SYNTHESIS, PHYSICOCHEMICAL PROPERTIES AND PHOTOCATALYTIC ACTIVITY OF ZIRCONIA-TITANIA HETEROSTRUCTURED NANOCOMPOSITE FOR DEGRADATION OF PARAQUAT DICHLORIDE

NUR AFIQAH BINTI BADLI

UNIVERSITI TEKNOLOGI MALAYSIA

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NUR AFIQAH BINTI BADLI

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ABSTRACT

The advanced oxidation process using heterogeneous photocatalyst has been proven as a promising technique for the wide range of organic pollutants degradation in aquatic environment. Paraquat dichloride is a highly toxic organic pollutant that is still being widely used in agricultural sectors. This could cause malicious effects to living things and should be treated immediately. In this study, nanocomposite TiO_2 based photocatalysts incorporated with transition metal oxides were synthesized using modified sol-gel and hydrothermal methods. The photocatalytic activity of the prepared catalysts was examined for the paraquat dichloride degradation in aqueous solution under UV lamp (λ = 365 nm, 12 watts) and fluorescence visible lamp (λ > 400 nm, Philips, 36 watts) for four hours. The photodegradation of paraquat dichloride was monitored using ultraviolet-visible spectrophotometer. The potential catalysts were further accomplished for several optimization studies inclusive of co-catalyst ratio, calcination temperature and catalyst dosage. From the screening results, ZrO_2/TiO_2 photocatalyst calcined at 750°C was found to give the best photocatalytic activity for both methods. The characterization analyses showed the presence of crystalline heterostructure $ZrTiO_4/Ti_2ZrO_6/TiO_2$ species with particle size in the range of 8-25 nm and band gap energy of 3.1 - 3.38 eV. The obtained species were confirmed by X-ray photoelectron spectroscopy and high resolution-transmission electron microscopy. The nano irregular morphology was observed with mesoporous mixtures of Type III and IV isotherms and H2 (b) type hysteresis loop with surface area of 49 m^2g^{-1}. The highest photodegradation of 98.45% was obtained using 0.3 g of ZrO_2/TiO_2 (40:60) prepared by hydrothermal method with 100% mineralization after irradiated for four hours. Meanwhile, for sol-gel method, only 84.51% of degradation was obtained over 0.3 g of ZrO_2/TiO_2 (20:80) catalyst. Response surface methodology with Box-Behnken design suggested that 0.3 g of ZrO_2/TiO_2 catalyst with 40:60 Zr to Ti ratio and calcination temperature of 815°C is required to achieve 98.43% of paraquat dichloride degradation. Under this condition, the paraquat dichloride photodegradation achieved 98.87%, higher than the recommended value. Furthermore, the advance optimization on the effect of pH, addition of H_2O_2, sonication treatment, hydrogenation process and immobilization on the support material were also studied but no significant increment was observed for the photodegradation. The suggested active species from the radical scavenger studies were in the order of $e^- > O_2^{\bullet-} > OH^\bullet > h^+$. From the mechanistic study, the paraquat cation was adsorbed on the ZrO_2/TiO_2 (40:60) photocatalyst surface while intermediates of monopyridone, $C_{12}H_{16}N_2O_4$ ion, 4-carboxyl-1-methylpyridium ion were validated by Gaussian 16 software. The mechanism was confirmed following the first-order kinetic in accordance to Langmuir-Hinshelwood model.

