

PREPARATION AND CHARACTERIZATION OF TITANIA BASED
TRIMETALLIC METAL OXIDE PHOTOCATALYSTS FOR
PHOTODEGRADATION OF 1,2-DICHLOROBENZENE
AND POLYCHLORINATED BIPHENYL
COMPOUNDS IN AQUEOUS PHASE

RENUGAMBAAL A/P K.NADARAJAN

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ABSTRACT

The deterioration of water quality has raised serious safety concerns due to the discharge of chlorinated industrial wastes such as 1,2-dichlorobenzene (DCB) and polychlorinated biphenyls (PCBs) which are highly toxic and cause dangerous effects on human health. The polluted water is usually treated using adsorption method, Fenton, ozonation and photocatalysis. Among these methods, photocatalysis is the most promising technique for the easy decomposition of pollutants in the presence of suitable photocatalyst. Hence, in this research, a series of titania based photocatalysts have been prepared and were utilized to investigate its efficiency in the photocatalytic degradation of DCB in aqueous solution. The influence of catalyst preparation methods (sol-gel, sol-immobilization and mechanical mixing) were explored under different calcination temperatures, ratios and a light source. Further, the potential photocatalyst was then investigated by hydrothermal and hydrogenation techniques. Relatively, trimetallic oxide $\text{SnO}_2/\text{WO}_3/\text{TiO}_2$ (10:10:80) prepared by mechanical mixing of hydrothermal SnO_2 , WO_3 , TiO_2 calcined at 850°C , 850°C and 950°C respectively, exhibited the highest degradation of 98.43% under visible light irradiation at the DCB concentration of 100 ppm. The high activity of mechanically mixed hydrothermal trimetallic oxide $\text{Sn}_{850}/\text{W}_{850}/\text{T}_{950}$ (10:10:80)HY was associated with the exposed surface with edges as observed in the field emission scanning electron microscope (FESEM) morphologies, and also the presence of Ti^{3+} analyzed by X-ray photoelectron spectroscopy (XPS). The existence of surface defects was further confirmed by photoluminescence (PL) spectroscopy. The reduction in the band gap energy of the trimetallic oxide and the absorption shift towards the visible light region was observed in the absorption band edge using diffuse reflectance-ultraviolet visible (DRUV) spectroscopy. Meanwhile, transmission electron microscope (TEM) images confirmed the absence of an interface gap between the metal oxides which is beneficial for the occurrence of charge transfer and enhancement of the activity. The effectiveness of this photocatalyst when immobilized on polyvinyl chloride (PVC) film, nevertheless decreased the photocatalytic activity to 93.67%. Eventually, the degradation activity of DCB was improved to 95.70% upon increasing the photocatalyst loading on PVC film of up to 0.25 g and under neutral pH. The optimization utilizing response surface methodology with Box-Behnken design was in good agreement with the obtained experimental result. The degradation of DCB in water was justified by the identification of two intermediates using gas chromatography-mass spectrometry (GCMS) analysis. Consequently, the investigation on removal of PCBs from green mussels using polyethylene glycol (PEG), and subsequent degradation of PCBs in aqueous phase utilizing immobilized photocatalysts, capable to degrade 83% of the total PCBs content under the optimized conditions.

