

CHAPTER 4

Results and Discussions

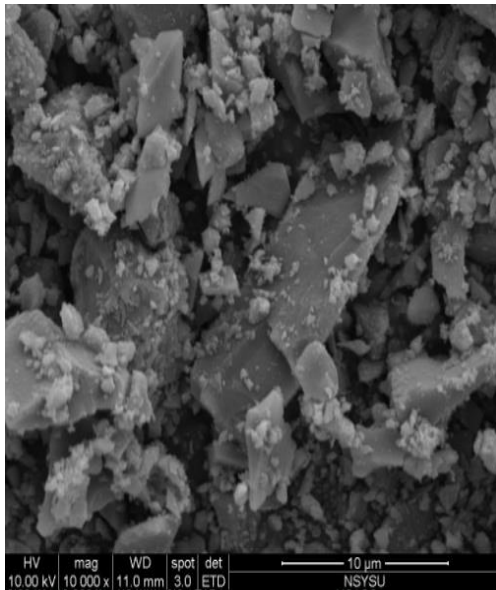
4.1. Characterization analysis

4.1.1 Scanning electron microscopy (SEM) analysis

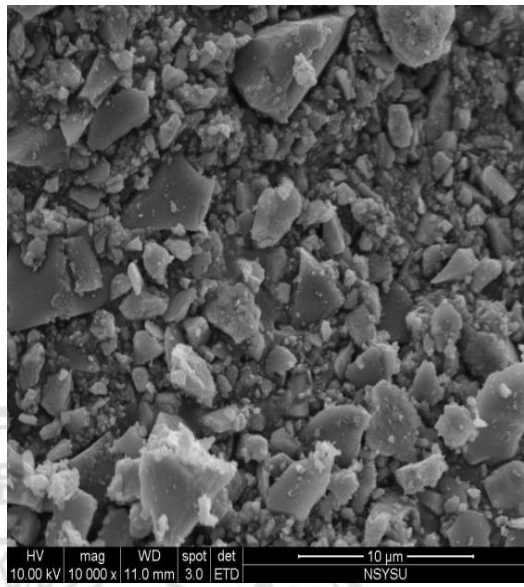
The SEM micrographs of different synthesized TiO₂ catalysts doped with Cerium(iii) nitrate hexahydrate are shown in Figure 4.1 and Figure 4.2. They illustrate are a lot of shape particles formed from the synthesized TiO₂ catalysts. All of the synthesized TiO₂ samples agglomerated into smaller particles. The particles of photocatalysts appear to have an effect on its photocatalytic performance and depended on the concentration of Cerium (iii) nitrate hexahydrate.



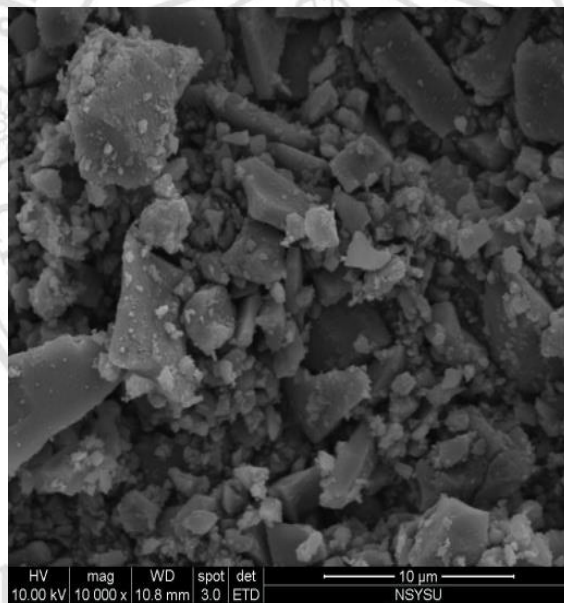
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TiO₂/Ce; 0.07 %mol

