OPTIMIZATION OF REACTION CONDITIONS ON TITANIUM DIOXIDE WITH VARIOUS CO-CATALYSTS FOR PHENOL REMOVAL

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Specially dedicated to my beloved parents, Mr. Danuri bin Kanapi and Mrs. Jamilah binti Suliman, my sisters and brother, as well as my friends.

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ABSTRAK

Titanium Dioksida, TiO_2 amnya digunakan sebagai pemangkin foto untuk proses fotodegradasi pencemar organik seperti fenol melalui proses pemangkinan-foto. Bagi meningkatkan tahap kecekapan proses pemangkinan-foto TiO_2, pengubahsuaian dan pengoptimuman keadaan tindak balas pemangkin foto tersebut telah dijalankan. Dalam kajian ini, tiga fasa darjah penghabluran TiO_2 telah digunakan, iaitu anatas, rutil dan campuran anatas dan rutil. Hasil kajian mengesahkan TiO_2 fasa anatas memberikan hasil proses pemangkinan-foto yang tinggi iaitu sekitar 22% selepas dua jam tindak balas di bawah radiasi ultra lembayung. Pengubahsuaian TiO_2 fasa anatas telah dijalankan mengunakan pelbagai ko-mangkin iaitu Platinum (Pt), Nikel (Ni), Zink Oksida (ZnO) dan Ferum Oksida (Fe_2O_3). Hasil kajian yang dijalankan diantara beberapa ko-mangkin menunjukkan hanya Pt berpotensi sebagai ko-mangkin untuk TiO_2 dalam proses pemangkinan-foto. Siri pemangkin foto Pt/TiO_2 telah dicirikan menggunakan teknik Pembelauan Sinar-X (XRD), penciri saiz partikel, Pantulan Serakan Ultra Lembayung-Cahaya Nampak dan Spektroskopi Fluorosensi. Corak XRD menunjukkan bahawa deposisi Pt pada TiO_2 menyebabkan intensiti puncak yang tinggi pada puncak TiO_2, tanpa pengesanan puncak pembelauan lain. Hasil pencirian ini mencadangkan penambahan Pt mungkin mendorong menghasilkan darjah penghabluran yang lebih tinggi serta meningkatkan saiz partikel sampel. Peningkatan saiz partikel melalui pencirian XRD adalah dalam persetujuan yang baik dengan taburan saiz partikel. Pencirian menggunakan pantulan serakan ultra lembayung-cahaya nampak menunjukkan puncak penyerapan TiO_2 yang tinggi pada aras 320 nm, menunjukkan kesemua sampel berupaya untuk aktif pada wilayah ultra lembayung. Peningkatan serapan pada aras 400 nm ke atas juga mencadangkan kehadiran Pt dalam sampel Pt/TiO_2. Spektra fluoresensi menunjukkan intensiti emisi TiO_2 meningkat dengan penambahan Pt, sekaligus mencadangkan Pt boleh bertindak sebagai penjebak elektron. Kesan penambahan ko-mangkin ke atas TiO_2 telah dijalankan dan didapati bahawa dengan penambahan 0.5w% (Pt) menghasilkan penyingkiran fenol yang lebih tinggi pada sekitar 28% berbanding TiO_2 yang tidak diubahsuai. Pengoptimuman tindak balas telah dijalankan dengan memanipulasikan jumlah pemangkin, pH larutan dan penambahan hidrogen peroksida (H_2O_2) ke atas larutan fenol. Hasil kajian menunjukkan keadaan terbaik untuk Pt/TiO_2 menghasilkan fotodegradasi yang tinggi adalah melalui penggunaan jumlah pemangkin sebanyak 50 mg, larutan fenol dengan pH pada 6.4 dan kadar H_2O_2 kepada larutan fenol sekitar 10.5. Kajian kinetik menunjukkan tindak balas foto-pemangkinan mengikut tindak balas bertertib pertama dan kadar tindak balas meningkat dengan penambahan H_2O_2 dibawah kawalan optimum.