ABSTRAK

Kemerosotan kualiti air telah menimbulkan kesedaran yang tinggi terhadap kepentingan keselamatan disebabkan oleh pelepasan bahan sisa industri berklorin seperti 1,2-diklorobenzena (DCB) dan bifenil poliklorinat (PCBs) yang sangat toksik dan mengakibatkan kesan yang berbahaya kepada kesihatan manusia. Air tercemar biasanya dirawat dengan menggunakan kaedah penjerapan, Fenton, pengozonan dan fotopemangkinan. Antara kaedah-kaedah ini, fotopemangkinan merupakan teknik yang paling menjanjikan penguraian mudah bahan pencemar dengan kehadiran fotomangkin yang sesuai. Maka, dalam penyelidikan ini, satu siri fotomangkin berasaskan titania telah disediakan dan digunakan untuk mengkaji keberkesanan degradasi fotopemangkinan sebatian DCB di dalam air. Pengaruh kaedah penyediaan mangkin (sol-gel, pemegunan-sol dan pencampuran secara mekanikal) telah diteroka pada suhu kalsin, nisbah dan sumber cahaya yang berbeza. Seterusnya, fotomangkin yang berpotensi kemudiannya dikaji menggunakan teknik hidroterma dan penghidrogenan. Secara relatif, trilogam oksida $\text{SnO}_2/\text{WO}_3/\text{TiO}_2$ (10:10:80) yang disediakan melalui pencampuran mekanikal SnO_2 , WO_3 , TiO_2 hidroterma yang dikalsin pada suhu 850°C , 850°C dan 950°C masing-masing, mempamerkan degradasi yang tertinggi iaitu 98.43% di bawah penyinaran cahaya nampak pada kepekatan DCB 100 ppm. Aktiviti tinggi trilogam oksida hidroterma yang disediakan secara pencampuran mekanikal Sn850/W850/T950 (10:10:80)HY mempunyai kaitan dengan morfologi permukaan yang terdedah dengan bucu, yang dicerap menggunakan mikroskop imbasan elektron pancaran medan (FESEM) dan juga kehadiran Ti^{3+} yang dianalisis menggunakan spektroskopi fotoelektron sinar-X (XPS). Kewujudan cacat permukaan selanjutnya telah disahkan dengan spektroskopi fotopendarcahaya (PL). Pengurangan tenaga jalur bagi trilogam oksida dan penganjakan serapan kepada kawasan cahaya nampak telah diperhatikan dalam penyerapan pinggir jalur menggunakan spektroskopi pantulan serakan ultralembayung-cahaya nampak (DRUV). Manakala, imej daripada mikroskop penghantaran elektron (TEM) mengesahkan bahawa tiada ruang antara muka di antara logam oksida yang bermanfaat bagi berlakunya pemindahan cas dan peningkatan aktiviti. Keberkesanan fotomangkin ini yang dipegunkan di atas filem polivinil klorida (PVC) bagaimanapun, telah menurunkan aktiviti fotopemangkin kepada 93.67%. Akhirnya, aktiviti degradasi DCB telah meningkat kepada 95.70% dengan pertambahan muatan fotomangkin pada filem PVC kepada 0.25 g pada pH neutral. Pengoptimum menggunakan kaedah respon permukaan (RSM) dengan reka bentuk Box-Behnken (BBD) didapati bertepatan dengan keputusan eksperimen. Degradasi DCB di dalam air telah dibuktikan dengan pengenalpastian dua bahan perantaraan dengan menggunakan analisa gas kromatografi-spektrometri jisim (GCMS). Oleh yang demikian, kajian terhadap penyingkiran PCBs dari kupang dengan menggunakan polietilina glikol (PEG) dan seterusnya degradasi PCBs di dalam fasa akueus dengan menggunakan fotomangkin pegun, mampu mendegradasikan 83% daripada jumlah kandungan keseluruhan PCBs pada keadaan optimum.

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LIST OF ABBREVIATIONS

ACN	-	Acetonitrile
ANOVA	-	Analysis of Variance
a.u.	-	Arbitrary unit
BBD	-	Box-Behnken design
BET	-	Brunnauer, Emmet and Teller
BE	-	Binding energy
CB	-	Conduction band
CCD	-	Central composite design
cm	-	Centimeter
CO ₂	-	Carbon dioxide
conc.	-	Concentration
DCB	-	1,2-Dichlorobenzene
e ⁻	-	Electron
ECD	-	Electron capture detector
EDX	-	Energy dispersive X-ray analysis
EPA	-	Environmental Protection Agency
Eq.	-	Equation
EtOH	-	Ethanol
eV	-	Electron volt
FDA	-	Food, Drug and Additive
g	-	Gram
h ⁺	-	Positive hole
H ₂ O ₂	-	Hydrogen peroxide
HCl	-	Hydrochloric acid
hν	-	Photon energy
<i>I</i>	-	Intensity
M	-	Mol
mg	-	Milligram

mmol	-	Millimole
mmolL ⁻¹	-	Millimole per Litre
mL	-	Millilitre
m/z	-	Mass/charge
nm	-	Nanometer
o	-	Ortho
OC	-	Organochlorine
P/P _o	-	Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure P _o of the adsorbate at the temperature where the isotherm is measured
PDF	-	Powder diffraction file
rpm	-	Rate per minute
TOC	-	Total organic carbon
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet-visible
VB	-	Valence band
W	-	Watt
wt %	-	Weight percentage
zpc	-	Zero point charge
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Over the past decades, mankind has observed an unprecedented and remarkable growth in industry, resulting in generation of organic toxic wastes. Toxic waste has been relentlessly released into air and water leading to serious and devastating environmental and health problem (Anpo and Kamat, 2010). Some of the organochlorine compounds used in industrials have been detected to bioaccumulate in the environment and living organisms and cause many toxic actions. Such compounds have been identified as persistent organic pollutants (POP). Polychlorinated biphenyls (PCBs) and dichlorobenzene (DCB) are among the identified toxic organochlorine pollutants (OCP) under this category. Figure 1.1 shows the chemical structure of DCB and PCB.

