Platinized Titanium Dioxide Photocatalyst for Degradation of Phenol

Leny Yuliati[1-3, a)] and Herlin Noorain Danuri[4, b)]

[1]*Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung,*
Malang 65151, East Java, Indonesia
[2]*Department of Chemistry, Faculty of Science and Technology,*
Universitas Ma Chung, Malang 65151, East Java, Indonesia
[3]*Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research,*
Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[4]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia,*
81310 UTM Johor Bahru, Johor, Malaysia

[a)] Corresponding author: leny.yuliati@machung.ac.id
[b)]herlin_danuri@yahoo.com

Abstract. Titanium oxide (TiO_2) is widely used as a photocatalyst for 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 with different crystal structures were investigated, which were anatase, rutile, and a mixture of anatase and rutile. It was confirmed that the anatase phase structure gave a higher photocatalytic activity than other TiO_2 phases for phenol degradation after 2 h-reaction under UV light irradiation. Modification of anatase TiO_2 was conducted by the addition of platinum (Pt) as a co-catalyst by impregnation method, followed by the calcination under the flow of hydrogen. The platinized titanium dioxide (Pt/TiO_2) photocatalysts were then characterized by X-ray diffraction (XRD), particle size analyser, diffuse reflectance UV-Visible (DR UV-Visible) and fluorescence spectroscopies. The phenol degradation was analyzed by a gas chromatography equipped with a flame ionization detector (GC FID). Several parameters were examined, which were Pt amount, photocatalyst amount, solution pH, and the addition of hydrogen peroxide. The kinetic of the phenol degradation was also examined and compared to the one after the hydrogen peroxide addition.

INTRODUCTION

Phenol is considered as a priority organic pollutant since it is harmful and hazardous to the living beings and environment even at low concentration [1,2]. 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 degradation are still highly required.

Many treatment methods have been reported in order to degrade phenol from water and wastewater [3-6]. Photocatalysis by using titanium dioxide (TiO_2) as a photocatalyst is one of the treatment methods for degradation of organic pollutants [7,8]. 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. This research is focused on the degradation of phenol by using TiO_2 photocatalysts with platinum (Pt) as the co-catalysts. Furthermore, 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 effect of

pH reported was different from each other and it should be clarified. Therefore, this study would investigate the optimum condition for the mentioned parameters.

MATERIALS AND METHODS

General

The chemicals used in this study were commercial chemicals without any purification. The commercial TiO_2 with three different phases; pure anatase (Aldrich, 99.7%), pure rutile (Aldrich, 99.5%) and mixture of anatase and rutile phase (Aldrich, $\geq$ 99.5%) were used as photocatalysts. The co-catalysts used were Pt, which precursor was platinum(IV) hexachloride 89.9% ($H_2PtCl_6 \cdot 6H_2O$, Across Organic). For the photocatalytic degradation of phenol, the materials used were phenol 99.5% (C6H5OH, Scharlau) and acetonitrile as solvent. The pH was adjusted with hydrochloric acid 37% (HCl, QRëC), and ammonium hydroxide 35% (NH_4OH, Fisher Scientific). As the oxidant, hydrogen peroxide 30% (H_2O_2, Fisher Scientific) was used.

Preparation and Characterizations of Platinized Titanium Dioxide

Supported monometallic Pt/TiO_2 photocatalysts were prepared using the conventional impregnation method. A certain amount of platinum hexachloride, $H_2PtCl_6.6H_2O$ was dissolved in 40 mL of double distilled water as solvent with the aid of ultrasonic mixing for 15 minutes. The TiO_2 (1 g) was added slowly to the solution that consisted of the Pt with loading amount was 0.1 wt% to TiO_2. The mixture was put on the hot plate, heated and stirred at temperature about 80-90 ºC until all the water was evaporated. The obtained powder was collected, ground, and reduced under the flow of hydrogen (30 mL/min) at 200 ºC for 30 minutes. The procedure was repeated for various Pt loading amounts (0.5 and 1.0 wt%). The prepared sample was labelled as $Pt(x)/TiO_2$, in which x shows the loading amounts of Pt (wt%). The prepared photocatalysts were characterized by using X-ray Diffraction (XRD, Bruker AXS Diffrac plus release 2000), particle size analyser (Nanosight, NS300), diffuse reflectance (DR) UV-visible spectroscopy (Perkin-Elmer, Lambda 900), and fluorescence spectroscopy (JASCO, FP-8500).

Photocatalytic Activity Tests

The photocatalytic degradation of phenol was conducted in a closed box reactor. Photocatalyst of 50 mg was dispersed in a 50 ml of phenol (50 ppm) that had been put in a 100 mL jacketed beaker equipped with water cooling system to maintain the reaction temperature to be at room temperature. Prior to the reaction, the solution was stirred in the dark condition for 1 hour to let the adsorption equilibrium to be reached. The reaction then was carried out for 2 hours under UV light irradiation. After the reaction, the solution was taken and separated from the photocatalyst. The solution was analysed by using GC-FID in order to determine the phenol degradation. The percentage of phenol degradation was determined by comparing the removed phenol concentration after reaction to the initial concentration.