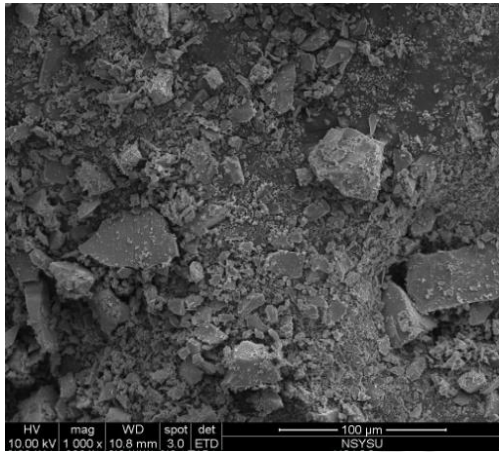


TiO₂/Ce; 0.28 %mol

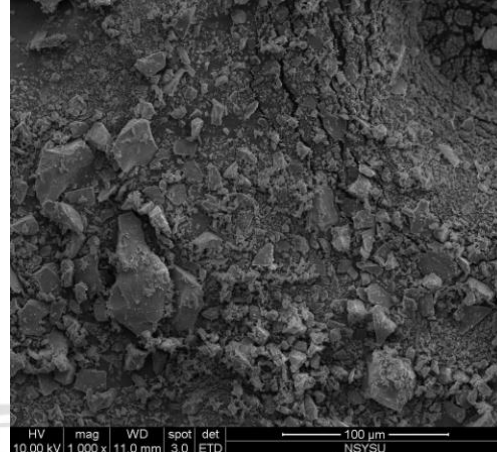


TiO₂/Ce; 0.35 %mol

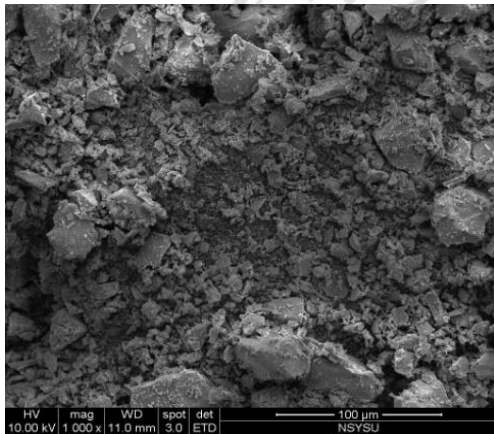
Figure 4.1 SEM micrographs at a magnification of 10,000X showing the morphological structure and texture of the synthesized TiO₂ catalysts with Ce-doping at various concentrations (0.07, 0.28 and 0.35% mol)



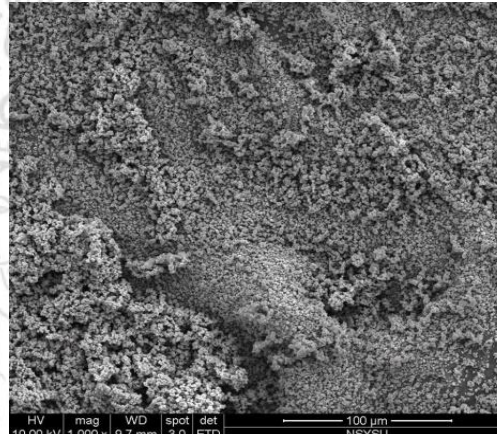
TiO₂/Ce; 0.07 %mol



TiO₂/Ce; 0.28 %mol



TiO₂/Ce; 0.35 %mol



Degussa – P25

Figure 4.2 SEM micrographs at a magnification of 1000X showing the morphological structure and texture of the synthesized TiO₂ catalysts with Ce-doping at various concentrations (0.07, 0.28 and 0.35% mol)

The SEM micrographs show that the Degussa P-25 had better regularity than the TiO₂/Ce. All particles were in nanogranular form, rough surface with smaller size with response to TiO₂/Ce catalysts (Figure 4.2). In fact, Degussa P-25 powder, produced through hydrolysis of TiCl₄ in a hydrogen flame (Datye et al., 1995), does not contain pore in each TiO₂ crystallites. Therefore, the formation of the pore structures in the samples could be attributed to the aggregations of TiO₂ crystallites (Lu et al., 1993).