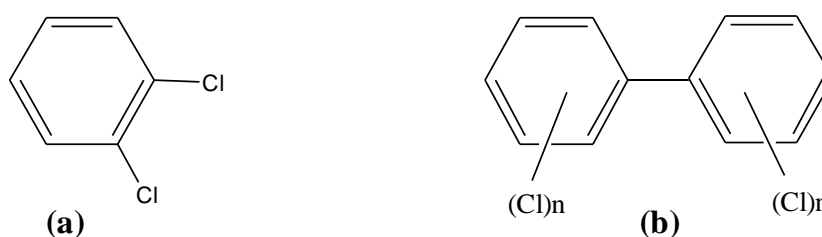


Figure 1.1 Chemical structure of (a) 1,2-dichlorobenzene (DCB) and (b) polychlorinated biphenyl (PCB)

PCB with chlorine attached to 2 benzene rings and DCB with chlorine attached to one benzene ring, are man-made organic compounds for wide application in industries as dielectric fluids or transformers and capacitors, in paints, inks and

pesticides. The number of chlorine at different positions in PCB leads to 209 different isomers and toxicity. DCB having three isomers with chlorine atom either at ortho, meta or para position is less toxic compared to PCB. These contaminants have very low solubility in water and thus are highly lipophilic and have long biological half-lives. Moreover, PCBs are extremely stable compounds under environmental conditions (WHO, 1998).

Organochlorine pollutants (OCP) can enter the aquatic system in a variety of ways, run-off from run-point sources, discharge of industrial and sewerage wastewater and wet/dry disposition. Due to their high persistence, these pollutants tend to bioaccumulate in fatty tissue of aquatic lives and subsequently into the food chain. Despite of the low concentrations (ppb to ppt), PCBs and DCB have high toxicity, carcinogenicity and mutagenicity. Toxic actions to humans include reproductive and developmental effects, neurological and behavioural effects, dermal toxicity, immunomodulatory and carcinogenic effects (Costopoulou *et al.*, 2016; ATSDR, 2002). Due to their potential detrimental effects on both environment and human health, PCBs and DCB have been listed as priority pollutants by United States Environmental Protection Agency (EPA, 2001) and Environmental Quality Standards Directive 2008/105/EC (Directive 2008; Directive 2013). In 2004, Stockholm Convention has urged many countries to reduce and eliminate POP. Nevertheless, despite the ban and restriction on the use of these chemicals, their contamination in air, sediment, water, biota and humans are still being reported.

In view of its toxicity, many studies were conducted worldwide monitoring the level of PCBs in marine/river water, fish, shellfish and also in human (from breast milk). Relatively very few data concerning the occurrence of DCB in water and fish has been reported, which is not surprising as the partitioning and accumulation characteristics of highly toxic PCBs makes it more attractive for study. Nevertheless, the contamination effect of those compounds should not be ruled out since, even at low doses, a long term exposure to it could bring various problems to humans. Some of the studies have shown that DCB has been detected in drinking water (Abdullah *et al.*, 2011; Dwiyitno *et al.*, 2016). Consequently, a detailed comparative account of DCB and PCBs worldwide has been summarized in Table 1.1 which delineates wide variations between different regions.

Table 1.1 Concentration level of PCBs in water, fish, mussels and human while DCB in water

Country	PCBs				DCB in water (ppb)
	Water (ppt)	Fish (ppb)	Mussel (ppb)	Human (ppb)	
Malaysia	1.4 - 14 (Huang <i>et al.</i> , 2014)	0.2 - 2.6 (Mohamad <i>et al.</i> , 2015)	5 - 250 (Yap, 2014)	80 (Tanabe & Kunisue, 2007)	0.01 - 64.1 (Abdullah <i>et al.</i> , 2011)
Indonesia	0.5 - 420 (Ilyas <i>et al.</i> , 2011)	10 - 2700 (Sudaryanto <i>et al.</i> , 2007)	6.7 - 250 (Bayen <i>et al.</i> , 2003)	6.7 - 250 (Sudaryanto <i>et al.</i> , 2006)	10 - 20 (Dwiyoitno <i>et al.</i> , 2016)
India	2 - 779 (Kumar <i>et al.</i> , 2012)	9 - 90 (Ahmed <i>et al.</i> , 2016)	10 - 2200 (Bayen <i>et al.</i> , 2003)	3.1 - 5400 (Devanathan <i>et al.</i> , 2012)	N.A.
China	0.2 - 2473 (Xing <i>et al.</i> , 2005)	6.3 - 199 (Sun <i>et al.</i> , 2014)	2.8 - 2480 (Xing <i>et al.</i> , 2005)	26 - 130 (Haraguchi <i>et al.</i> , 2009)	1 - 138 (Huang <i>et al.</i> , 2015)
Japan	9.6 - 133 (Yamamoto, 2014)	61.6 - 85.2 (Matsumoto <i>et al.</i> , 2014)	20 - 3100 (Ueno <i>et al.</i> , 2010)	14 - 360 (Haraguchi <i>et al.</i> , 2009)	N.A.
Korea	2.9 - 3.1 (Hong <i>et al.</i> , 2011)	2.9 - 96.6 (Yim <i>et al.</i> , 2005)	17 - 1000 (Ramu <i>et al.</i> , 2007)	20 - 128 (Haraguchi <i>et al.</i> , 2009)	N.A.
Hong Kong	N.A.	40 - 710 (Bayen <i>et al.</i> , 2003)	170 - 1000 (So <i>et al.</i> , 2005)	0.3 - 87 (Qin <i>et al.</i> , 2011)	N.A.
United State	N.A.	28 - 1337 (Greenfield & Allen, 2013)	576 - 1220 (Subedi <i>et al.</i> , 2014)	76 - 856 (Subedi <i>et al.</i> , 2014)	N.A.
Europe	1.4 - 264 (Montuori <i>et al.</i> , 2014)	1 - 1672 (Bettinetti <i>et al.</i> , 2016)	0.6 - 107.5 (Carro <i>et al.</i> , 2010)	N.A.	N.A.