ABSTRACT

Titanium oxide, TiO_2 is commonly used as a photocatalyst for photocatalytic degradation of organic pollutants such as phenol. In order to improve the photocatalytic efficiency of TiO_2, modification and reaction condition optimizations were carried out in this study. Three types of TiO_2 were used, which were anatase, rutile, and mixture of anatase and rutile. It was confirmed that the anatase structure gave the highest photocatalytic activity with 22% of phenol removal after 2 hours reaction under UV light irradiation. Modification of anatase TiO_2 was conducted using various co-catalysts, such as Pt, Ni, ZnO, and Fe_2O_3. Among the examined co-catalysts, only Pt showed its potential as co-catalyst for TiO_2 in this photocatalyst system. The Pt/TiO_2 series were then characterized by X-ray diffraction (XRD), particle size analyser, Diffuse Reflectance UV-Visible spectroscopy (DR UV-Visible), and fluorescence spectroscopy. XRD patterns showed that the addition of Pt resulted in the higher peak intensity of the TiO_2, without detection of other diffraction peaks. This result suggested that the addition of Pt might induce the high crystallinity and increase the particle size of prepared samples. The increase of the particle size was in good agreement with the particle size distribution. DR UV-visible spectra showed the strong absorption peak of TiO_2 at 320 nm, indicating that all of these samples possess the ability to be active in UV light region. Additional of absorbance at background level above 400 nm suggested the presence of Pt in the Pt/TiO_2 samples. Fluorescence spectra showed that the emission intensity of TiO_2 increased with the addition of Pt, suggesting the Pt can act as an electron trapper. The effect of co-catalyst loading on TiO_2 anatase was then investigated and it was found that 0.5 wt% loading on TiO_2 gave higher photocatalytic phenol removal (28%) than the unmodified TiO_2. Optimization of the reaction conditions was carried out by varying the amount of catalyst, pH of the solution, and addition of H_2O_2 into the phenol solution. It was observed that the best condition for the Pt/TiO_2 to give the highest activity (54%) was obtained when using 50 mg of catalyst, phenol solution pH of 6.4 and ratio of H_2O_2 to phenol solution of 10.5. The kinetic study showed that the reactions followed first order reaction and the rate of reaction increased with the addition of H_2O_2 under optimized conditions.

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LIST OF ABBREVIATIONS

arb.u	-	Arbitary unit
CB	-	Conduction Band
DR UV-Vis	-	Diffuse Reflectance Ultra Violet-Visible
e_{CB}^-	-	Electrons
g	-	Gram
h	-	Hours
h_{VB}^+	-	Holes
min	-	Minutes
mL	-	Mililiter
nm	-	Nanometer
ppm	-	Part per million
pzc	-	Point of Zero Charge
TOC		Total Organic Carbon
UV	-	Ultra Violet
VB	-	Valence Band
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, industrial processes generate a variety of molecules that may cause air and water pollution due to their negative impacts for ecosystems and human. Phenol is one of the most common organic water pollutants due to its toxicity and high solubility in water (Ahmed *et al*., 2010). It is a simplest aromatic compound that contains of a benzene ring and hydroxyl group that attached to it and also known as carbolic acid or phenic acid (Busca *et al*., 2008). Phenol compounds are widely used as raw material in petrochemical, chemical and pharmaceutical industries. Some of the phenol compounds which are most toxic such as chlorinated and nitro-substituted phenols are used as pesticides and anti-bacterial (Liotta *et al*., 2008).

Phenol and its derivatives are being introduced continuously into the aquatic environment through various anthropogenics inputs (Ahmed *et al*., 2010). Due to the toxicity of phenol compounds, it affects the health of ecosystems and is present as a threat to humans through contamination of drinking water supply *e.g*., surface and ground water. According to Liotta *et al*., 2008, the presence of organic compounds in water and wastewater was reported to be a major problem to the widespread acceptance of water cycling. The industries that generate a wide variety of highly toxic organic wastes are chemical and petroleum industries. Therefore, the extensive studies have been reported on the removing of organic compounds from industrial process waters and wastewaters.

Photocatalysis is a promising method to treat the contaminated water. It has several advantages over conventional oxidation processes such as complete mineralization of pollutant, the utilization of near UV light and no addition of chemicals (Ksibi *et al*., 2003). When there is photon with equivalent energy or energy greater than band gap (ΔE) of a semiconductor, the electrons can excite from Valence Band (VB) to Conduction Band (CB) and promote possible reaction. The excitation of electrons will leave a positive hole in the VB (Priya *et al*., 2006), which will be responsible for oxidation reactions.