The optimization of reaction condition was conducted by using the best photocatalyst. Three parameters were monitored, which were catalysts loading, pH, and addition of H_2O_2. The effect of catalyst loading on the photocatalytic degradation of phenol was analysed by a series of catalyst loading ranges. Variations of catalyst loadings (10, 50, 70 and 100 mg) were put in a jacketed beaker containing 50 mL of 50 ppm phenol. To examine the pH effect, different series of pH ranges (3, 6.4, 8, and 10) for phenol solution were prepared for this study. The pH values of the solutions were adjusted either with sulphuric acid, H_2SO_4 or ammonium hydroxide, NH_4OH solution and monitored by a pH meter. The effect of hydrogen peroxide addition (H_2O_2) was analysed by using various ratio of H_2O_2 to phenol solution (3.5, 7, 10.5 and 14). The reaction was conducted with constant catalyst loading (50 mg), pH value (6.4) and phenol concentration (50 mL, 50 ppm). Prior to the reaction, the dark condition was carried out for 1 hour to let the adsorption equilibrium to be reached. The reaction then was carried out for 2 hours under UV light irradiation. After the reaction, the solution was taken and separated from the photocatalyst. The solution was analysed by using GC-FID in order to determine the phenol degradation.

The kinetic studies were carried out for both reactions condition, with or without the addition of H_2O_2 in order to determine the order and the rate of reaction. The studies were conducted by using $Pt(0.5)/TiO_2$ as photocatalyst and pH 6.4 as the pH of the phenol solution. Prior to the reaction, the solution was stirred in the dark condition for 1

hour to let the adsorption equilibrium to be reached. The reaction was then carried out for 2, 3, 6, and 12 hours under UV light irradiation in a closed reactor. After the reaction, the solution was taken and separated from the photocatalyst. The solution was analysed by using GC-FID in order to determine the phenol degradation. The percentage of phenol degradation was determined by comparing the removed phenol concentration after reaction to the initial concentration.

RESULTS AND DISCUSSION

Effect of Crystal Phase of Titanium Dioxide

The commercial TiO_2 photocatalysts with different phases of anatase, rutile, and mixture of anatase and rutile phases were characterized by using XRD and DR UV-Visible spectroscopy in order to study the properties of the materials. The anatase TiO_2, which is labelled as TiO_2 (A), exhibited diffraction peaks at 2θ of $25°$ (101), $38°$ (004), $48°$ (200), and $75°$ (215). On the other hand, rutile TiO_2 that is labelled as TiO_2 (R) showed diffraction peaks at 2θ of $27°$ (110), $36°$ (101), $54°$ (211), $63°$ (204), and $70°$ (116) [9]. The mixture of anatase and rutile that is labelled as TiO_2 (AR) gave diffraction peaks of both anatase and rutile. In order to determine the percentage of anatase and rutile phases in the TiO_2 (AR) sample, the percentage of anatase, A %, was determined using the equation (1) as has been reported elsewhere [10]. The main diffraction peaks at 2θ of $25°$ (101) for TiO_2 (A) and $27 °$ (110) for TiO_2 (R) were used for the calculation.

$$A (\%) = 100 (1 + 1.265 \, I_R/I_A) \qquad (1)$$

It can be obtained that the composition of anatase and rutile phase in the TiO_2 (AR) is 77 and 23%, respectively.

The optical properties of all TiO_2 samples were studied using DR UV-Vis spectroscopy by measuring the absorption peaks and determining the band gap energy. From the DR UV-Vis spectra of the TiO_2 samples. All TiO_2 samples only absorbed light at UV region and did not show the absorption in visible light region, indicating their limited ability to be only active in the UV region. In order to determine the band gap energy (E_g) of the TiO_2 samples from DR UV-Vis spectra, some calculation methods can be used. The determination of the E_g values can be made by a direct extrapolation of the Kubelka-Munk function, $F(R)$ spectrum or the wavelength corresponding to the maximum absorption. One of the most applied methods is the one proposed by J. Tauc, in which the Eg can be obtained from extrapolating the linear region in the graph of $(\alpha h\nu)^2$ versus $h\nu$, which is called as Tauc plot. The point of the extrapolation of the linear part that meets the abscissa will give the value of the band gap energy of the material (Rusdi *et al*., 2011). The values of the E_g were obtained by extrapolating the graph and the values for TiO_2 (A), TiO_2 (R), and TiO_2 (AR) were 3.47, 3.2, and 3.46 eV, respectively. The TiO_2 (A) has the highest value of Eg, while TiO_2 (R) shows the lowest value of Eg. The TiO_2 (AR) showed very similar value of Eg to that of TiO_2 (A) due to the fact the composition of anatase in the TiO_2 (AR) is much higher than the rutile phase (77%).

The commercial TiO_2 samples with various types of phases were tested for photocatalytic degradation of phenol under UV light irradiation in order to confirm the efficiency of the samples. It was confirmed that no reaction was observed in the dark or without the photocatalysts, suggesting that the reaction occurred photocatalytically. The TiO_2 with anatase phase, the TiO_2 (A), has the highest percentage degradation of phenol about 22% within 2 hours reaction, followed by TiO_2 (AR) about 8%. However, there was no activity in the degradation of phenol on the TiO_2 (R). Since the TiO_2 (A) showed the highest photocatalytic activity, the modification was carried out only on the TiO_2 (A) photocatalyst.

Effect of Platinum on the Titanium Dioxide

The photocatalytic percentage degradation of phenol on the TiO_2 (A) decreased with the addition of small amount of Pt. When the Pt amount loading increased from 0.1 to 0.5 wt%, the percentage degradation of phenol increased from 11 to 28 %. However, further increase in Pt content (1.0 wt%) caused the decrease of percentage degradation of phenol to 10%. Pt could improve the performance of photocatalytic efficiency in degradation of phenol because it plays a role in increasing the formation of hydroxyl radicals and oxygen species by trapping the photoinduced electrons. Besides, Pt also could provide catalytic sites for target degradants and reaction intermediates. The higher activity on the Pt(0.5)/TiO_2 (A) sample showed that the Pt with the optimum amount acted

as the electron trapper that can improve the photocatalytic efficiency. However, the excess amount of Pt loading on the surface of TiO_2 (A) may also cause the Pt act as a recombination center.

