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The effect of calcination temperature on the phase transformation of titanium dioxide for photodegradation of paraquat dichloride

Nur Sakinah Binti Masri and Rusmidah Ali
Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
Corresponding Author: rusmidah@kimia.fs.utm.my

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GRAPHICAL ABSTRACT

ABSTRACT

Paraquat dichloride is an herbicide which is harmful and toxic which polluted the water system and give negative impact to the health of ecosystems and human and must be treated. In this research, photocatalytic degradation of paraquat dichloride (PQ) solution was conducted and assessed using Uv-vis spectrometer measured at λ_{max}, 257 nm under 365 nm UV light irradiation for 3 hours using single TiO_2 and coupled TiO_2/ZrO_2 catalysts. This research focused on the effect of calcination temperature on the phase transformation of TiO_2 and their performance on the photodegradation of PQ. Single TiO_2 was synthesized using sol gel method while TiO_2:ZrO_2 (90:10) using impregnated method. The synthesized catalysts were calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C and were compared with TiO_2 Aldrich and P25 Degussa. The transformation of anatase to rutile phase was increased by increasing the calcination temperature for all the photocatalysts. Zr used as a dopant on the TiO_2 has delayed the formation of the rutile phase. Among this photocatalysts, synthesized TiO_2/ZrO_2 and commercial catalyst (P25 Degussa) those calcined at 700°C and 450°C gave highest percentage of photodegaradation with 54.87% and 83.66% respectively at original reaction pH at 7.70. Addition of H_2O_2 gave better performance on photodegradation. XRD analysis has proven the transformation of 75% anatase to 57% anatase at 450°C for P25 Degussa. FESEM-EDX showed TiO_2/ZrO_2 and P25 Degussa has a spherical morphology and particle size range between 20 - 35 nm. BET analysis showed surface area for TiO_2/ZrO_2 and P25 Degussa range between 25 - 44 m^2/g. The data obtained showed that the best catalyst for degradation of PQ is P25 Degussa calcined at 450°C, pH 7.70 which gave 83.66%.

Keywords: Photocatalyst, paraquat dichloride, zirconia, titania, effect of calcination temperature, phase transformation, hydrogen peroxide, pH.

1. INTRODUCTION

Paraquat dichloride (N, N'-dimethyl-4, 4'-bipyridinium dichloride) is one example of herbicides used in agricultural practise (Figure 1). In acute toxicity studies using laboratory animals, paraquat has been shown to be highly toxic by the inhalation route and has been placed in Toxicity Category I (the highest of four levels) for acute inhalation effects. However, the Environmental Protection Agency (EPA) has determined that particles used in agricultural practices (400 to 800 μm) are well beyond the respirable range and therefore inhalation toxicity is not a toxicological endpoint of concern. Paraquat is toxic (Category II) by the oral route and moderately toxic (Category III) by the dermal route. Paraquat will cause moderate to severe eye irritation and minimal dermal irritation, and has been placed in Toxicity Categories II and IV (slightly toxic) respectively for these effects [1].

Advanced oxidation processes (AOPs) employing heterogeneous catalysts have been used extensively for various types of degradation of organic pollutants in water. This is due to the ability of the catalyst to generate a strongly oxidizing hydroxyl radical with high oxidative power of E_o =2.8 eV and thus acts to degrade various organic pollutants. Among the semiconductor photocatalyst used, titania (TiO_2) has been promoted as a potential photocatalyst that can be used for the degradation of the paraquat dichloride due to the ability to completely oxidize a large number of hazardous organic pollutants to non-toxic products [2]. AOPs in general are cheap to install but involve high operating costs due to the input of chemicals and energy [3].

Generally, TiO_2 exists in three most commonly polymorphs: brookite, anatase and rutile. Among the three polymorphs only brookite has not been employed as the photocatalyst because of its metastable structure. According to the previous research, the pure anatase shows the higher photoreactivity than the single rutile structure [2]. The poor photocatalytic activity of the rutile is mainly attributed to its higher recombination rate of the photoinduced electron–hole pairs and the greater crystallite size, which can be transformed from brookite and anatase when increasing the calcination temperatures. Furthermore, a biphase of anatase–rutile TiO_2 with a singularly high photocatalytic performance can be obtained by controlling the calcinating temperature [4]. The phase transformation from anatase to rutile nanoparticles is associated to the increase of the calcination temperature [5]. In addition, the presence of zirconium has delayed the anatase phase transformation of TiO_2 at high temperature [6].