ABSTRAK

Proses pengoksidaan termaju menggunakan fotomangkin heterogen telah terbukti sebagai teknik yang menyakinkan bagi degradasi pelbagai pencemar organik di dalam persekitaran akuatik. Paraquat diklorida adalah bahan pencemar organik yang sangat toksik yang masih digunakan secara meluas dalam sektor pertanian. Ia boleh menyebabkan kesan buruk kepada benda hidup dan perlu dirawat dengan segera. Dalam kajian ini, fotopemangkin nanokomposit berasaskan TiO_2 yang digabungkan dengan oksida logam peralihan telah disintesis menggunakan kaedah sol-gel yang diubah suai dan hidroterma. Aktiviti fotopemangkinan mangkin yang disediakan telah diuji bagi degradasi paraquat diklorida di dalam larutan akueus di bawah lampu UV (λ = 365 nm, 12 watt) dan lampu pendarfluor nampak (λ > 400 nm, Philips, 36 watt) selama empat jam. Fotodegradasi paraquat diklorida telah dipantau dengan menggunakan spektrofotometer ultraungu-cahaya nampak. Mangkin yang berpotensi kemudiannya dilengkapi dengan beberapa kajian pengoptimuman termasuk nisbah ko-mangkin, suhu kalsinasi dan dos mangkin. Daripada hasil saringan, ZrO_2/TiO_2 dikalsin pada 750°C didapati memberikan aktiviti fotomangkinan terbaik bagi kedua-dua kaedah. Hasil analisis pencirian menunjukkkan kehadiran struktur hetero berhablur spesies $ZrTiO_4/Ti_2ZrO_6/TiO_2$ dengan saiz zarah antara 8-25 nm dan tenaga luang jalur 3.1 - 3.8 eV. Spesies yang diperoleh telah disahkan dengan spektroskopi fotoelektron sinar-X dan mikroskopi electron penghantaran resolusi tinggi. Morfologi nano tidak sekata diperhatikan dengan campuran liang meso isoterma jenis III dan IV dan keluk histeresis jenis H2 (b) dengan luas permukaan 49 m^2g^{-1}. Fotodegradasi tertinggi iaitu 98.45% telah diperoleh menggunakan 0.3 g ZrO_2/TiO_2 (40:60) yang disediakan melalui kaedah hidroterma dengan pemineralan 100% selepas penyinaran selama empat jam. Sementara itu, bagi kaedah sol-gel, hanya 84.51% degradasi diperoleh menggunakan 0.3 g pemangkin ZrO_2/TiO_2 (20:80). Kaedah permukaan gerak balas dengan reka bentuk Box-Behnken mencadangkan bahawa 0.3 g mangkin ZrO_2/TiO_2 dengan nisbah Zr kepada Ti 40:60 dan suhu pengkalsinan 815°C diperlukan untuk mencapai 98.43% degradasi paraquat diklorida. Di bawah keadaan ini, fotodegradasi paraquat diklorida telah mencapai 98.87%, lebih tinggi daripada nilai yang disyorkan. Tambahan pula, pengoptimuman kesan pH, penambahan H_2O_2, rawatan sonikasi, proses penghidrogenan dan pemegunan pada bahan sokongan juga telah dikaji namun tiada kenaikan ketara fotodegradasi diperhatikan. Spesies aktif yang dicadangkan daripada kajian pemerangkapan radikal adalah mengikut urutan $e^- > O_2^{\bullet-} > OH^{\bullet} > h^+$. Dari kajian mekanistik, kation paraquat telah terjerap pada permukaan fotomangkin ZrO_2/TiO_2 (40:60) manakala sebatian pertengahan monopiridon, ion $C_{12}H_{16}N_2O_4$, ion 4-karboksil-1-metilpiridium pula telah disahkan dengan perisian Gaussian 16. Mekanisme telah disahkan mengikuti kinetik kelas pertama sesuai dengan model Langmuir-Hinshelwood.

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LIST OF ABBREVIATIONS AND SYMBOL

ANOVA	-	Analysis of Variance
a.u.	-	Arbbitary unit
BBD	-	Box-Behnken design
BE	-	Binding energy
CB	-	Conduction band
CO_2	-	Carbon dioxide
e-	-	Electron
Eq.	-	Equation
h^+	-	Positive hole
H_2O_2	-	Hydrogen peroxide
HCl	-	Hydrochloric acid
$h\nu$	-	Photon energy
m/z	-	Mass/charge
PDF	-	Powder diffraction file
rpm	-	Rate per minute
TOC	-	Total organic carbon
UV-Vis	-	Ultraviolet-visible
VB	-	Valence band
W	-	Watt
wt %	-	Weight percentage
zpc	-	Zero point charge
λ	-	Wavelength

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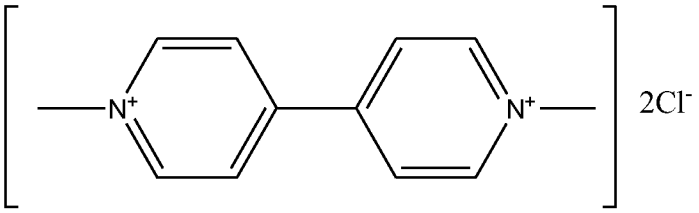
CHAPTER 1

INTRODUCTION

1.1 Background of study

Water is one of the most crucial sources in an ecosystem. About 70 % of the Earth's surface is covered by water. Water pollution has become one of the severe global issues due to the toxic contaminants discharge directly or indirectly from industries or domestic activities without proper treatment. Subsequently causes the consumption of polluted or infected aquatic life and water, resulting in long term illness on the human being. Direct contaminant such as effluent from factories and sewage treatment plants is regulated under the Environmental Quality Act 1974 and Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. Meanwhile, indirect contaminant source is difficult to be identified and this contamination usually comes either from the soil, groundwater and atmosphere via rainwater or agricultural practices like fertilizers and herbicides. These pollutants commonly lead to soil and groundwater contamination leading to ill-associated towards human health and aquatic biodiversity. In common, agricultural residues such as herbicides are strongly adsorbed by soil and may leach into the water bodies by rainfall or runoff which could give a nasty effect on living things mainly for humans.

