_2 (Tennakone, et al., 1997). The band gap radiation incident on TiO_2 generates electron-hole pairs of which the electrons tunnel into the solution reducing Pb^{2+} to metallic Pb. The holes react with hydroxyl ions producing highly oxidative hydroxyl free radicals which reacts with calcium oxalate yielding carbon dioxide (shown below in equation 1.13 and 1.14);



The experiments carried out showed the feasibility of using a solid hole-consuming agent to attract holes. This system was also able to remove Hg and Ag under solar irradiation.

Tanaka et al., (1986) found efficient transformation of lead ion into metallic lead under the illumination of Pt- TiO_2 suspensions. The reaction was found to have been enhanced by continuous bubbling of air through the suspension, whereas it decreased when argon or nitrogen gas was bubbled before illumination PbO_2 was identified as the product when Pt/ TiO_2 was the photocatalyst. Other metal ions were also transformed according to Equation 1.15, especially at low concentrations in the following order; $Pb^{2+} > Mn^{2+} > Ti^+ > Co^{2+}$.



Another study was carried out by Vohra, et al., in investigating the employment of TiO_2 -assisted photocatalysis in treating aqueous Pb-EDTA (Vohra, et al., 2000). Strong ligand-type Pb-EDTA adsorption onto TiO_2 had

been observed. It was found that lead became adsorbed onto the TiO₂ surface as complexed intermediates at higher pH. This study focused on the fate of lead which represents the primary toxicity concern.

Removal of lead from solutions by photocatalysis using irradiated platinized TiO₂ was carried out by Lawless et al (Lawless, et al., 1990). Upon irradiation of anatase platinized TiO₂, in an air-equilibrated or oxygen purged suspension containing 100 mg/l of lead, electrons and holes were trapped at surface sites (the catalytic sites) where the redox chemistry occurred. Lead was found reduced to Pb⁰ on the platinum islands and also oxidized to PbO₂ by a valence band process as well as by oxygen radical species. The results showed that the optimal condition for lead removal occurred at pH 3.7 with 2 g/l of TiO₂/Pt catalyst.

Dingwang Chen and Ajay K. Ray discussed the possibility of photocatalytic reduction for various metal ions (Chen, et al., 2001). Among the discussed metal ions, lead was one of them. According to them it is very unlikely for lead to be reduced under most pH conditions due to its extremely low driving force. This was based on the thermodynamic analysis which claims that the reduction of Pb (II) is impossible. However in their conducted experiments, the concentration of lead did decrease with the illumination time despite at a very slow rate

Many other reports of Pb²⁺ reduction to metallic lead on TiO₂ surfaces using various modified methods have been reported elsewhere in depth (Lawless, et al., 1990; Horvath, et al., 2001; Tanaka, et al., 1986).

In the various literature reviewed, it was found, very few articles reported on the photocatalytical removal of lead using TiO₂ as most of the papers

reported on conventional methods such as adsorption, ion-exchange, coagulant usage and precipitation. However the various photocatalytic removal methods for lead are found to be effective and practical for today's fast developing industries. Due to lead's redox position as claimed by Chen and Ray earlier, they reported that according to the thermodynamic analysis, reduction of lead is said to be impossible. Even if it is possible, the removal rate is found to be very slow.

1.7 Objective Of Research

A number of attempts are made to study the immobilization method. The usage of suspension as mentioned before has its own disadvantages such as the suspension requires separation and recycling of the ultra fine catalyst from the treated liquid and this can post inconvenience besides being a time consuming expensive process. In addition, the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved organic species. However the concept of immobilization overcomes most of these problems. Therefore an effective method of immobilization technique should be developed to overcome the loopholes of suspension usage.

Today in the waste water treatment field, a technology which is cost, energy and time saving is needed in the market. This capabilities and abilities are found in immobilized TiO_2 methods. However the immobilized methods have many weakness and limitations which need to be examined and studied. For an example, the usage of calcium oxalate which was introduced by Tennakone, is an interesting new modified method for lead removal (Tennakone, et al., 1997). However, the usage of paper as a base for its coating is found to be a weak corner of the experiment itself as the usage of paper as a