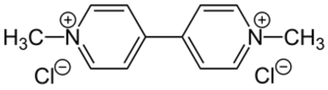


Figure 1 Chemical structure of paraquat dichloride

In this research, single TiO_2 and coupled TiO_2/ZrO_2 (90:10) catalysts were successfully prepared using sol-gel method and impregnated method respectively and the photocatalytic activity was tested on the degradation of paraquat dichloride solution (1×10^{-4} M) under UV irradiation for 3 hours. The synthesized catalysts were calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C and were compared with commercial 99% TiO_2 and P25 Degussa in order to observe the effect on phase transformation of TiO_2 and surface area of the prepared photocatalyst. Interestingly, the transformation of anatase to rutile phase was increased by increasing the calcination temperature for all the photocatalysts.TiO_2/ZrO_2 and P25Degussa catalysts calcined at 700°C and 450°C respectively has given positive effect on the degradation of paraquat dichloride. In this research, Zr used as a dopant on the TiO_2 has delayed the formation of the rutile phase. Among these photocatalysts, synthesized TiO_2/ZrO_2 and commercial catalyst (P25 Degussa) calcined at 700°C and 450°C gave highest percentage of photodegaradation respectively at original reaction pH. Addition of H_2O_2 gave better performance on photodegradation. Various characterization techniques were employed to reveal their physicochemical properties such as XRD analysis which has proven the transformation of the anatase to rutile phases, FESEM-EDX analysis showed morphology and particle size range of the catalyst and BET analysis showed surface area of the catalyst.

2. EXPERIMENTAL

The experiment was divided into three main stages. In the first stage the research involves the preparation of single TiO_2 and coupled TiO_2/ZrO_2 (90:10) photocatalysts using sol-gel method and impregnation method respectively which were calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C and were compared with TiO_2 Aldrich and P25 Degussa. In second stage, the photocatalytic activity of all the photocatalysts were studied on the photodegradation of paraquat dichloride in aqueous solution (1×10^{-4} M) under UV-light irradiation and monitored by using Uv-vis spectrophotometer. The percentage of photocatalytic activity was calculated using Eq 1. All photodegradation processes of paraquat dichloride were conducted in the photoreactor system at room temperature and pressure and also under the sunlight. In the third stage, the characterization of the photocatalysts were conducted by using field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) analyser, X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area analyser.

$$D\% = \frac{(A_0 - A_t)}{A_0} \times 100\% \qquad (1)$$

where D % is the percentage of degradation, A_o is the initial absorbance of sample before irradiation under UV light and A_t is the absorbance of sample after irradiation under UV light (t-minutes).

3. RESULTS AND DISCUSSION

From the previous research, zirconium was added to TiO_2 photocatalyst for further investigation towards the effect of ZrO_2/TiO_2 ratios on the formation of ternary species which are $ZrTiO_4$ and $ZrTi_2O_6$ in the photocatalyst system towards the degradation of paraquat dichloride. The experiment was run for 240 min under UV irradiation. They had reported that the trend of degradation was 450 >750 > 1000°C for TiO_2 and 750> 450 >1000 °C for ZrO_2/TiO_2 (10:90) were observed which indicated that addition of zirconium at certain ratio had remarkable improvement over degradation of paraquat dichloride compared to the single TiO_2 [2]. In the current study was focused more on the effect of calcination temperature on the phase transformation of TiO_2 and the comparison of the performance for all the catalysts that were calcined at various temperatures.

3.1. Comparison of the Activity of Synthesis Single and Couple Catalyst

Figure 2 shows the activity of the synthesized single TiO_2 catalyst and coupled TiO_2/ZrO_2 catalyst calcined at 700°C. Figure shows that coupled catalyst gave 54.87% which was higher removal of paraquat dichloride solution while, single TiO_2 gave only 37.71% removal. According to these results, the synthesized coupled catalyst acted better catalyst to degrade paraquat dichloride solution to harmless compound. This observation has also been reported by Zhang *et al*., for coupled catalyst of ZnO/SnO_2 which has higher photocatalytic activity efficiency compared to ZnO and SnO_2 alone. This is due to the utilizing single photocatalyst has greater chances for recombination of photogenerated electrons with holes. In this study, recombination of photogenerated electrons and holes was reduced to increase the photocatalytic degradation efficiency. The coupled catalyst was able to overcome this problem by supplying an h^+ from TiO_2 with band gap 3.2 MeV to ZrO_2 with band gap 5.2 MeV and the electron of ZrO_2 to TiO_2. This is due to the different between the band gap energy of coupled catalyst which be able to induce the effective charge separation by trapping the photogenetrated electrons, so that, the photogenerated electrons and holes were move in opposite direction. These results were also observed by Zhang *et al*., whereby the holes generated of SnO_2 was trapped in TiO_2 and the electrons generated by TiO_2 trapped in SnO_2 [7].

Furthermore, based on the theory, the coupled semiconductor can increase the efficiency of a photocatalytic process by increasing the charge separation. The various displacement of electrons and holes provide more efficient charge separation and increases the charge lifetime. Recombination in TiO_2/ZrO_2 is suppressed therefore increased the charge transfer between the adsorbed substrate and catalyst. The electron transfer occurred from the conduction band of ZrO_2 to the conduction band of TiO_2 and conversely, the holes move in the opposite direction from the electron which will reduce the electron hole recombination.