Recently, the statistic of herbicide usage increased rapidly along with the world population thus increases the food consumption's demand (Diaz Kirmser *et al.*, 2010). Among the herbicide used, paraquat dichloride is one of the active ingredients that was widely used for the agricultural and non-agricultural sectors. This compound is known as methyl viologen with the IUPAC name of 1,1-dimethyl-4,40-bipyridylium dichloride. The structural formula for paraquat dichloride is shown in Figure 1.1



1, 1'-dimethyl-4, 4'-bipyridinium dichloride

Figure 1.1 Structure formula of Paraquat dichloride

Paraquat dichloride is harmful to humans and could lead to fatal injury if they exceed the lethal dosage. Paraquat poisoning can lead to dysfunctional kidney and liver in humans and animals. Besides that, it also might cause Parkinson's disease (Mandel, Adami and Cole, 2012). However, paraquat dichloride demand increased due to the low-cost and high efficiency to eliminate a wide range of weed made it popular for massive applications. Widespread use of paraquat dichloride application on the soil surface resulted in contamination of water bodies due to heavy rainfall and thus penetrates into the food chain. It also shows high persistence and toxicity in the environment, which has an impact on the environment (Huston and Pignatello, 1999). Hence, it is important to control water contamination to keep the reservoir from being polluted. At present, paraquat dichloride has been banned in certain countries which are Austria, European Union and South Korea (Santos *et al.*, (2013),Cha *et al.*, (2016) and Veríssimo, Bast and Weseler, (2017). Malaysia has also had decided to ban the use of paraquat dichloride starting in January 2020 (The Sun Daily, 2020) but it can be only used for the selected agricultural sector and must be controlled under Pesticide Act 1974.

According to the United States Environmental Protection Agency (2018) the maximum contamination levels (MCL) for paraquat in drinking water is 20 µg/L. While, based on the National Water Quality Standards for Malaysia the maximum concentration level for water resource was set at 10 µg/L (Huang et al., 2012). In Malaysia, the concentration of paraquat dichloride detected is at ranging from1.49 – 2.29 µg/L (Iguegbe and Mohd, (2008), . Ismail, Sameni and Halimah, (2011)). Eventhough the concentration detected still in ppb level but the half-life of paraquat in

the soil can be up to 6 years which might cause a serious impact on humans and other living things in the futures and must be treated (Alexander. M, 1999).

The development in science and technology causes an increase in demand to solve the paraquat dichloride contamination in the aquatic environment. Numerous treatments have been done to overcome these contaminations either by physical, biological or chemical methods. Generally, biological treatment methods such as using enzymes and microorganisms are not effective, because biological methods might produce secondary pollutants after the reaction that need further treatment which will be an additional cost (Han *et al.*, 2009). Besides, some of the organic pollutants are chemically stable and difficult to be degraded by these methods. Moreover, a long retention time is required for the degradation of organic pollution by using biological methods (Wu *et al.*, (2013) and Li *et al.*,(2017)).

The physicochemical method has emerged as a promising method to degraded paraquat dichloride due to its high efficiency and non-toxic properties. Heterogeneous photocatalyst has received considerable attention among researchers. This was due to its effectiveness to degrade and mineralize a wide range of organic and inorganic contaminations in the aquatic environment to harmless by-product(Ahmed *et al.*, 2011). Heterogeneous photocatalytic oxidation is a reaction that involves the use of catalyst that has a different phase from the reactant. Catalyst is a substance that increases the reaction rate by providing an alternate mechanism pathway. Meanwhile, photocatalysis is a process of acceleration of the photoreaction in presence of light. In photogenerated catalysis, the photocatalytic activity depends on the ability of the catalyst to create electron-hole pairs in producing free radicals (hydroxyl radicals, OH•). It will decompose and remove the toxicity of harmful organic chemical substance into carbon dioxide and water (Rauf and Ashraf, 2009).

Among semiconductor material, titanium(IV) dioxide (TiO_2) is the most favourable photocatalyst for heterogenous photocatalysis due to its non-toxicity, the capability of degrading a wide range of pollutants, insoluble in water, good reusability and photostable which makes it a suitable photocatalyst for applications in environmental remediation nowadays (Teh and Mohamed, 2011). Furthermore, an

extensive literature has shown many possibilities of improving the photocatalytic efficiency of TiO_2 especially by incorporating with transition metal oxide. The incorporation of titanium dioxide with transition metal oxide also had received much attention which mostly will contribute to better photocatalytic performance of either using UV irradiation or visible light (Han *et al.*, 2009).