The particles size of the TiO₂/Ce decreased with an increasing of doping concentration. As a result, is increased which provided more active sites for interfacial

reaction of degradation. Because the agglomeration of the crystallines on the surface to form larger particles. Nevertheless, the SEM micrographs show in insignificant a\effect on the specific surface area and performance of the photocatalyst. In order to that explain in the component of the dopant, structure of the TiO₂ dopants were analysed by XRD.

4.1.2 X-ray diffraction (XRD) analysis

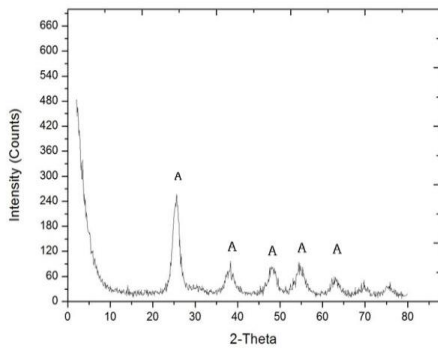
TiO₂ catalysts were calcined at different calcinations temperature (200, 300, 400, 500 and 600°C) as compared to the pure TiO₂. All of samples were analyzed by X-ray diffraction method as show in Figure 4.3. Characterization of a heterogeneous powder sample, that is to quantify the relative abundance of the crystalline TiO₂ catalyst. Synthesized TiO₂ calcined at different temperature was found to have high intensity peak and crystal growth were observed XRD patterns of the synthesized photocatalyst after calcinations with the diffraction angle (2θ).

The XRD patterns represent the principal crystal phase of anatase(A). Both of rutile and Brookite were not observed in the catalysts indicating that the TiO₂ catalysts were pure anatase and no rutile phase formed.

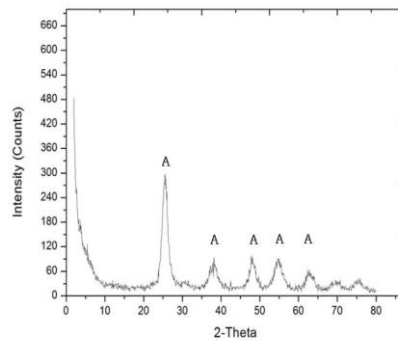
The diffraction angles (2θ) of 25.28 and 27.43 represent the crystal plane of anatase (1 0 1) and rutile (1 1 0). This peak was used to estimate the crystallite size by applying the Scherrer's equation, as follows (Brundle et al., 1992).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (eq. 4 - 1)$$

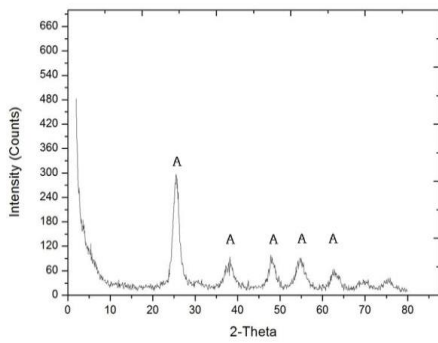
Where; λ wavelength of the X-ray radiation radiation (λ = 0.15406 nm), β is the full width at half maximum (FWHM) of which unit is in radians and θ is the corresponding diffraction angle. The full widths at half-maximum of the anatase, brookite, and rutile peaks could be obtained from the XRD pattern. The crystal structures are summarized as Apendix C. Table 4.1 shows the large peak at 2θ and the crystal sizes of the TiO₂ obtained from this study under various calcination temperatures.