Titanium dioxide (TiO_2) is one of the important photocatalysts for practical application in wastewater treatment (Jin and Shirashi, 2004). The TiO_2 photocatalysts are excited by ultraviolet (UV) light to generate electron-hole pairs, where positive holes (h^+) are in the (VB) and free electrons (e^-) are in the CB. The holes will move to the TiO_2 particle surface and react with adsorbed water molecules. Then, hydroxyl radicals are generated which can oxidize organic pollutants.

There are many researchers reported that TiO_2 is a good photocatalyst. It possesses ability to degrade variety toxic compounds due to its high photocatalytic activity, photo-stability and non-toxicity. However, TiO_2 practically suffers from certain drawbacks, such as a very short lifetime of photoinduced charge separation in bare TiO_2 particles because of the charge recombination. Therefore, some methods should be developed in order to enhance photocatalytic efficiency of TiO_2. The typical method to enhance the photocatalytic efficiency of TiO_2 is improving the separation of electron and hole by modification of TiO_2. There are various modification methods reported, which are noble metal deposition, composite semiconductors, ion-doping, dye sensitization, surface reductive treatment, and surface chelating (Zhang *et al*., 2011). However, the improved activity observed on TiO_2 would depend on the type of the modification as well as the type of the reaction. So far, there is no report on the comparison of using various types of metals and metal oxides co-catalysts to improve the efficiency of TiO_2 for photocatalytic removal of phenol under exactly the same reaction conditions. Hence, this study focuses on using the suitable co-catalyst to modify and enhance the photocatalytic activity of TiO_2 for removal of phenol.

In addition to the modification of the TiO_2, optimizations of the reaction conditions are playing important roles to enhance the efficiency of TiO_2 in the phenol removal. A number of studies have reported that the photocatalytic degradation rate initially increases with the increase in the catalyst loading. However, the degradation rate decreases at high values of catalyst loading due to the effect of light scattering and screening effects. Besides, the particles tend to interact among them and agglomerate at high solid concentration that result in a reduction of catalyst surface area available for light absorption and thus, a drop in the photocatalytic degradation rate (Ahmed *et al*., 2011).

Since industrial effluents may be in basic or acidic conditions, study on the effect of pH on the photocatalytic efficiency of TiO_2 is very important. It has been recognized that pH plays a major role in adsorption of organic pollutants when the adsorbant is a semiconductor, such as TiO_2. The surface of semiconductor TiO_2 will be negatively or positively charged when it exists over or below its isolelectric point. In adsorption reaction, both states that are the state of the phenol molecule and the load of the catalyst surface are bound directly to the value of pH and play important role in the adsorption process. Therefore, the effect of pH should be investigated (Bekkouche *et al*., 2004). There have been some studies reported about the effect of initial pH on the activity of TiO_2 for photocatalytic degradation of phenol. However, the reported pH values are different from each other. The acidic phenol solution with pH of 4 or 5 was reported to be the most appropriate condition for TiO_2 to have the highest efficiency for phenol degradation (Lin *et al.*, 2011; Kashif *et al.*, 2009). Other group reported that there was no effect of pH when the pH range was 3-5 (Silva *et al.*, 2009).On the other hand, pH of 7.4 was found to enhance the photodegradation of phenol while it was not favoured in acidic solution with pH of less than 3 (Chiou *et al.*, 2008). Contrast result showed that the best pH for phenol removal was 11 (Rahmani *et al.*, 2008). Since the effect of the pH on the removal of phenol on TiO_2 was not clear, it was also considered as one important parameter investigated in this study.

Another parameter that should be investigated to obtain better efficiency is the presence of oxidant. Generally, oxygen from the air as TiO_2 electron acceptor is

used in the photocatalytic process due to the good efficiency, availability, and low cost. However, hydrogen peroxide has been also reported as one of good electron acceptors since it can increase the production of active •OH radicals, which are able to mineralize phenol. This would be due to the fact that hydrogen peroxide has high oxidizing efficiency as a consequence of its high oxidation potential with a value of 1.78 eV at 25 ºC (Adan *et al*., 2009). Hence, in the present study, the effect of hydrogen peroxide on the photocatalytic removal of phenol was also investigated to improve the efficiency of TiO_2.