Transition metals exhibit more than one oxidation stated that enables to enhance the photocatalytic performance of TiO_2. This was due to ability to act as traps for photogenerated electron and hole pairs as well as charge traps in the lattice of TiO_2. The incorporating with transition metal was believed can prevent the agglomeration of particles thus forming well-defined nanocrystal with high surface area. Moreover, the incorporation of transition metal ions into the matrix could decrease the band-gap energy of TiO_2 and causes a red shift of the absorption edge to the visible-light region. This red shift is caused by the charge-transfer transition between the d electrons of the transition metals and the CB or VB of TiO_2. In addition, transition metal ions in the TiO_2 lattice could delayed the recombination rate of photogenerated electron and holes by act as traps thus improving the photocatalytic activity of single TiO_2.

Response surface methodology (RSM) is one of the computational method that has been used for designing the optimization of the experiment to obtain the optimum response (Sakkas *et al.*, 2010). This technique can be used to develop models from experimental or simulation data and evaluating the individual or interaction between the variables. Among the RSM design used, Bob-Behnken design (BBD) has proven as a useful technique for optimization process as it requires less experimental points with high efficiency (Toemen, Bakar and Ali, (2014)and Tantriratna *et al.*, (2011). RSM also had been used by researchers in photocatalysis field either for experimental design or for process optimization.

Therefore, the degradation of paraquat dichloride using the photocatalysis method could be the alternative and most effective method. Thus, our current research focus on the synthesize of high efficiency nanocomposite TiO_2 based photocatalyst prepared by sol-gel and hydrothermal methods using transition metal as co-catalyst and immobilized on the support material. In addition, optimization study was carried

out to check the suitability of this technique to optimize the photocatalytic performance of potential photocatalyst over degradation of paraquat dichloride via BBD.

The novelties of this research study are as follows:

1) The development of heterostructured $ZrTiO_4/ZrTi_2O_6/TiO_2$ photocatalyst that enhanced the degradation of paraquat dichloride.
2) The optimization of the experimental conditions towards the photocatalytic degradation of paraquat dichloride over the potential catalysts using BBD (RSM).
3) A proposed cyclic stepwise mechanism for paraquat dichloride degradation under UV irradiation using ZrO_2/TiO_2 (40:60) photocatalyst.
4) The new intermediate product for paraquat dichloride degradation and the structural confirmation test using Gaussian 16 software.

1.2 Problem Statements

Paraquat dichloride contamination in the aquatic environment could give dangerous effects on human beings and living things. Therefore, an immediate solution is needed to solve this problem. Although a few treatment methods have been investigated for the degradation of paraquat dichloride however all methods have their drawbacks. Thus in this study, it is proposed to use the photocatalysis technology to degrade paraquat dichloride in solution by using nanocomposite TiO_2 based photocatalyst.

Currently, TiO_2 photocatalyst had gained wide interest in the degradation of various aquatic contaminations. Meanwhile, it is still not suitable for practical application due to its lower photo utilization efficiency and relatively higher band gap (Horváth *et. al.*, 2003, Zu *et. al.*, 2009). However, incorporating with suitable transition metal oxide had shown promising technique to enhanced the efficiency. The incorporation with transition metal oxides will give the useful outcome that might improve the photocatalytic activity. This is due to either the reduction in the band-gap

energy or formation of heterostructured photocatalyst which will increase the generating hydroxyl radicals ($OH^{\bullet}$). Besides that, the existence of heterostructure might lead to charge transfer between species thus producing more active species and formation of nanoheterostured had reported could lead to improve the photocatalytic activity even the bad gap increases. This was due to cative species existed on the catalyst surface even the band gap energy increases (Li *et al.*, 2016). In addition, only a few studies on the degradation of paraquat dichloride were conducted employing nanocomposite TiO_2 photocatalyst. Furthermore, the synthesis of visible light driven photocatalyst is crucial for a practical use of photocatalysis technique for the degradation of paraquat dichloride in water since artificial UV light is costly and only 11% could be found in the sunlight. In addition, the immobilization of the photocatalyst on the support material also was proven would be useful for industrial application.