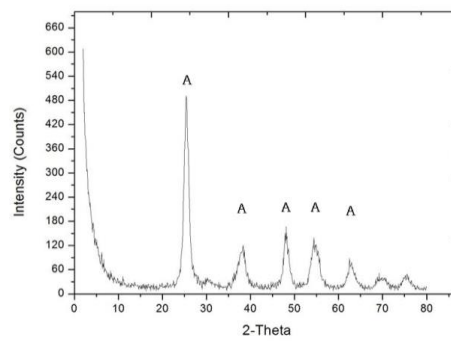
(a) 200 °C



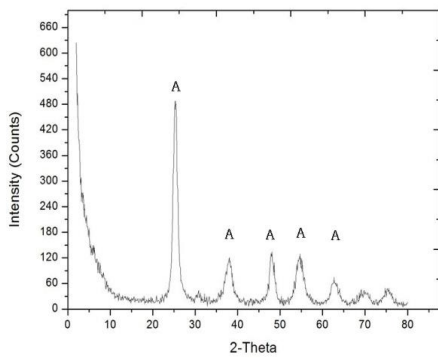
(b) 300 °C



(c) 400 °C



(d) 500 °C



(e) 600 °C

Figure 4.3 XRD spectra of synthesized TiO₂ catalyst calcined at different temperatures (a) 200°C; (b) 300°C (c) 400°C (d) 500°C and (e) 600°C

Table 4.1 Summary of the calculated structural parameters of synthesized TiO₂ catalysts

Calcination temperature	Crystal Structure	Crystal Phase	2θ	Crystallite Size (nm)
200	Tetragonal	anatase	25.63	9.93
300	Tetragonal	anatase	25.51	9.46
400	Tetragonal	anatase	25.22	10.25
500	Tetragonal	anatase	25.45	10.91
600	Tetragonal	anatase	25.44	11.66

Results reveal that in all cases, increasing the calcination temperature enhances the crystallinity of the ensuing photocatalyst. And there is increases transformation from amorphous to crystal phase TiO₂ as increasing calcination temperature. The crystal phase all of the samples calcined at different temperature as calcination temperature from 200 °C reached to 600°C contained only anatase and the crystal sizes were calculated to be 9.93, 9.46, 10.25, 10.91 and 11.66 nm, respectively. The reason of the broadening of the peaks was the presence of some impurities such as, amorphous hydroxide, amorphous carbon, etc. on the samples. Sikong, et al., (2008) also investigated the effects of various calcinations temperature (300-700 °C) when doped TiO₂ with SiO₂. The SiO₂-doped TiO₂ powder showed a phase transformation from amorphous to anatase phase at 300-600°C, thus producing photocatalysts with higher crystallinity. They were not able to observe rutile or brookite TiO₂ phase at these temperature range as well. The rutile phase only appeared when the photocatalyst was calcined at 700°C (Sikong, et al., 2008).

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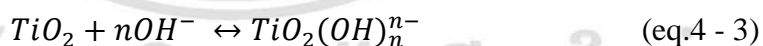
4.1.3 Point of zero charge (pzc) or surface charge

Semiconductors TiO_2 , reveal an electrical charge due to its amphoteric dissociation of the hydroxyl groups mixed with adsorption. The oxygen sites or hydroxide ions sites bonded the number of metal atoms and metal hydroxyl compound were obtained. These occasions were all pH dependent. The pH of the solution is one of the most important parameter in the photocatalytic oxidation of 2-chlorophenol. Therefore, photoredox process in TiO_2 as well as the interfacial electron transfer will be affected if the pH of the solution is varied from acidic to alkaline condition (Lu et al., 1993, Ku et al., 1996). However, chlorinated organic compounds will hydrolyze in alkaline media (Lu et al., 1993). The potential of the point of zero charge (pzc) or the surface charge is connected to the adsorption process (Lu et al., 1993, Reymond and Kolenda, 1999). The mass titration is the one method of determining the point of zero charge (pzc) of TiO_2 catalyst. This analysis describes which electrical charge density condition on the surface of the TiO_2 catalyst refers to. The positive properties of TiO_2 catalyst ($pH < pH_{PZC}$) and negative charge properties ($pH > pH_{PZC}$) both of them were expressed in the following equations.