Note : N.A. – Literature not available

Higher contaminant level of PCBs in fish was observed at industrialized and developed countries as Japan, China, United States and Korea. Although the usage of PCBs has been banned in those countries, the important sources such as older PCB-containing equipment, landfill, and incineration of e-waste are continuing to release

PCBs to the environment (Breivik *et al.*, 2007). A recent study suggested that large quantities of e-waste have been exported to Malaysia (Robinson, 2009). Due to PCBs lipophilicity, lipid containing food products such as meat and meat products, milk and dairy products, fish and seafood are responsible for at least 90% of human exposure to these toxic compounds (Bordajandi *et al.*, 2006). Among the 209 PCB isomers, PCB 28, 52, 101, 118, 138, 153 and 180 (Appendix A) were commonly detected at higher concentration in fish and shellfish. Nevertheless, research by Yap *et al.* (2014) only reported total PCBs in mussels at Malaysia and until now no report has been published on individual PCBs concentration.

The occurrence of these contaminants worldwide and its high risk on human health has caused several authorities to propose safety limits for PCBs and DCB in water and food products which vary according to the authorities. Most countries including Malaysia follow the standard by US Environmental Protection Agency (EPA) and European Commission Regulation (EC) which has stringent limitation for the concentration of DCB and PCB in drinking water and fishery product as shown in Table 1.2.

Table 1.2 The health problem and tolerable limit of DCB and PCB in drinking water and fishery product

Contaminant	Health problem	Drinking water	Fish and fishery products
1,2-DCB	Liver, kidney, or circulatory system problems.	0.6 ppm	NA
PCB	Skin problems, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer.	zero	2.5 ppt
Reference	EPA, 2001	EPA, 2001	Directive 2013

It has to be noted that the tolerable limit of PCBs in fish and fishery product has been narrowed from 6.5 ppt in EC 1881/2006 to 2.50 ppt on year 2013 which clearly shows the concern rose due to its adverse effect on human from daily intake.

Therefore, the concentration of this contaminant in water and seafood should be kept at recommended level to reduce its effect on human health.

1.2 Various Remediation Techniques

Numerous efforts have been made to remediate the contamination sources including soil, sediments and surface/ground water in order to improve the drinking water quality and reduce the contamination level into the aquatic biota. There are few remediation techniques which have been explored for the removal of DCB and PCBs from water source that involves biodegradation, physical adsorption, reductive dechlorination and advanced oxidation process. Although these methods are effective for the removal/degradation of DCB and PCBs, each has its advantages and limitations.

Biodegradation is a widely used method to treat organic pollutants that leads to a complete mineralization. Aerobic and anaerobic microbial conversions of chlorinated contaminant into nontoxic hydrocarbons have been studied for the potential application of in-situ treatment over the last few decades. The slower degradation rate associated with biodegradation limits large-scale application, and high concentrations of chlorinated solvents could have adverse effects on the microorganisms in the biodegradation media, resulting in a reduction in the efficiency of contaminant removal by this method (Huang *et al.*, 2014).

Physical adsorption method has high reliability due to a robust operating configuration and hence is widely used for the treatment of drinking water supplies and industrial wastewaters. Several adsorbents such as activated carbons (Sotelo *et al.*, 2002), multi-walled carbon nanotubes (Beless *et al.*, 2014), graphene (Wang *et al.*, 2013), cyclodextrin (Shao *et al.*, 2010) have been utilized for the removal of DCB and PCBs in aqueous medium. Adsorption using activated carbon has been recommended in EU directive 2001 for drinking water treatment (EPA, 2001). Compared to biodegradation, this process is considered a non-destructive method as this technique only transfers the contaminants from one phase to another. Therefore post-treatment

for the decomposition of the pollutants are necessary which leads to higher operating cost.

Reductive dechlorination has been intensively used for the remediation of DCB and PCBs due to the electronegative nature of chlorine. In reductive dechlorination, the chlorine ion is removed, forming non-toxic hydrocarbons. Most studies used zerovalent iron for the dechlorination of PCBs and DCB. The incorporation of noble metals (e.g. Cu, Pd, Ag, Ni) are often used in bimetallic system. Another reductive method is known as catalytic hydrodechlorination whereby external hydrogen source is employed as reducing agent. Palladium is found to be the best hydrodechlorination catalyst among other noble and transition metals. An obvious drawback of this technology is the relatively slow reaction rate as degradation process requires a couple of days to reach the desired level of completion. Besides, the reductive dechlorination also faces challenges such as corrosion of metals and passivation of catalyst surface as well as higher processing cost with the use of noble metals and hydrogen source (Ghosh *et al.*, 2012).