Figure 1 shows the XRD patterns of TiO_2 (A) and the $Pt(x)/TiO_2$ (A) series with various amounts of Pt loading. There was no diffraction peak of Pt and only diffraction peaks of TiO_2 (A) can be detected with the addition of Pt. The presence of Pt could not be detected by using the XRD, might be due to the low Pt content on the surface of TiO_2 (A). On the other hand, it is clear that the addition of Pt did not affect the phase of TiO_2, since only diffraction peaks of TiO_2 (A) can be observed with the addition of Pt. However, the addition of Pt on TiO_2 (A) resulted in the higher intensity for the diffraction peaks of TiO_2 (A). This result suggested that the addition of Pt might induce the high crystallinity or increase the particle size of prepared samples. In order to clarify the effect of Pt in the increase of the particle size, the particle size distribution of the $Pt(x)/TiO_2$ (A) series was measured.
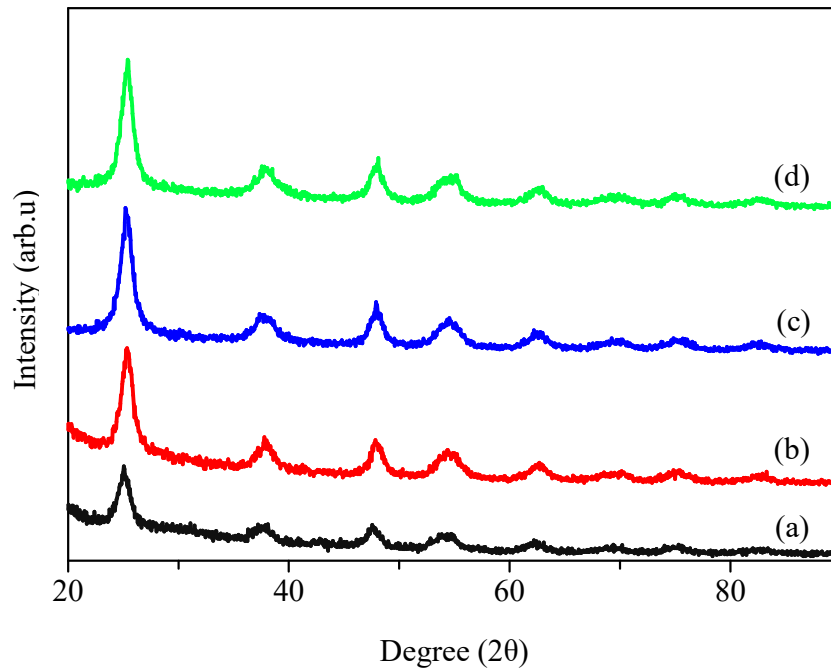

FIGURE 1 XRD patterns of (a) TiO_2 (A), (b) Pt (*0.1*)/TiO_2 (A), (c) Pt (*0.5*)/TiO_2 (A), and (d) Pt (*1.0*)/TiO_2 (A) samples

TABLE 1 Percentage of particle size distribution on TiO_2 (A) and $Pt(x)/TiO_2$ (A) samples

Samples	Percentage of particle size distribution (%)[a]	
	35-210 nm (small)	211-715 nm (large)
TiO_2 (A)	49.7	50.3
Pt(*0.1*)/TiO_2 (A)	42.2	57.8
Pt(*0.5*)/TiO_2 (A)	34.7	65.3
Pt(*1.0*)/TiO_2 (A)	28.8	71.2

[a]Percentage of particle size distribution was calculated as $\frac{C}{C_t} \times 100$, where C is the concentration of particle distribution at certain range and C_t is the total concentration of particle distribution

Particle size distribution is an index (means of expression) showing what sizes of particles are present in what proportions (relative particle amount as a percentage where the total amount of particles is 100%) in the measured sample. In this study, the particle size distribution was measured based on the diffusion coefficients of individual particles. The measurement results are summarized in Table 1. The concentration of particle size was taken from the range of 35 to 715 nm. The small particle size was defined as in the range of 35 to 210 nm, whereas the range from

211 to 715 nm indicated the large particle size. The percentage of the particle size distribution is shown in Table 1. It is clear that the percentage of small particle size distribution decreased while the large particle size distribution increased with the increase of Pt loading amount. The percentage of large particle size in TiO_2 (A) increased with the addition of Pt as this might occur during the heating treatment in the reduction process due to agglomeration and sintering. This process usually depends on the catalyst loading, and the catalysts with a higher metal loading are expected to have more agglomeration and sintering.