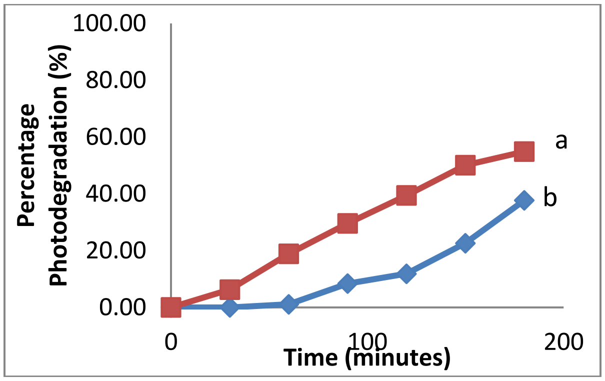


Figure 2 Activity of single TiO_2 and coupled catalyst TiO_2/ZrO_2 at 700°C a) TiO_2/ZrO_2 b) single TiO_2

3.2. The effect of calcination temperature

Figure 3 shows the percentage photodegradation of 1×10^{-4} M paraquat dichloride solution by using coupled catalyst TiO_2/ZrO_2 at different calcination temperatures. In this experiment, paraquat dichloride solution was degraded under UV irradiation with the presence of coupled catalyst, TiO_2/ZrO_2 which has been calcined for 5 hours at several temperatures of 450°C, 700°C, 800°C, 900°C, and 1000°C, which gave 20.45%, 54.87%, 16.25%, 12.04% and 7.12% respectively. Coupled catalyst which was calcined at 700°C for 5 hours gave the highest percentage photodegradation for paraquat dichloride solution. Based on the Figure 3, it showed that the efficiency of photodegradation increased as the calcination temperature of the catalyst was increased up to 700°C. However, the efficiency of the photodegradation was decreased as the calcination temperature was increased greater than 700°C. Hence, the percentage photodegradation for the paraquat dichloride solution was dependent on the calcination temperature of the catalyst.

The particle size and the surface area are important factors in order to act as a good catalyst. Since the reaction is heterogeneous catalysis which involving two different phases of the catalyst and the substrate (paraquat dichloride solution), the reaction only occurs on the surface of the active site of the catalyst. Particle size of the catalyst was in the range of 18 – 26 nm and the surface area was 25.6 m^2/g (Refer Figure 13 and Table 6). According to the group research, increasing the calcination temperature were resulting increasing the particle size. Therefore, the calcination temperature affects the efficiency of the catalyst in the photodegradation process. Higher calcination temperature causes the growth of particle size through agglomeration and a drop of surface area (as discussed in Section 3.5.2 and 3.5.3). Thus, this leads to decrease in photodegradation activity. As a whole, varying the calcination temperature would affect the morphology of photocatalyst that plays a vital role in the catalyst performance. This is in agreement with the result obtained in this study that shows the calcination at various temperatures may cause several successive structural changes such as the evaporation of water, decomposition of manganese compounds. In this research, enhancement of ZrO_2 crystallization, and the crystal phase transformation of ZrO_2 and TiO_2 may occur. Some agglomeration of TiO_2/ZrO_2 occurs at higher calcination temperature, resulting in the drastic decreases of BET surface area and pore volume. Meanwhile, the particle sizes greatly increase with the increasing calcination temperature.

Figure 4 shows the percentage of photodegradation for paraquat dichloride solution using Degussa of TiO_2 catalyst calcined for 5 hours at 450°C, 700°C, 800°C, 900°C, and 1000°C were 83.66%, 76.65%, 80.51%, 81.84% and 15.68% respectively. This results obtained were not in good agreement with previous coupled TiO_2/ZrO_2 (90:10) catalyst and single TiO_2 catalyst. Figure 4 showed that the degussa of TiO_2 that was calcined at 450°C gave the highest percentage photodegradation for paraquat dichloride. Result from XRD data showed that it has the presence of 57% anatase and 43% rutile was responsible for the highest activity (Refer Table 1 and 2). Figure 5 shows that the uncalcined Degussa catalyst has lower percentage photodegradation compared to the calcined Degussa. The percentage of photodegradation for uncalcined was much lower which was only 17.20% due to the catalyst was inactivated. For the heterogeneous catalyst, in order to make the catalyst active, the catalyst needs to be calcined at appropriate temperature. Photocatalysts calcined at 800°C and 900°C were also given comparable results.

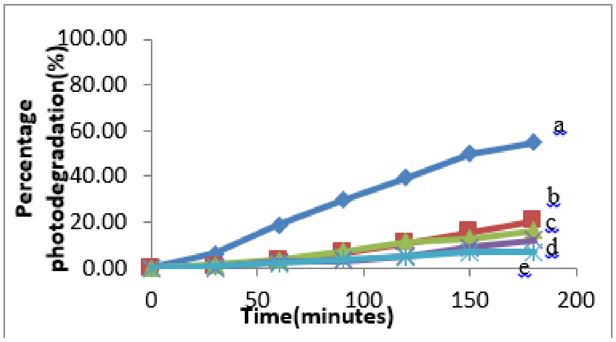


Figure 3: Percentage photodegradation of paraquat dichloride by using coupled catalyst TiO_2/ ZrO_2 at different calcination temperature a) 700°C b) 450°C c) 800°C d) 900°C e) 1000°C