Advanced oxidation processes (AOPs) has been suggested as one of the most promising technology for the abatement of chlorinated compounds which includes ozonation, Fenton oxidation and photocatalysis techniques. These methods principally take advantage of the strong oxidation capacity of hydroxyl radical ($\cdot\text{OH}$) to decompose the chlorinated compounds and even complete mineralize of the contaminants to carbon dioxide and water.

The use of ozone in conjunction with UV light has been reported to completely remove chlorinated compounds in water. However, the low solubility of ozone in water is the major limitation in the ozonation process, besides the presence of CO_2 in environment restricts its efficiency in practical application (Kasprzyk-Hordern *et al.*, 2003).

Fenton based oxidation process has attracted a significant amount of attention for the decomposition of chlorinated compound due to its simplicity and efficiency. In Fenton process, mixture of H_2O_2 and Fe^{2+} (Fenton reagent) is used in acidic medium

to generate hydroxyl radicals for the decomposition of pollutants. The generation of hydroxyl radicals are further enhanced by irradiation of UV light, and it is known as photo-Fenton process and could be used at neutral pH. The main drawbacks of this process are the fast consumption of Fe^{2+} in comparison with its regeneration rate, the limited pH range to operate (pH 2.5 - 3), the complications of some iron species and the possible waste of oxidants as well as the inadequacy of dissolved oxygen in aqueous limiting the efficiency of Fenton reaction (Nidheesh & Gandhimathi 2012; Ribeiro *et al.*, 2015).

Photocatalysis technique with the use of heterogeneous photocatalyst has gained much popularity in the degradation of organochlorine in aqueous medium. In photocatalytic oxidation, the hydroxyl radical is generated upon light irradiation on photocatalyst which then decomposes the chlorinated compounds. The choice of suitable photocatalyst is the main concern for selective contaminants. The main advantage of heterogeneous photocatalysis process is its efficiency, fast degradation process and the complete mineralization to CO_2 and H_2O . In addition, sunlight could also be used as one of the light source in the presence of appropriate photocatalyst. This method is economic and has sustainability advantages in comparison with processes involving ozone or oxidant which requires high operational costs. Another advantage is the possible disinfection of water contaminated with pathogenic microorganisms (McCullagh *et al.*, 2007). The drawback of this method is the recovery of catalysts used in slurry batch system and regeneration that incur additional cost.

1.3 Semiconductor Photocatalysis

Semiconductor based photocatalysis has received increasing attention because of its promising applications in energy generation and environmental purification. Usually semiconductor metal oxides including TiO_2 , Fe_2O_3 , WO_3 , ZnO , CeO_2 , CdS , Fe_2O_3 , ZnS , MoO_3 , ZrO_2 , and SnO_2 are selected as photocatalysts due to their band gaps. In general, when a semiconductor metal oxide is irradiated by an input light with energy equal or higher than the band gap ($h\nu > E_g$), an electron (e^-) from valence band

(VB), is excited to the conduction band (CB), leaving behind a photogenerated hole (h^+) at the VB (Figure 1.2 and Eq. 1.1).

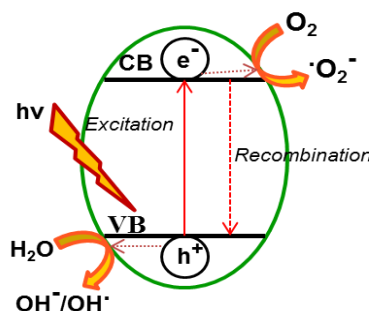
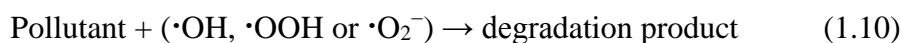
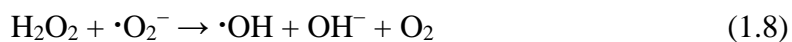


Figure 1.2 Absorption of photon energy by semiconductor and formation of electron-hole pairs

Consequently, the produced e^-/h^+ pairs migrate to the surface of the semiconductor leading to several reactions that generate active species as hydroxyl radical ($\cdot OH$) and superoxide radical ($\cdot O_2^-$). In aqueous medium, H_2O and OH^- that adsorb on photocatalyst surface are oxidized by photogenerated h^+ to form $\cdot OH$ radicals while dissolved oxygen is reduced by the photogenerated e^- to form $\cdot O_2^-$ radical (Refer Eq. 1.2 - 1.5). Protonation of $\cdot O_2^-$ yields hydroperoxide radical $\cdot OOH$ (Eq. 1.6) which is then further decomposed to produce $\cdot OH$ radicals (Eq. 1.7 - 1.9). The $\cdot OH$, $\cdot OOH$ and $\cdot O_2^-$ play an important role in initiating oxidation reactions, especially for substances that adsorb weakly on the semiconductor surface and facilitate the photodegradation of pollutants (Eq. 1.10). The oxidation-reduction reaction that occurs at the photo-activated surface of photocatalyst has been broadly proposed as following (Dong *et al.*, 2015):



It has to be noted that the separated photogenerated electrons and holes have characteristic lifetimes on the order of nanoseconds and could easily recombine after their generation in the absence of electron or hole scavengers. In this regard, the presence of specific scavengers or surface defects is vital in suppressing the charge recombination rates and in enhancing the efficiency of photocatalysis (Chong *et al.*, 2010).