Figure 2 shows the DR UV-Vis spectra of TiO_2 (A) and $Pt(x)/TiO_2$ (A) samples. The TiO_2 (A) exhibited the sharp absorption edge at about 370 nm as can be seen in Figure 2(a). The addition of Pt slightly shifted the absorption edge of the TiO_2 (A) to the longer wavelength. Besides the shifting, the deposition of Pt gave additional absorption band level after 400 nm, which intensity increased with the increase of the Pt loading amounts. The absorption in the visible region showed the presence of Pt in the samples, as can be also supported by the grey colour observed in the samples after the reduction process.In this study, the band gap energy, E_g, was determined by plotted a graph $(\alpha h\nu)^2$ $(eV/cm)^2$ versus $h\nu$ (eV). The value of the band gap (E_g) was obtained by extrapolating the graph. The E_g value of TiO_2 (A) was slightly changed with the addition of Pt. The value of E_g decreased with the increase in the amount of Pt loading. This result is in good agreement with the discussion mentioned above, that the addition of Pt increased the particle size.
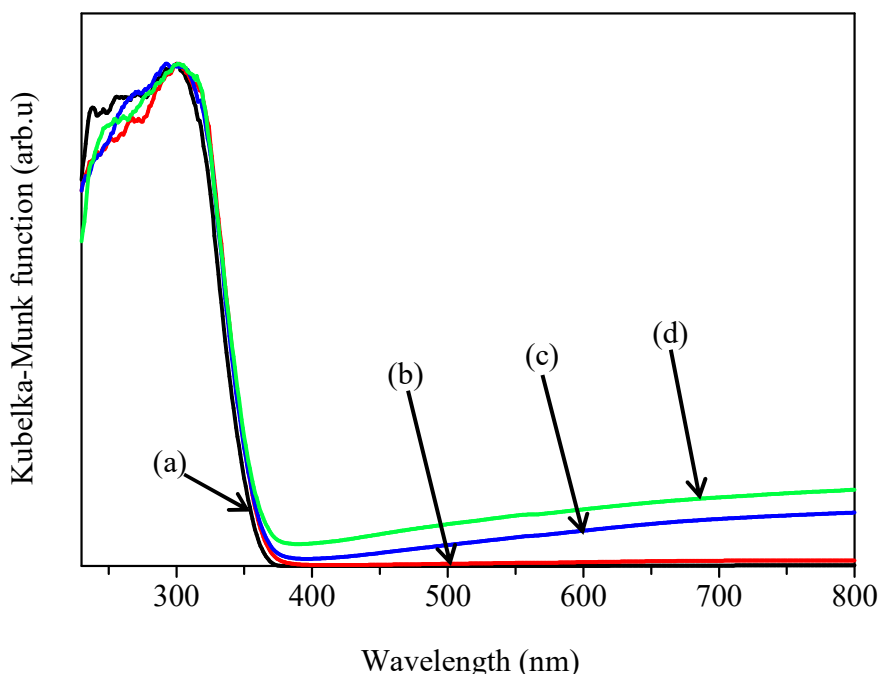

FIGURE 2 DR UV-Vis spectra of (a) TiO_2 (A), (b) $Pt(0.1)/TiO_2$ (A), (c) $Pt(0.5)/TiO_2$ (A), and (d) $Pt(1.0)/TiO_2$ (A) samples

In order to elucidate the fate of electron/hole pairs in the TiO_2 (A) and $Pt(x)/TiO_2$ (A) samples, the emission spectra were measured, as shown in Figures 3 and 4. The TiO_2 (A) and $Pt(x)TiO_2$ samples showed similar excitonic fluorescence emission spectra, demonstrating that the Pt species did not cause the new fluorescence phenomena. In addition, there was no shifting in the fluorescence emission spectra, indicating that the presence of Pt did not affect the emission sites of TiO_2. Based on the results, it was found that all of the photocatalysts have two excitation sites at 215 and 233 nm. The excitation at 215 nm gave the three emission sites at 236, 273, and 281 nm, while the excitation at 233 nm gave the emission sites at 247, 270, and 283 nm. While there was no effect observed on the position and peaks of the excitation and emission spectra, the intensity of the spectra was affected with the addition of Pt.
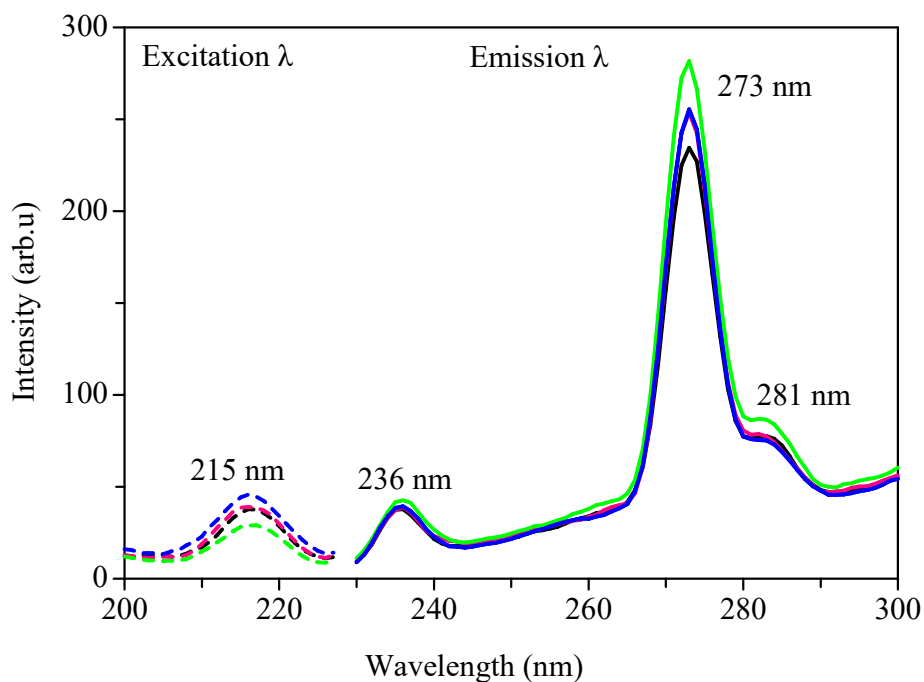
FIGURE 3 Excitation and emission spectra of TiO$_2$ (A) (black), Pt(0.1)/TiO$_2$ (A) (red), Pt(0.5)/TiO$_2$ (blue), and Pt(1.0)/TiO$_2$ (A) (green) samples. The monitoring wavelengths for excitation and emission spectra were 273 and 215 nm, respectively.
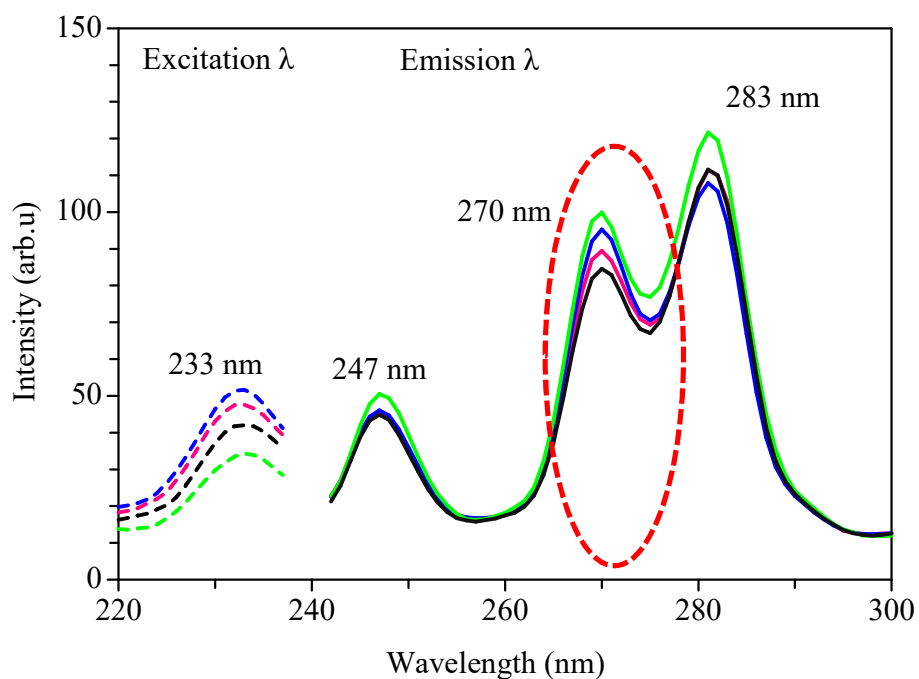