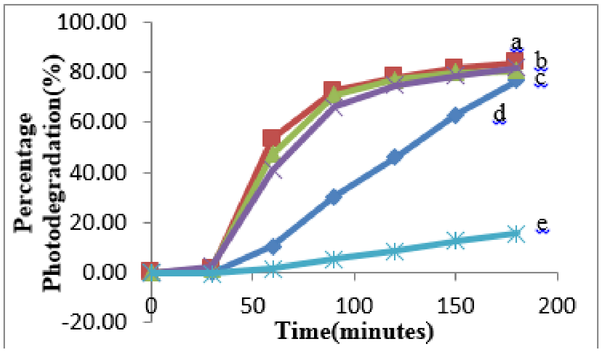


Figure 4: Percentage photodegradation of paraquat dichloride by using Degussa of TiO_2 at different calcination temperature a) 450°C b) 900°C c) 800°C d) 700°C e) 1000°C

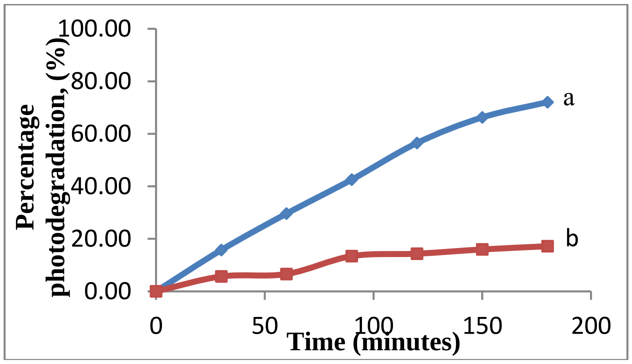


Figure 5: Percentage photodegradation of paraquat dichloride by using commercial 99% of TiO_2 and Degussa of TiO_2 without undergo calcination a) Percentage photodegradation commercial 99% TiO_2 b) Percentage photodegradation Degussa of TiO_2

The effect of the calcination temperature had also been investigated by Tianliang *et al.* Calcination was found to be an important step in most synthesis methods of solid catalysts. Calcination has great effects on the decomposition of inorganic or organic compounds such as carbonate, hydrate and ammonium ions, phase transformation of crystal or stabilization of solid materials. The increment of the temperature will cause the lowering of surface area and consequently lower the activity. Tianliang *et al.*, obtained surface area for TiO_2 calcined at 600°C was 35 $m^2 g^{-1}$ while uncalcined TiO_2 was 325 $m^2 g^{-1}$ [9].

3.3. The effect of pH

The effect of initial pH on paraquat dichloride solution was shown in Figure 6 and Figure 7. The original pH of paraquat dichloride solution was pH 7.74. The effect of pH on the photodegradation of paraquat dichloride solution was investigated over the acidic pH (3) and basic pH (10). According to the Figure 6 and Figure 7, the percentage photodegradation of paraquat dichloride solution without adjusting the pH was 65.51%. Meanwhile, when the initial pH was adjusted to pH 3 and pH 10, the percentage photodegradation of paraquat dichloride solution was 72.22% and 81.42% respectively. In acidic condition, the positive charge on the photocatalyst surface would only attacks anion, while in basic solution the surface on the photocatalyst was negative charge and hence easily adsorb the cation species. Paraquat dichloride has positively charge in aqueous solution, therefore easily adsorb on the catalyst surface to be degraded. Therefore the percentage was higher in basic solution. The experiment was repeated by using 450°C of the commercial 99% TiO_2, and it gave the same trend of result as shown in Figure 7. The increment of degradation in acidic solution is very small gave the surface is positive and the adsorption is less.

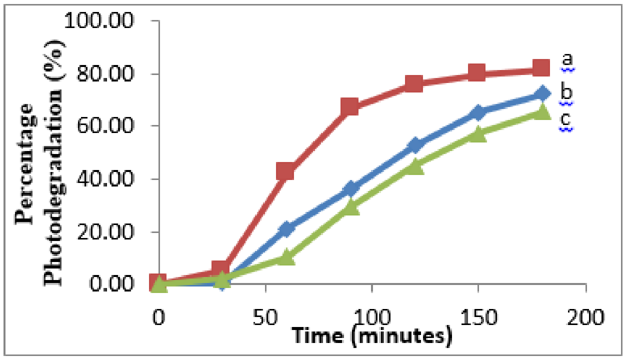


Figure 6: Percentage photodegradation of paraquat dichloride by using 700°C commercial 99% of TiO_2 with manipulating the intial pH a) basic b) acidic c) original pH

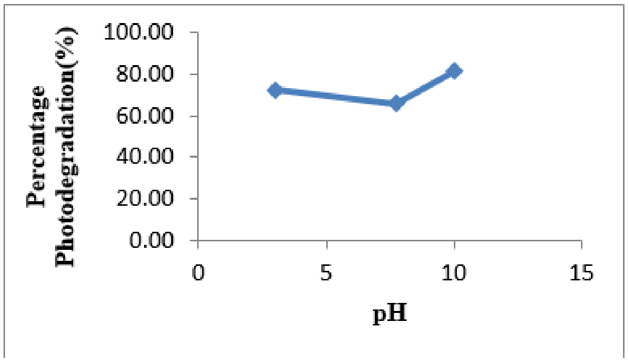


Figure 7: Percentage photodegradation of paraquat dichloride by using commercial 99% of TiO_2 at various pH.