In the other hence, the mechanistic study of paraquat dichloride is still vague due to limited research had been conducted using photocatalysis technology especially, using nanocomposite TiO_2 based photocatalyst. Therefore, this study is important to reveals the reaction pathway and the intermediate products formed during the photocatalytic degradation reaction. Thus, giving an insight on effect of the photocatalytic process on surface of the catalyst which can be an added valuable knowledge for the degradation study of paraquat dichloride using photocatalysis process.

1.3 Objective of the research

The objectives of the research are as follow:

1. To synthesize and characterize nanocomposite TiO_2 photocatalyst with transition metal oxides as co-catalyst via modified sol-gel and hydrothermal methods

2. To test and optimize the photocatalytic performance of the prepared photocatalyst for degradation of paraquat dichloride
3. To investigate the kinetic reactions and postulate a mechanism for photodegradation of paraquat dichloride through the analysis on the photocatalyst surface and intermediate products obtained

1.4 Scope of the research

This research was focused on developing a photocatalyst toward the degradation of paraquat dichloride. Therefore, a series of photocatalysts were prepared using TiO_2 as a based catalyst while transition metal oxide was selected as co-catalysts. All single, bimetallic and trimetallic oxide photocatalysts were prepared by sol-gel and hydrothermal methods. The TiO_2 and MO/TiO_2 (MO = NiO, Sc_2O_3, ZrO_2, CoO, CuO, ZnO, MoO_3, RuO, Fe_2O_3, and V_2O_5) photocatalysts were prepared based on the atomic weight percentage.

The photocatalytic performance of the synthesized catalysts was tested under UV irradiation and visible light using a home built a reactor and was monitored by UV-Vis spectrophotometer and total organic carbon (TOC) analysis. The UV lamp (λ =365nm, 12 watts) and compact fluorescence visible lamp (λ> 400 nm, Philips, 36 watts) were used as light sources. Then, the best prepared photocatalysts were characterized by using different techniques to study the physicochemical properties which are X-ray diffraction (XRD), field emission scanning electron microscopy-energy dispersion X-ray (FESEM-EDX), transmission electron microscopy (TEM), diffuse reflectance ultraviolet-visible (DR UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS) and nitrogen absorption-desorption (NA). Next, the photocatalyst obtained from both methods were optimized on the preparation of photocatalysts using various co-catalysts loading (10:90, 20:80, 30:70, 40:60 and 50:50), calcination temperature (450 - 1000°C) and catalyst dosage (0.1 g to 0.4 g. The reusability testing and mineralization study were carried out using the best catalyst obtained from both methods. Validation

of experimental results was done using response surface methodology (RSM) via Box-Behnken design (BBD).

Then, the best photocatalyst was optimized on the photocatalytic degradation activity. The five studied parameters are initial pH (pH 5,6,7, 8 and 9), hydrogen peroxide concentration (2, 3, 4, 5, 10, 15 and 20 ppm), sonication time (30, 45, and 60 minutes), hydrogenation (700, 750, 800 and 900 ℃) and immobilization on PVC and chitosan bead as the supported material using one factor at a time method. Lastly, the mechanistic study was determined by using liquid chromatography-mass spectrometer quadrupole time-of-flight (LCMS-QTOF) and the structural confirmation test was done with Gaussian 16 software to identify the intermediate species and fourier transform infrared spectroscopy–attenuated total reflectance (FTIR–ATR) was used to monitor the adsorbed species on the catalyst surface. The active species was investigated using benzoquinone, ammonium oxalate, silver nitrate and tert-butyl alcohol as scavengers for superoxide radical, holes, electron and hydroxyl radical, respectively.

1.5 Significance of the research

The study gave valuable contributions on the developed preparation method of nanocomposite TiO_2 photocatalyst incorporating with transition metal oxide that have high stability and good photocatalytic performance. The characterizations of the prepared TiO_2-based photocatalyst will provide valuable knowledge on the. fundamental requirements for the physicochemical properties of the material prepared either by sol-gel or hydrothermal methods and photocatalytic activities for paraquat dichloride degradation.

This study can be considered as one of the environmentally friendly technologies since photocatalysts are able to degrade harmful pollutants into non-hazardous compounds utilizing light as an energy source. Finally, the success of this

study will contribute to solving water pollution caused by pesticides, especially from the agriculture sector.

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Appendix O Publications and Conferences

Nur Afiqah Badli, Rusmidah Ali, Wan Azelee Wan Abu Bakar and Leny Yuliati. Role of Heterojunction $ZrTiO_4/ZrTi_2O_6/TiO_2$ Photocatalyst towards the Degradation of Paraquat Dichloride and Optimization Study by Box–Behnken Design. Arabian Journal of Chemistry, 10(2017): 935–943.(I.F 3.298) (Q1).

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