FIGURE 4 Excitation and emission spectra of TiO$_2$ (A) (black), Pt(0.1)/TiO$_2$ (A) (red), Pt(0.5)/TiO$_2$ (A) (blue), and Pt(1.0)/TiO$_2$ (A) (green) samples. The monitoring wavelengths for excitation and emission spectra were 283 nm and 233 nm, respectively.

As can be seen in Figure 4, when the excitation wavelength was 233 nm, the main emission sites shown as the highest intensity can be observed at 283 nm. It can be seen that the addition of small amount of Pt (0.1 wt%) did not affect much the intensity of the emission spectrum. With the addition of Pt (0.5 wt%), the intensity of the emission spectrum for TiO_2 decreased, suggesting that the Pt may act as a trapping site to capture photogenerated electron from TiO_2 conduction band, thus the electron/hole recombination can be suppressed. On the other hand, with further addition of Pt (1.0 wt%), the intensity of the emission spectrum increased. The increase in the emission spectrum intensity suggested the increase in the recombination of electron/hole pairs, which may occur due to the possibility of Pt to act as the recombination center when the amount of Pt was too high. This result was in good agreement with the results from the photocatalytic activity tests.

Optimized Reaction Conditions

The catalyst loading is one of the crucial parameters in photocatalytic degradation of phenol. In order to avoid an ineffective excess of catalyst and to ensure maximum total absorption of efficient photons, the optimum mass of catalyst needs to be investigated. Various amounts of Pt(0.5)/TiO_2 (A) loading were investigated for the photocatalytic degradation of phenol under UV light irradiation for 2 hours. The results are shown in Figure 4.5. It was confirmed that there was no activity in the absence of catalyst in the solution of phenol. Initially, when the loading amount of Pt(0.5)/TiO_2 (A) increased from 10 to 50 mg, phenol degradation increased from 12 to 28%. The increase in the photocatalytic degradation of phenol due to the increase of catalyst loading can be associated to an increment of the active sites available for phenol adsorption and degradation processes. The increase of the catalyst loading also led to the increase in the generation rate for electron/hole pairs, and consequently enhancing the photocatalytic reaction. When the loading amount was further increased to 70 mg, the rate of photocatalytic degradation of phenol was decreased. This is due to the aggregation of Pt(0.5)/TiO_2 (A) particles that make a significant fraction of the catalyst to be inaccessible to either adsorbing phenol molecules or absorbing UV light which results in a decrease in the number of active sites available for catalytic reactions. Furthermore, the increase in the catalyst loading may lead to the excessive opacity and screening effect of excess catalyst, which acts as shield, and consequently hinder the light penetration. Therefore, there is a decrease in the number of available surface area for light-harvesting and results in a reduction of the photocatalytic degradation of phenol. Further increase in the catalyst loading (100 mg) did not give much different result compared to that using the 70 mg of catalyst loading. Based on these results, it can be shown that 50 mg is the optimum amount for catalyst loading in this reaction condition.