1.4 Photocatalyst

The use of metal oxides as catalysts for the degradation of DCB and PCBs showed the increasing attraction because of their relatively low costs and high level of activity. TiO₂ is one of the most widely used semiconductor metal oxide with lowered activation energy and higher oxygen uptake that has significant effect on photocatalytic reaction. Commercial TiO₂ (Degussa P25) with mixture of anatase and rutile has been mostly utilized in the degradation of DCB and PCBs (Lin *et al.*, 2002; Zhu *et al.*, 2012) in gas phase and aqueous medium. However better photocatalytic activity was observed by the doping or coupling of titanium dioxide with other semiconductor metal oxides.

In this context, a series of transition metal oxides (Cr₂O₃, V₂O₅, MoO₃, Fe₂O₃ and Co₃O₄) supported on TiO₂ have been tested in catalytic oxidation of DCB by Krishnamoorthy (2000), and among them Cr₂O₃ and V₂O₅ supported TiO₂ catalyst showed the best activity in gas phase. However these metal oxides are highly toxic. Considerable catalytic activity was reported with the utilization of TiO₂/WO₃ and TiO₂/SnO₂ in gas phase (Bertinchamps *et al.*, 2006). Noble metals based catalysts such as Pd, Pt, Rh or Au, on the other hand could be easily poisoned by chloride ion during the decomposition process (Krishnamoorthy *et al.*, 1998). Thus, the type of semiconductor material used for coupling/doping with titanium dioxide is particularly important in term of the redox reaction which determines the overall efficiency of the photocatalyst. Extensive studies on the catalysts focused on the dispersion, surface structure and oxidation state of the supported catalyst and these properties have been correlated with the oxidation reactions.

Recently, surface modifications to the electronic structure of titanium dioxide in order to shift the absorption into the visible range and to reduce the charge recombination are under intense study in the photocatalysis field. The most common type of alteration involves structural defects with exposed facets and surface defects, which could be achieved by modifying the preparation method and calcination temperature. On this basis, the most studied metal oxides with exposed facets and surface defects are TiO₂, WO₃, SnO₂, and ZnO which have contributed to high catalytic activity by improved charge carrier separation. Wang *et al.* (2015a) reported that the presence of Ti³⁺ in anatase TiO₂ with (001) exposed facet demonstrated higher degradation of 4-chlorophenol under visible light irradiation. The efficient photocatalytic degradation of methylene blue by utilizing ZnO nanorods with higher aspect ratio and surface defects was reported by Zhang *et al.* (2014). Wang *et al.* (2015b) revealed that the enhanced photocatalytic performance of SnO₂ on photodegradation of Rhodamine B was attributed to the presence of high oxygen vacancies as surface defect.

Even though the toxicity of DCB and PCBs is of great concern and photocatalysis been known as an effective decomposition technique, yet research on these pollutants in aqueous medium is still in scarce. Most of the research works conducted on DCB was in gas phase using catalytic oxidation method while PCBs decomposition in soil and sediment was of higher interest. In view of this, semiconductor metal oxide TiO₂, WO₃, SnO₂ and ZnO have been explored for their efficiency in the degradation of DCB and PCBs in aqueous medium with the appliance of bimetallic and trimetallic systems.

Tungsten with narrow band gap is widely known to absorb visible light and its high surface acidity would enhance the adsorption of water molecule and organic pollutant (Grabowska *et al.*, 2012). Meanwhile SnO₂ was reported to be active under visible light when doped with TiO₂ and the most important is that it could avoid the poisoning of chloride ion (Sasikala *et al.*, 2009; Li *et al.*, 2014). On the other hand, doping of TiO₂ with ZnO has been widely used in photocatalytic study yet has not been reported for the degradation of DCB. Besides, this would be the first instance of trimetallic oxide been investigated for the photodegradation of DCB and PCB in aqueous medium. In addition the influence of the preparation method used to

synthesize the bimetallic and trimetallic oxides photocatalysts indicates the effects on the structure and active phase.