3.4. The effect of hydrogen peroxide addition

Figure 8 shows the effect of hydrogen peroxide addition in percentage photodegradation of 1×10^{-4} M of paraquat dichloride solution. The addition of hydrogen peroxide in the paraquat dichloride solution which consists of photocatalyst and UV irradiation gave greater removal of toxic in paraquat dichloride. After the addition of hydrogen peroxide, the degradation for 700°C of single TiO_2 and 700°C of coupled catalyst TiO_2/ZrO_2 was increased from 37.71% to 43.96% and from 54.87% to 74.19% respectively. The efficiency of catalyst increased with the addition of hydrogen peroxide. Hydrogen peroxide is a powerful oxidant and electron acceptor.

The presence of oxidant hydrogen peroxide in the photocatalytic system has been proven to enhance the rate of photodegradation by increasing the number of ●OH radical as shown on Equation 3.1-3.3:

$$H_2O_2 + h\nu \rightarrow 2\ \bullet OH \qquad (3.1)$$
$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \qquad (3.2)$$
$$H_2O_2 + \bullet\ O_2^- \rightarrow \bullet OH + OH^- + O_2 \qquad (3.3)$$

Every addition of one mol of H_2O_2 will produce four mol of ●OH radical. This resulted in an increase of paraquat dichloride being attack by their radicals. Recombination of h^+ and e^- are one of the main drawbacks in the application of the photocatalyst. However, the presence of the proper electron acceptor or donor are be able to overcome the problems encountered while using photocatalyst and this have been proven in this experiment. Hydrogen peroxide wills also retard the electron-hole recombination by accepting the conduction band electron. As a whole, the generation of hydroxyl radical is significant to transform toxic compound to harmless compound. Dionysiou *et al.*, has reported that the addition of hydrogen peroxide at small concentrations had a synergistic effect and increased considerably the rates of photocatalytic reactions [10].

3.5. Characterization

In this section, it will focus on the surface topology and morphology by using field emission scanning electron microscope energy dispersive X-ray spectroscopy (FESEM-EDX) analysis, phase structure of the catalyst using X-ray diffraction analyzer (XRD) and the surface area of the catalyst using Brunauer-Emmet-Teller surface area analyzer.

3.5.1 X-Ray Diffraction (XRD) Analysis

The synthesis catalysts and the commercial catalysts were analysed by using XRD. This XRD analysis is mainly for the determination of active phases that was present to give a good performance in the photodegradation process. The structural and the phases of the catalyst were identified by this method. In this experiment, the based catalyst used was titanium dioxide.

TiO_2 forms three different phases which are anatase, rutile and brookite, but in the catalyst under observation, only rutile and anatase phase were observed.

The X-ray diffraction pattern for all catalysts which was synthesized single TiO_2, synthesized coupled catalyst TiO_2/ZrO_2, commercial 99% TiO_2 and Degussa, calcined at 700°C were shown in Figure 9. Based on Figure 9 (a), it shows that there are 8.70% of ZrO_2, 21% of anatase phase and 69% of rutile phase, while Figure 9 (b) shows 100% of the rutile phases for single TiO_2. In Figure 9 (c), it shows that 100% of anatase phase formed for commercial 99% TiO_2. Figure 9 (d) shows 24% of anatase and 76% of rutile for Degussa (Refer Table 1). According to the percentage degradation of these four catalysts at 700°C, it found that 54.87%, 37.71%, 65.51% and 76.65% respectively were degraded. By comparing the synthesized catalysts which are the single TiO_2 and coupled catalyst TiO_2/ZrO_2, the results show that having all rutile phases gave lower performance in the percentage photodegradation compared to catalyst that have both anatase and rutile phases, but with the higher percentage of anatase would gave the better performance (Refer Table 1 and 2). So it is proven in this experiment that the catalyst which having a both anatase and rutile phase would increase the percentage of the photodegradation of paraquat dichloride solution.

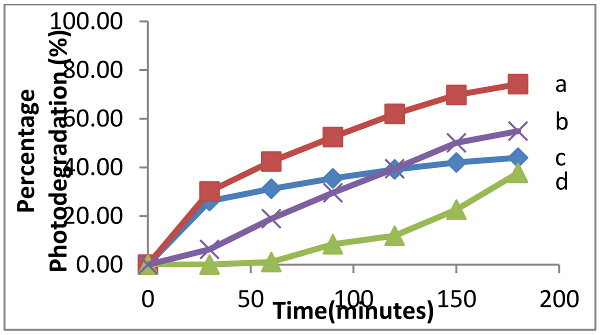


Figure 8: Percentage photodegradation of paraquat dichloride by using 700°C single TiO_2 and 700°C coupled catalyst TiO_2/ZrO_2 with H_2O_2 a) TiO_2/ZrO_2 + H_2O_2 b) TiO_2/ZrO_2 c) single TiO_2 + H_2O_2 d) single TiO_2

By comparing the commercial catalysts which is the commercial 99% of titanium dioxide and degussa, it shows that having all the anatase phases gave a low performance in the percentage of photodegradation compared to catalyst with both anatase and rutile phases (Refer Table 1 and 2). Data also showed that for commercial 99% TiO_2 at 1000°C only the rutile phase was observed while for Degussa, the rutile phase was observed at 450°C and a complete transformation was observed at 1000°C.