The pH of the solution also plays an important role in the photocatalytic degradation since it can affect the adsorption of phenol on the photocatalyst surface. This is because pH strongly affects the properties of semiconductor's surface charge state, flat band potential, and dissociation of the solution. Therefore, it is necessary to study on the effect of pH solution in order to get maximum photocatalytic efficiency. Figure 6 shows the influence of solution pH on the phenol degradation over the Pt(0.5)/TiO_2 (A) catalyst. The reaction was carried out for 2 hours under UV light irradiation with the constant concentration of phenol (50 ppm) and 50 mg of catalyst was dispersed in the solution. An increase in solution pH enhanced the photocatalytic degradation of phenol and it reached the maximum at pH of 6.4. However, the photocatalytic degradation of phenol decreased when the pH was further increased. On the other hand, phenol exists as phenolate anions at higher pH values. At higher pH, low degradation rate can be observed due to the fact when the concentration of OH⁻ is higher in the solution, it prevents the penetration of UV light to reach the catalyst surface. At high pH, there is Columbic repulsion force occurred between the negatively charged surface of TiO_2 particles and the hydroxide anions that could prevent from the formation of hydroxyl radical, hence reducing the photocatalytic degradation of phenol. Phenol is completely in the form of phenolate anions while the surface of TiO_2 is negatively charged at pH more than 11 developing repulsive forces between catalyst and phenol, and consequently decreasing the photocatalytic degradation of phenol. In this regard, pH of 6.4 is suggested to be the optimum pH for the high degradation of phenol using Pt(x)/TiO_2 (A) photocatalyst under UV light irradiation.
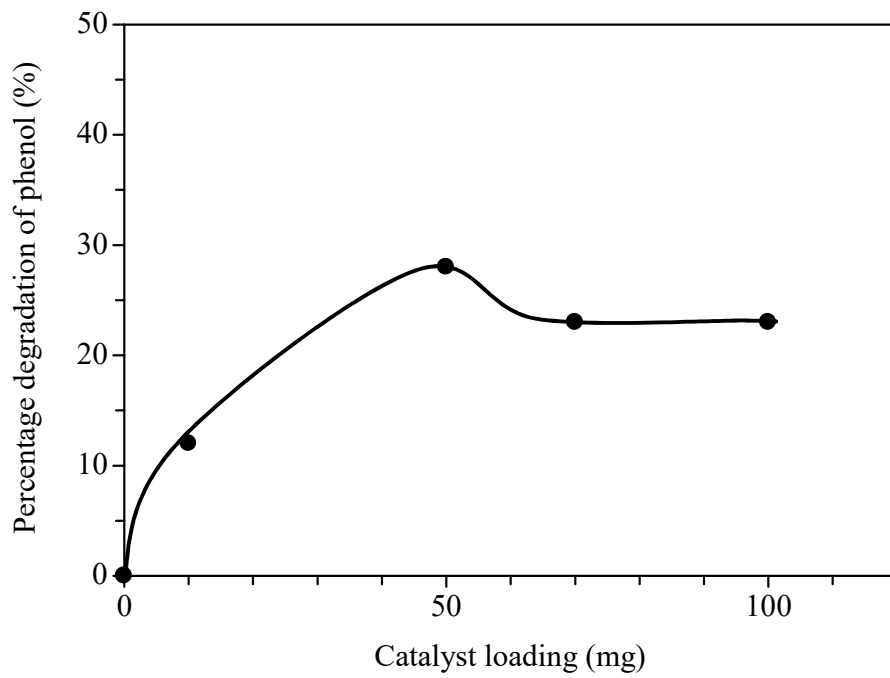
FIGURE 5 Effect of the catalyst loading using Pt(*0.5*)/TiO$_2$ (A) catalyst on the photocatalytic degradation of phenol for 2 hours under UV light irradiation
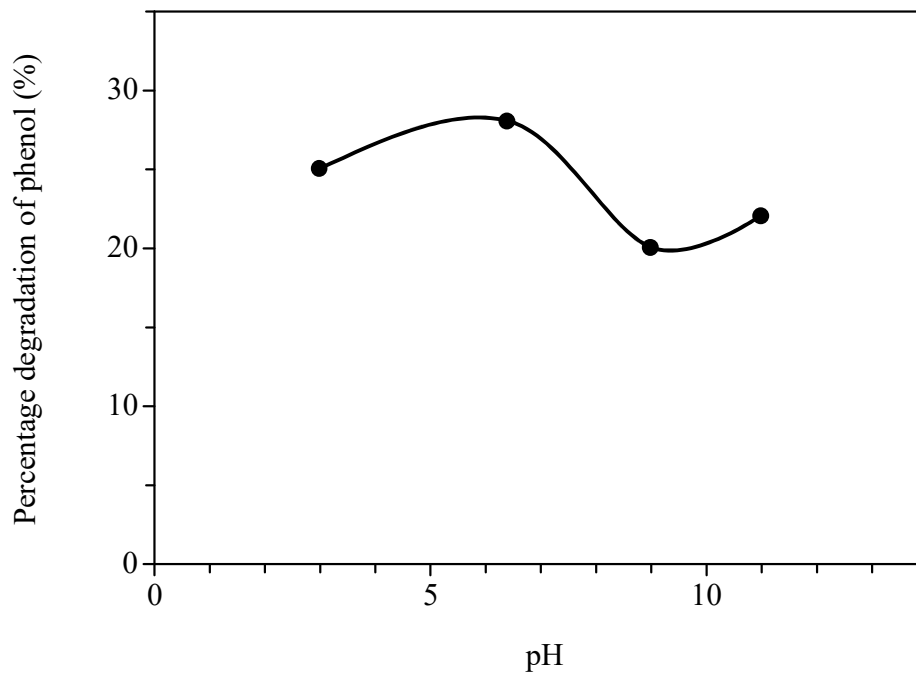