1.2 Statement of Problem

Phenol is considered as a priority organic pollutant since it is harmful and hazardous to the living beings and environment even at low concentration. It is a toxic and mutagenic substance at high concentrations and may be absorbed through the skin. Phenol can cause toxicity, persistence and bioaccumulation effects in animal and vegetable organisms and may be dangerous for human health. In addition, phenol is known as common water pollution because it presents in wastewater and even in drinking water. Therefore, the developments of effective method as well as the appropriate material for phenol removal are still highly required.

Many treatment methods have been reported in order to degrade phenol from water and wastewater. Photocatalysis by using TiO_2 as a photocatalyst is one of the treatment methods for degradation of phenol. It has been extensively investigated in the recent years because it is able to completely oxidize organic molecule at low energy cost. However, due to some drawbacks of TiO_2, some modifications must be done in order to improve the efficiency of TiO_2 for photocatalytic degradation of phenol. While addition of co-catalysts would be one of the answers for the problem, there is still no report on the activity comparisons when using various metals and metal oxides as co-catalysts under the same reaction conditions. The lack of knowledge on this field led to the lack of information to explore the efficient co-

catalyst for TiO_2. This research is focused on the degradation of phenol by using TiO_2 photocatalysts with various metals and metal oxides as co-catalysts. The study on the activity comparisons using these modified TiO_2 would help answering the most suitable co-catalyst for TiO_2 in the photocatalytic phenol removal.

There are some important parameters that need to be investigated, such as effect of catalyst dosage, pH, and hydrogen peroxide. Some of the parameters were unclear and reported to have contradiction results. For example, the optimum solution pH was reported differently, either in acid, neutral, or basic condition, thus, needs to be clarified. This study would investigate the optimum condition for the mentioned parameters.

1.3 Objectives

The main objectives in this study can be shown as below:

1. To modify TiO_2 with addition of various metals and metal oxides as co-catalysts.
2. To study the properties of modified TiO_2 photocatalysts.
3. To investigate the photocatalytic degradation of phenol by using modified TiO_2 photocatalysts.
4. To obtain the optimum reaction condition by varying the catalyst dosage, amount of co-catalyst loading, pH, and the amount of added H_2O_2.

1.4 Scope of Study

Various types of commercial TiO_2 were used in this study, which were anatase, rutile, and a mixture of anatase and rutile. The co-catalysts were introduced on the best TiO_2 by impregnation method, followed by reduction process for Pt and Ni and oxidation process for Fe_2O_3 and ZnO. The TiO_2 and modified photocatalysts

were characterized by X-ray diffraction (XRD), particle size analysis, diffuse reflectance UV-Visible spectroscopy (DR UV-Vis), and fluorescence spectroscopy. The TiO_2 and the modified photocatalysts were tested for photocatalytic removal of phenol at room temperature under UV light irradiation. Several parameters such as amount of co-catalyst, catalyst dosage, pH and addition of hydrogen peroxide were varied in order to obtain the optimum photocatalytic reaction conditions for removal of phenol. The removal of phenol was analysed by a gas chromatography equipped with flame ionization detector (GC-FID).

1.5 Significance of Study

Due to the facts that phenol is toxic, highly soluble in water, and widely used in industries, the removal of phenol before its disposal to our environment is very important. Photocatalytic technique has been reported as an efficient method in degradation of phenol as it provides environmental friendly process. Besides, phenol can be mineralized completely by using photocatalytic technique. Thus, this study is very important for both environmental and photocatalytic science.

One of the active photocatalysts is TiO_2. Some studies showed that degradation of phenol can be enhanced by addition of metals and metal oxides as co-catalysts onto the surface of TiO_2 photocatalysts. Since we need to have efficient photocatalysts, the study on the modification of TiO_2 so that the activity can be improved is required. The same goes to the study on the optimized parameters of the reaction conditions that will give significant impacts on providing the fundamental knowledge to improve the performance of the photocatalysts on the photocatalytic removal of phenol.

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