Based on Table 1 and Table 2, it clearly shows that having all rutile phase and anatase phase will gave a low performance compared on having both of the anatase and rutile phase. However, the smaller percentage of anatase phase would increase the percentage of photodegradation of paraquat dichloride solution.

Table 1: Percentage of anatase phase and rutile phase transform at different calcination temperature

		TiO_2/ ZrO_2 (%)	**Single TiO_2 (%)**	**Commercial 99% TiO_2 (%)**	**Degussa (%)**
450°C	Anatase	100	100	100	57
	Rutile	-	-	-	43
700°C	Anatase	21	-	100	24
	Rutile	69	100	-	76
1000°C	Anatase	-	-	65	-
	Rutile	100	100	35	100

3.5.2 Field Emission Scanning Electron Microscope & Energy Dispersive X-ray Spectroscopy (FESEM-EDX) Analysis

The chemical composition of single TiO_2, TiO_2/ZrO_2, commercial 99% TiO_2 and Degussa with different activation temperature of 450°C, 700°C and 1000°C were identified by using Energy Dispersive X-ray (EDX) Spectroscopy. Figure 10, and 11 demonstrate EDX spectra of two catalysts which was TiO_2/ZrO_2 catalyst and Degussa catalyst with activation temperature at 700°C Another activation temperature at 450°C and 1000°C were conducted by group member (Refer Table 4 and 5). From the spectra in Figure 10 the complete catalyst showed only the presence of O, Ti and Zr were observed while the Ti and O for other catalyst as shown in Table 4 and 5. The composition of the element in the catalysts calcined at 700°C was summarized in Table 3.

Table 2: Percentage of photodegradation of paraquat dichloride at different calcination temperature

	TiO_2/ ZrO_2	**Single TiO_2**	**Commercial 99% TiO_2**	**Degussa**
450°C	20.45	18.38	64.02	83.66
700°C	54.87	37.71	65.51	76.65
1000°C	7.12	1.42	68.38	15.68

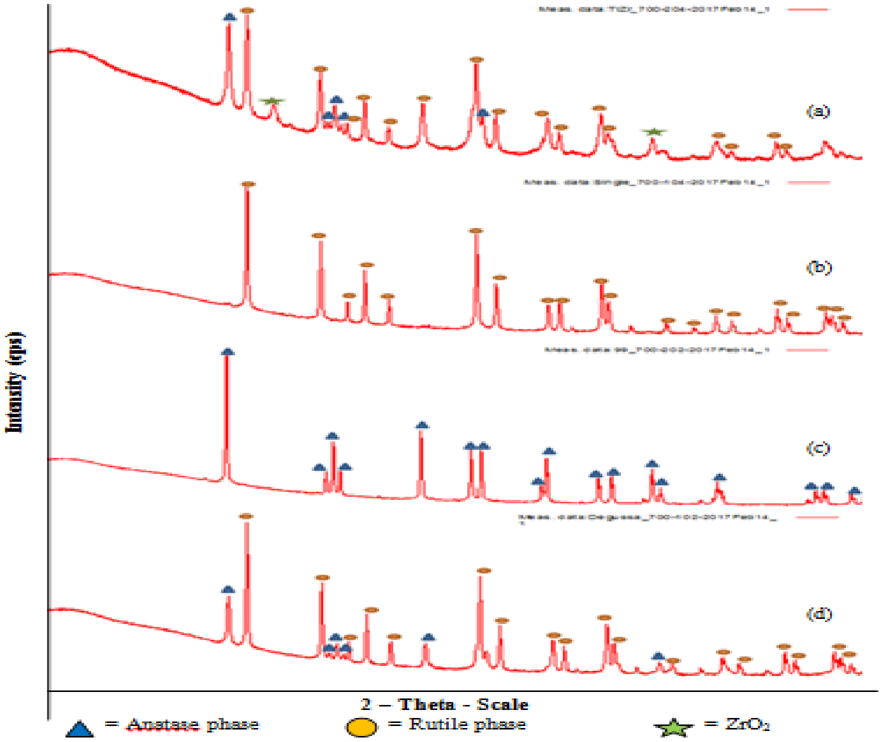


Figure 9: XRD diffractograms of (a) TiO_2/ ZrO_2 (90:10), (b) synthesized single TiO_2 prepared by sol gel, (c) Commercial 99% TiO_2, and (d) Degussa 75% TiO_2 those calcined at 700°C.

Table 3: Composition of element in various TiO_2 catalysts at 700°C

Photocatalyst	**Ti (%)**	**O (%)**	**Zr (%)**
TiO_2/ ZrO_2	47.1	49.0	3.8
TiO_2 synthesized	52.6	47.4	-
Commercial 99% TiO_2	42.0	58.0	-
75% P25 Degussa	56.4	43.6	-

Field emission scanning electron microscopy (FESEM) analysis provides a view of the topology and morphology of the catalysts. In this study, the surface morphology for all catalysts at 700°C was only being characterized by FESEM. Selected images of the catalysts were compared in the Figure 12 – 15.