FIGURE 6 Effect of the pH solution on the photocatalytic degradation of phenol for 2 hours under UV light irradiation

H_2O_2 is one of the oxidant species that can increase the photocatalytic reaction efficiency. It can also act as electron scavengers to prevent the electron/ hole recombination. Therefore, in this study, the effect of addition H_2O_2 was studied in order to get the high photocatalytic degradation of phenol. Figure 7 shows the effect of added H_2O_2 with various mol ratios to phenol solution of 3.5, 7.0, 10.5 and 14.0. The experiments were carried out by using 50 mg catalyst that was dispersed in the 50 ml of 50 ppm phenol solution. Based on the results, it can be observed that percentage degradation of phenol increases with the increasing ratio of H_2O_2 added into the phenol solution. The ratio addition of H_2O_2 from 3.5 to 10.5 led to an increase in degradation efficiency from 29 to 54% within 2 hours reactions. The increase of ratio H_2O_2 being added into the phenol solution could increase the production of •OH radicals, thus increased the degradation of phenol. Further increase in the ratio of H_2O_2 did not increase the degradation of phenol and there was no significant drop in percentage degradation of phenol with the increasing ratio of H_2O_2 added from 10.5 to 14.0. This was due to the dual roles played by H_2O_2 in the photocatalytic degradation of phenol. The H_2O_2 can act as electron acceptor and also promotes the charge separation, being also able to be decomposed to produce •OH radicals by absorption of light at 254 nm. Based on these results, the optimum ratio of H_2O_2 to phenol that was used in this study was about 10.
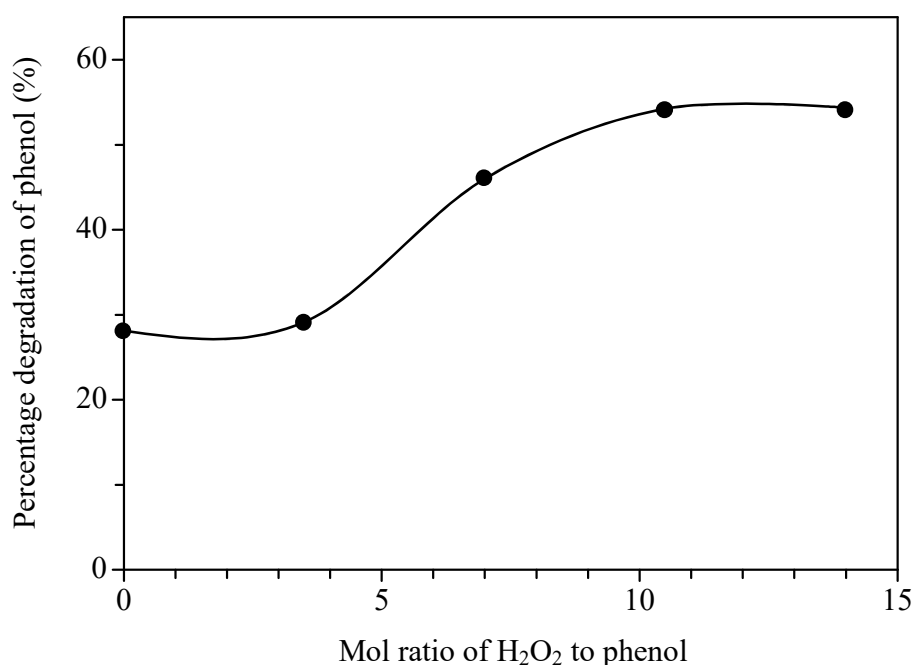

FIGURE 7 Effect of H_2O_2 on the photocatalytic phenol degradation for 2 hours under UV light irradiation.

Kinetic Study and Proposed Mechanism

The kinetic study showed that the degradation reactions followed first order reaction. Without H_2O_2, the kinetic graph (not shown) gave linear relationship up to 12 hours reaction, while in the presence of H_2O_2, deviation from the linear plot was observed after 3 hours reactions. The rate constant of the reaction can be obtained from the slope of linear region, where the value can be determined as 0.13 and 0.08 h^{-1} for the reaction with and without H_2O_2, respectively. In the presence of H_2O_2, the initial rate was found to be 0.24 h^{-1}, which decreased to 0.13 h^{-1} from 3 to 12 hours reaction. The difference in the reaction rate would be due to the difference of the H_2O_2 concentrations in the initial time. In this study, it was demonstrated that the constant rate of reaction increased with the addition of H_2O_2 under optimized conditions.