1.5 Response Surface Methodology

Response surface methodology (RSM) is a widely accepted statistical-based method for designing experiments, evaluating the individual and interaction effects of independent variables, and optimizing the process parameters with limited number of experiments. Chemometric techniques such as central composite design (CCD) and Box-Behnken design (BBD) have been proven to be useful techniques to evaluate optimal conditions in the photocatalysis process, as reported by Hamed *et al.* (2014) and Chaibakhsh *et al.* (2015). With the aid of this experimental design, results are quantitatively correlated to several experimental factors, and optimum conditions are achievable with savings of time and cost, since few distinctly varied experiments are carried out. In comparison, BBD was preferred due to the lesser number of experiments involved, yet provides good evaluation analysis. However most of the photocatalytic optimization was done on slurry mode using powder photocatalyst. Consequently, in this study, BBD was employed for optimization of DCB degradation in aqueous medium with immobilized photocatalyst.

1.6 Mechanistic Study

In semiconductor photocatalysis, there are three main path of reactions that occur during the reaction; adsorption of pollutant on the catalyst surface, desorption of the pollutant and diffusion of the by-products. These are the fundamental steps which are in accordance to Langmuir-Hinshelwood (LH) mechanism. It has to be noted that the catalysts has different surface properties which would lead to different reaction pathways. Therefore the study of the detailed processes of reaction mechanisms is important, including in understanding the reaction pathways as well as validation of the overall process. Several mechanistic studies have been conducted on catalytic oxidation of DCB in gas phase (Krishnamoorthy, 1999; Wang *et al.*, 2015). The

photocatalytic degradation mechanism of DCB in aqueous utilizing supported photocatalyst has not been reported. Thus, this present study might provide an underlying insight on the mechanism of DCB decomposition on immobilized photocatalyst.

1.7 Statement of Problem

Environmental pollutant has raised much concern towards its remediation techniques. Organochlorine pollutants such as DCB and PCBs are highly lipophilic, stable and persistence which facilitate their accumulation in the environment and aquatic ecosystem. As shown in Table 1.1, studies have reported the occurrence of DCB and PCBs contaminant in drinking water, fish and mussels which led to the detection of these compounds in human body. Despite of their low concentration, these contaminants have raised substantial health effect which emphasizes the necessity for further research on the removal and degradation of trace contaminants in water and fishery products to minimize their detection according to the EC standards.

Photocatalysis has been considered as sustainable and green chemistry technique for water treatment which leads to total mineralization of the pollutants. Nevertheless, up to now few research studies were done on the removal of DCB and PCBs from water using photocatalysis technique. One of the reasons could be due to the deactivation of the catalyst by chloride ion released during the reaction. As such, the selection of catalyst is crucial to avoid deactivation by the released chloride ion during the reaction. From the previous reports, high catalytic activity was not achieved by using TiO_2 alone. However, coupling with other semiconductor improved its performance. Besides, most of these studies utilized UV light source in the photocatalytic reaction which consume large amount of energy. Therefore, the development of visible light active photocatalyst with high efficiency and stability is desired. The synergistic effect by formation of heterojunction through coupling of two or more metal oxides has been shown to enhance the catalytic activity. This inspired the utilization of multi component semiconductor metal such as WO_3 , SnO_2 and ZnO in this study which leads to the formation of multi-heterostructure $\text{SnO}_2/\text{WO}_3/\text{TiO}_2$

and ZnO/WO₃/TiO₂ photocatalyst which are active under visible light. These photocatalysts have not been reported yet elsewhere and therefore they were studied in this research as based on previous studies, this type of co-catalyst have capability to mineralize the pollutants into harmless species such as H₂O and CO₂. In addition, the development of supported photocatalyst is crucial in this study for practical application. Several support materials have been reported, among which immobilization on glass plate, chitosan bead and PVC film has increased the photocatalytic activity. Thus this support material is employed with slight modification in the immobilization technique.

Meanwhile until now, there is no literature published on the removal of PCBs from the dietary intake as shellfish and fishery products. Instead study on PCBs remediation was done on sediments in order to reduce the accumulation of these contaminants in the aquatic life. However, the large area coverage incurs high cost and might not be efficient. The detection of toxic PCBs in fishery products not only cause health problem but also affect seafood business. Due to the high contaminant in fishery product, European United (EU) had banned the import of fishery product from Malaysia on year 2008 to year 2009 which had resulted in a huge loss of business for Malaysian seafood processors (Retnam *et al.*, 2013; EC No 1252/2008). Due to inadequate risk measurement on the contaminant levels, the Malaysian seafood industry is facing another challenge as the EU has withdrawn its generalised system of preferences for Malaysian seafood exporters in January 2014 (David, 2013). In view of this, research on in-situ removal and degradation of PCBs from fishery product is essential on the effort to minimize the contaminant in food intake. In this regard, photocatalysis technique which is known as environmental friendly and sustainable treatment technology has been explored by employing immobilized photocatalyst and visible light.