For positively surface charged, $pH < pH_{pzc}$



For negatively surface charged, $pH > pH_{pzc}$



The pH of the aqueous solution during the oxidation varies from acidic to basic depending on the type of organic contaminants. The estimation of the point of zero charge of the synthesized TiO_2 catalyst is shown in Figure 4.4.

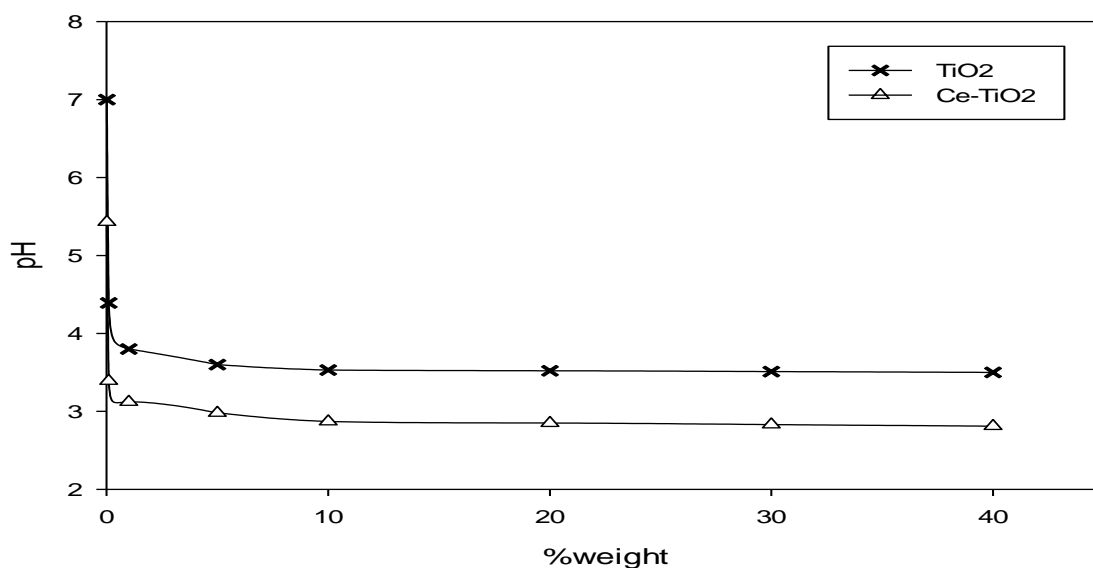


Figure 4.4 Point of zero charge of the synthetic TiO₂

Table 4.2 pH_{pzc} values for TiO₂ synthesized

TiO ₂ Catalysts Sample	pH _{pzc}
Pure TiO ₂	3.51
TiO ₂ /Ce; 0.28 %mol	2.83

The pH_{pzc} of photocatalyst synthesis for pure TiO₂ and TiO₂/Ce (0.28 %mol) were 3.51 and 2.83 respectively as shown in Table 4.2. The operated as high effective condition was at acidic condition (pH lower than 3) in catalyst surface. Some studies reported that at alkaline condition in solution, which have chlorinated organic compounds hydrolyze. Thus, to minimize hydrolysis of the organic compounds, the working pH during the oxidation process should be in acidic condition. So the condition of TiO₂/Ce 100:0.28 %mol catalyst was in acidic condition more than Pure TiO₂, which have advantage was the solution have not chlorinated organic compounds hydrolyzed that make removal effective of 2-chlorophenol decrease. The latter was expected to maintain the surface charge of the catalyst (Reymond and Kolenda, 1999; Lu et. al., 1993).

4.2 Feasibility of dopants on TiO₂ with 2-CP degradation

The sol-gel method was most widely used because of its possible capability in controlling the textural and surface properties of composite oxides. However, it can lead to particle agglomeration, small surface area and anatase structure transform to rutile structure, which adversely affect photocatalytic activity of the catalyst. The hydrothermal process has been represented to high-temperature calcination for crystallization of TiO₂. It has been widely applied in the synthesis of zeolites and in the production of advanced ceramic powders with ultrafine particle size. The hydrothermal process can be useful in controlling grain size, particle morphology, crystalline phase, and surface chemistry.