Figure 8 shows the proposed mechanism of photocatalytic degradation of phenol over Pt/TiO_2 (A). During the exposure of UV light, electron from VB of TiO_2 is excited to the CB, generating electron-hole pairs. Then, the electron from CB of TiO_2 is transferred to the Pt deposits, which is slightly lower in energy in order to reduce the

rate of photogenerated electron-hole recombination. This indicates that Pt metal acts as an electron trapper. Therefore, due to enhanced time in excitation state lead to oxidation of phenol to carbon dioxide and water. This significant enhancement of photocatalytic activity would be due to deposition of Pt on the surface of TiO_2 that produced high efficiency of induced charge separation.
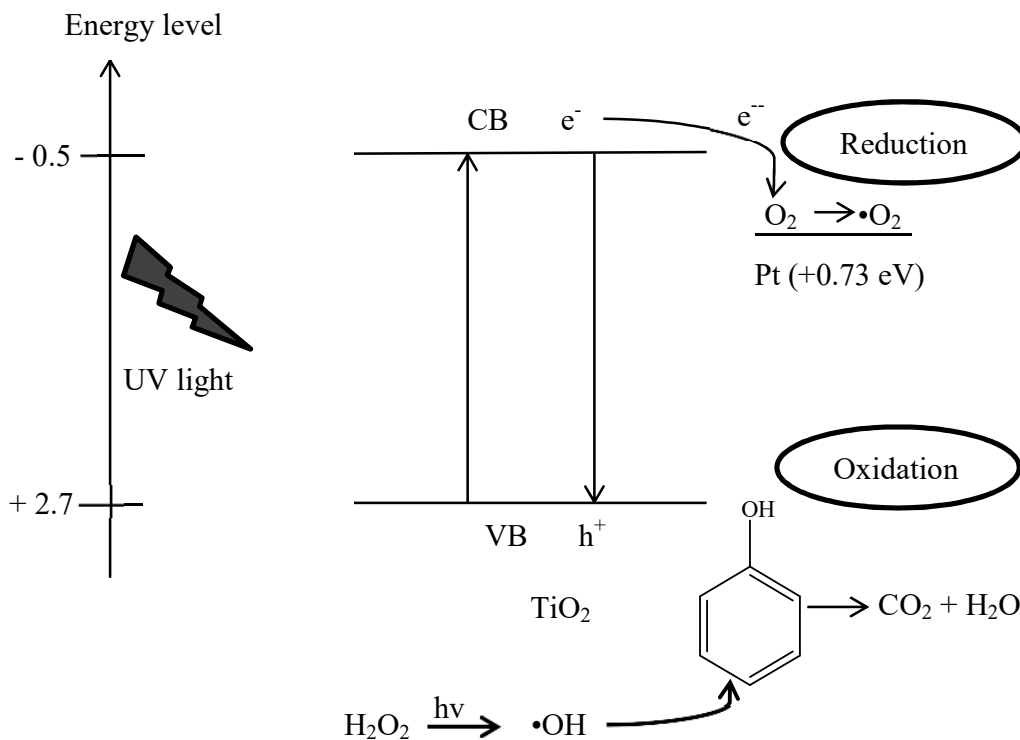

FIGURE 8 Proposed mechanism of photocatalytic degradation of phenol over Pt/TiO_2 (A) with low loading of Pt

CONCLUSION

TiO_2 (A) was found to give the highest percentage degradation of phenol (22%) among the TiO_2 samples. The higher activity obtained on the TiO_2 (A) than the TiO_2 (AR) might be due to the smaller crystallite size of the TiO_2 (A) than the TiO_2 (AR). The addition of Pt (0.5wt%) increased the activity of TiO_2 (A). XRD patterns revealed that the addition of Pt did not change the crystal phase of the TiO_2 (A), but induce to the high cystallinity or increase the particle size of the prepared samples.This result was supported with the measurement results of the particle size distribution, which showed that the addition of Pt resulted in the larger distribution of large particle size. The presence of Pt can be also confirmed by DR UV-visible spectra that showed the additional of absorbance at the background level above 400 nm with the addition of Pt. The addition of optimum amount of Pt (0.5%) was found to lower the emission intensity, suggesting that the Pt can act as a good electron trapper that can suppress the electron/hole recombinations, so that the photocatalytic activity can be increased. Optimization of the reaction conditions were 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 most appropriate 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 of photocatalytic degradation of phenol showed that the reactions followed first order reaction. The constant rate of with and without the addition of H_2O_2 are 0.1495 and 0.0823 h^{-1}, respectively. Therefore, it can be concluded that the constant rate of reaction increased with the addition of H_2O_2 under optimized conditions.

REFERENCES

1. M. Thayi, N. Kumari and S. Jagavedan, J. Water Proc. Eng. **37,** 101475 (2020).
2. R. Liu and S. A. Mabury, Environ. Sci. Technol. **54**, 11796–11719 (2020).
3. M.F. Hanafi and N. Sapawe, Mater. Today: Proceed. **31**, A141–A150 (2020).
4. W. F. Elmobarak, B.H. Hameed, F. Almomani and A. Z. Abdullah, Catalysts **11**, 782 (2021).
5. E. Brillas and S. Garcia-Segura, Sep. Pur. Technol. **237**, 116337 (2020).
6. K. Subramaniam, S. A. Ahmad and N. A. Shaharuddin, AsPAc. J. Mol. Biol. Biotechnol. **28**, 77–89 (2020).
7. D. Chen, Y. Chen, N. Zhou, P.Chen, Y. Wang, K. Li, S. Huo. P. Cheng, P. Peng, R. Zhang, L.Wang, H. Liu, Y. Liu and R. Ruan, J. Cleaner Prod. **268**, 121725 (2020).
8. K. S. Varma, R. J. Tayade, K. J. Shah, P. A. Joshi, A. D. Shukla and V. G. Gandhi, Water-Energy Nexus **3**, 46–61 (2020).
9. W. R. Siah, H. O. Lintang, M. Shamsuddin and L. Yuliati, IOP Conf. Series: Mater. Sci. Eng. **107**, 012005 (2016).
10. P.W. Koh, C.Y. Leong, L. Yuliati, H. Nur and S. L. Lee, Malay. J. Anal. Sci. **24**, 1045–1060 (2020).