Table 4: Composition of element in various TiO_2 catalysts at 450°C

Photocatalyst	**Ti (%)**	**O (%)**
Commercial 99% TiO_2	52.6	47.4
75% P25 Degussa	50.8	49.2

Table 5: Composition of element in various TiO_2 catalysts at 1000°C

Photocatalyst	**Ti (%)**	**O (%)**
Commercial 99% TiO_2	57.9	42.1
75% P25 Degussa	57.0	43.0

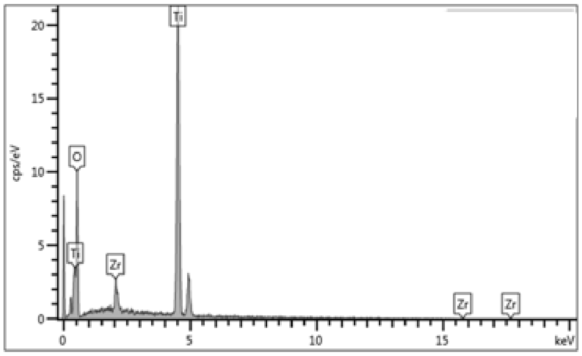


Figure 10: EDX spectrum for couple catalyst, TiO_2/ ZrO_2 (90:10) calcined at 700°C

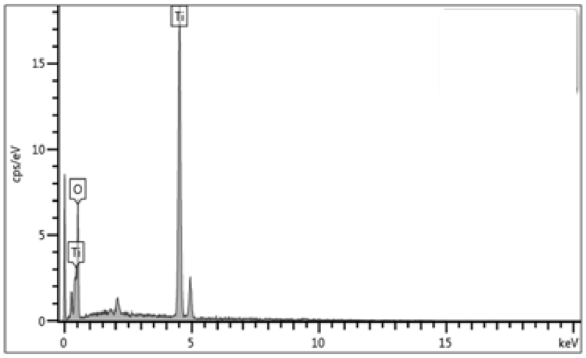


Figure 11: EDX spectrum for Degussa catalyst calcined at 700°C

Figure 12, 13, 14, and 15 shows the surface morphology of the coupled catalyst, single TiO_2 catalyst, commercial 99% TiO_2 catalyst and degussa respectively. The FESEM micrographs show that the coupled catalyst, commercial 99% TiO_2 and degussa consists of small spherical particles with non-uniform sizes from particle size range 18.9 nm for coupled catalyst to 54.6 nm for synthesized single TiO_2. Furthermore, Figure 13 showed the particle size of single TiO_2 was larger than the other catalysts. In the other word, the catalyst of TiO_2/ZrO_2, commercial 99% TiO_2 and degussa consists of larger surface area than single TiO_2 (Refer Table 6). This observation was supported the result obtained in photodegradation for single TiO_2 which has the lowest percentage in photodegradation process. At 450°C the particle size of 75% Degussa was in the range of 29 – 35 nm (Group research data). The group research data has proven that the degussa calcined at 450°C has the smallest particle size which result in high degradation efficiency (Refer Section 3.2). It can be concluded that smaller particle size gives the larger surface area. The larger surface areas give more active site on the surface of catalyst which enhances the photodegradation reaction. Calcination process favored the formation of bigger TiO_2 crystal through agglomeration crystals of TiO_2. This led to the formation of bigger mesopores between TiO_2 crystals [9].

3.5.3 Brunauer-Emmet-Teller (BET) Analysis

The coupled catalyst TiO_2/ZrO_2, single catalyst TiO_2, commercial 99% TiO_2 and degusa were calcined for 5 hours at different calcination temperature. These catalysts were analysed by using BET mainly to determine the surface area. The single point surface area data was tabulated in Table 6. The larger of the surface area give the more active site on the surface of the catalyst [11].

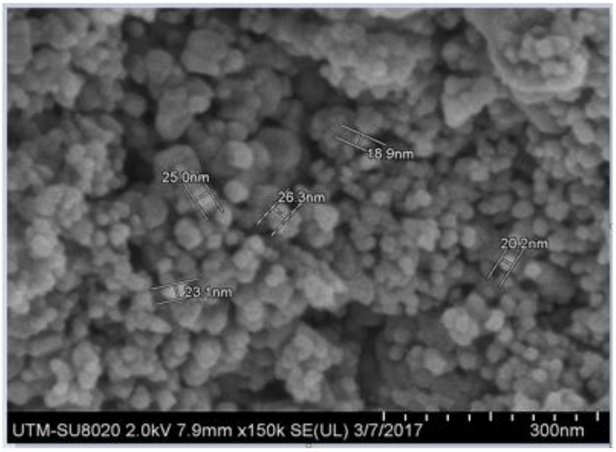


Figure 12: FESEM micrograph for couple catalyst TiO_2/ZrO_2 (90:10) calcined at 700°C