1.8 Objectives of the Study

Based on the problem statement, the main goal of this research was to develop a potential visible light active photocatalyst for the decomposition of DCB and PCB in aqueous medium. Thus, the objectives of this research are:-

- i. To study the effect of calcination temperature on structural defects and towards the degradation of 1,2-dichlorobenzene (DCB) using monometallic oxides (TiO_2 , WO_3 , SnO_2 and ZnO), bimetallic oxides (WO_3/TiO_2 , $\text{SnO}_2/\text{TiO}_2$, ZnO/TiO_2) and trimetallic oxides ($\text{SnO}_2/\text{WO}_3/\text{TiO}_2$ and $\text{ZnO}/\text{WO}_3/\text{TiO}_2$) under UV light.
- ii. To investigate the influence of preparation methods (sol-gel, sol-immobilization, mechanical mixing) of bimetallic and trimetallic oxides; with further evaluation on potential photocatalysts using hydrothermal and hydrogenation method.
- iii. To determine the optimum working conditions for the degradation of DCB in aqueous phase over the best immobilized photocatalyst under visible light and to optimize the photocatalytic degradation by using Response Surface Methodology (RSM) via Box-Behnken Design (BBD).
- iv. To propose mechanism for the decomposition of DCB in aqueous using the best immobilized photocatalyst under visible light.
- v. To apply the photocatalytic technology for in-situ removal and degradation of PCBs from green mussels by employing the best immobilized photocatalyst and visible light.

1.9 Scope of the Study

This research was aimed at developing a potential visible light photocatalyst for application in aqueous medium. A comprehensive study was conducted on degradation of 1,2-dichlorobenzene (DCB) and was then opted for study on polychlorinated biphenyl (PCBs) removal and decomposition in aqueous medium. In line with this, the efficiency of TiO_2 , WO_3 , SnO_2 and ZnO photocatalyst prepared by sol-gel method were explored under monometallic, bimetallic and trimetallic oxide

system for the degradation of DCB under UV light. The percent degradation of DCB was determined from the absorbance obtained using UV spectrophotometer. The effect of calcination temperature was exploited throughout the study while deviation in ratios was investigated on bimetallic and trimetallic oxides. As preparation method was known to cause physical modification on the catalyst, several preparation techniques (sol-gel, surface immobilization and mechanical mixing) were examined on bimetallic and trimetallic oxides. The effect of hydrothermal method was scrutinized on the potential photocatalysts. Stimulation of surface defects by hydrogenation and its effect on photocatalytic activity was inspected. Efficiency of the potential photocatalysts was then tested under visible light. The best photocatalyst subsequently was immobilized on several support materials (PVC film, chitosan beads and glass plate) to determine the suitable support material. The immobilized photocatalyst was then utilized for optimization study by the aid of response surface methodology technique. The reusability of the immobilized photocatalyst was also evaluated.

In order to study the physical properties of the photocatalysts, characterization analysis were carried out using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), X-ray Diffraction (XRD), Nitrogen Adsorption (NA), UV-Vis Diffuse Reflectance (DRUV), Photoluminescence (PL), X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The by-products obtained from DCB degradation were determined using gas chromatograph with mass spectrometer (GC-MS). A mechanism for DCB degradation in aqueous using immobilized photocatalyst was then proposed by using information from Fourier Transform Infra-Red (FTIR) spectroscopy. In the final stage of the study, the aptness of photocatalysis technique for in-situ removal and degradation of PCBs were conducted using green mussels collected from Sungai Melayu. The removal of PCB from mussels was done using food grade polyethylene glycol (PEG) and simultaneous decomposition with the presence of photocatalyst and visible light. The decomposition of five PCBs (PCB 15, 28, 52, 138 and 153) that are usually detected in fishery products according to EU directive was monitored using gas chromatograph with electron capture detector (GC-ECD).

1.10 Significance of the Study

Most of the water treatment plant uses biodegradation and adsorption method to remove/reduce the pollutants; however these methods are time consuming and not cost effective. Furthermore, organochlorine pollutants that exist in water are not easily degraded. In view of that, a simple photocatalysis technique with suitable catalyst was employed which leads to the degradation of chlorinated compound. The reactions could be conducted with a potential photocatalyst which is immobilized on suitable support material, under visible light and at ambient temperature and pressure. In addition, in this reaction other materials as oxidant or ozone are not necessary since they are not cost effective. The photocatalyst could be easily prepared using cheap metal oxides that are highly stable in aqueous and not easily poisoned. This potential technology was also explored on fishery product, which in fact is the first attempt in this field and has proven to be viable in removal of toxic compound as PCB. Accordingly, the novelties of this research study could be listed as following:

1. The development of new hybrid trimetallic oxide photocatalyst $\text{SnO}_2/\text{WO}_3/\text{TiO}_2$ in the ratio of 10:10:80 which are active in visible light region.
2. The significant appliance of immobilized photocatalyst on PVC in photodegradation of DCB in aqueous under visible light.
3. The proposed mechanism of DCB decomposition in aqueous under visible light using immobilized photocatalyst.
4. The application of photocatalytic technique for in-situ removal and degradation of PCB from green mussels which is environmental friendly method.

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