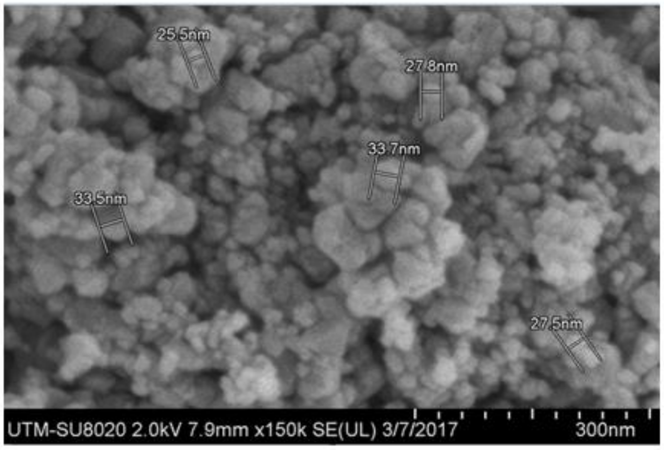
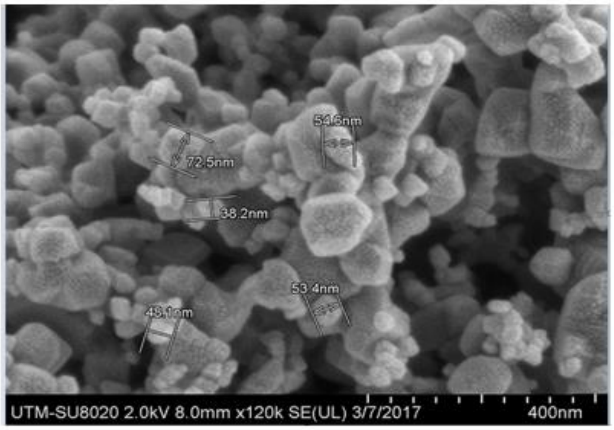


Figure 14: FESEM micrograph for commercial 99% TiO_2 catalyst calcined at 700°C



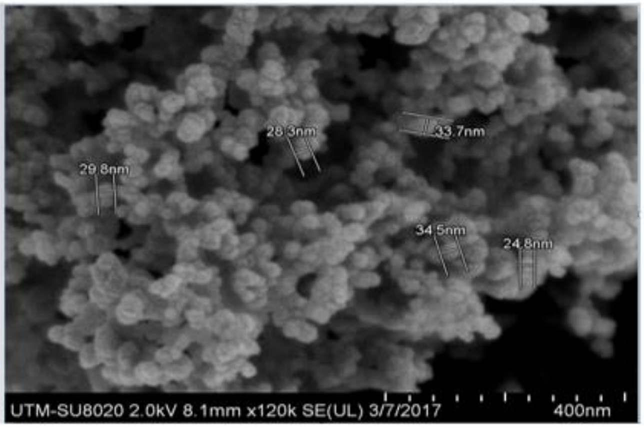


Table 6: Single point of surface area data for 700°C

Type of catalysts	Surface area (m^2/g)
TiO_2/ ZrO_2	25.61
Single TiO_2	4.26
Commercial 99% of TiO_2	11.67
Degusa	22.50

The single point surface area with nitrogen gas flow being used to obtain the surface area of the catalyst at 24°C room temperature and 130°C outgas temperature. According to the Table 6, it shows that the surface area for coupled catalyst TiO_2/ZrO_2, single catalyst TiO_2, commercial 99% of TiO_2 and Degussa calcined at 700°C were 25.61 m^2/g, 4.26 m^2/g, 11.67 m^2/g and 22.50 m^2/g respectively. From group research data, the surface area of degussa calcined at 450°C was 44.91 m^2/g. This high surface area of degussa calcined at 450°C compared to the other photocatalysts indicates that larger surface area would gave high degradation rate. This data was in agreement with the FESEM where single catalyst has the highest particle size compared to the others, therefore it has the lowest surface area.

4. CONCLUSION

From the results has proven that synthesized couple catalyst TiO_2/ ZrO_2 was more effective compared to synthesized single catalyst TiO_2. It gave 54.87% removal of 1×10^{-4} M of paraquat dichloride solution. By comparing performance between these four catalysts which were single TiO_2, couple TiO_2/ZrO_2 catalyst, commercial 99% TiO_2 and Degussa, Degussa gave the highest percentage photodegradation of all with 83.66% calcined at 450°C. In this studied, these catalysts were calcined at various temperature which were 450°C, 700°C, 800°C, 900°C, and 1000°C. The percentage of degradation for paraquat dichloride by using Degussa catalyst calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C were found to be 83.66%, 76.65%, 80.51%, 81.84% and 15.68% respectively. Hence, Degussa catalyst calcined at 450°C gave the highest percentage photodegradation. Besides, the percentage of degradation for paraquat dichloride by using coupled catalyst TiO_2/ZrO_2 (90:10) calcined at 450°C, 700°C, 800°C, 900°C, and 1000°C were found to be 20.45%, 54.87%, 16.25%, 12.04% and 7.12% respectively. Hence, coupled catalyst calcined at 700°C gave the quite highest percentage photodegradation. The calcination temperature gave high impact on the percentage photodegaradtion of paraquat dichloride. Addition of H_2O_2 gave better performance on photodegradation. In this study was proven that hydrogen peroxide would increase the percentage of photodegradation of paraquat dichloride. Characterization by using XRD, FESEM, and BET surface area have proven that the catalyst activity was determined by the type of TiO_2 structural phase either anatase or rutile. Results showed that a combination of anatase and rutile phase gave synergy effect which increases the percentage degradation. FESEM and BET data have also supported the finding whereby the smaller the particle size with the larger surface area will enhance the photocatalytic activity.

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