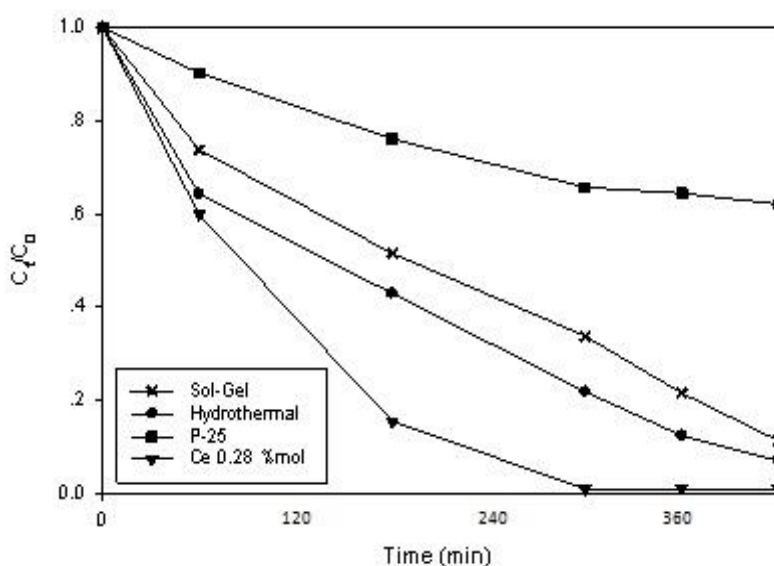


Figure 4.5 Photodegradation of 2-chlorophenol at various doped TiO₂ compared to undoped TiO₂ under blue light irradiation (3g/L TiO₂, initial pH 5.5 and 40°C)

In this part, the efficiency of the sol-gel process was expected to be lower than the hydrothermal process due to the difference in the purity and consistency in particle size. The experiment was conducted to find out the efficiency of the hydrothermal process and to compare it with that of sol-gel process by using undoped-TiO₂. Figure 4.5 represents the difference between photocatalyst synthesis performance in 2-chlorophenol removal at 490 minutes and it could be arrayed in order by cerium 0.28%mol doped TiO₂ with hydrothermal process > undoped TiO₂ with hydrothermal process > undoped TiO₂ with the sol-gel process > P25 with the efficiencies of 100.00%, 93.06%, 88.78%, 37.95%, respectively. The % 2-chlorophenol degradation at various doped TiO₂ compared to

undoped TiO₂ with different synthesis methods was observed. 2-CP reduced rapidly during the first hour of reaction. The degradation rates of them are sharply at 0 – 60 minutes. The photocatalyst dopants of cerium 0.28%mol doped TiO₂ with hydrothermal process and undoped TiO₂ with hydrothermal process, both of them, can decrease amount of 2-chlorophenol rapidly until irradiation time between 1- 3 hours, the degradation rates are obviously different. Besides, the efficiencies of cerium 0.28%mol doped TiO₂ with hydrothermal process is very high. However, for catalyst P-25, the removal efficiency was very low at 0 – 60 minutes and the degradation rate is rough.

Thus, in this experiment, cerium doped TiO₂ with hydrothermal process as different ratios were focused to find percent degradation of 2-chlorophenol using 2^k factorial design.

4.3 Control experiments 2^k factorial design

The independent variables were calcined temperature (A), Amount of cerium (B) and Amount of Nitric acid (C) as shown in Table 4.3. The response variable is a percent degradation of 2-chlorophenol using 2^k factorial design. The experiments were done using 100 mL of 20 ppm initial concentrations of 2-chlorophenol, amount of HNO₃ was 0.10 vol HNO₃/Ti(OBu)₄, operating temperature of 40 °C, light intensity of 16.85 mW/cm² and the initial pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH.

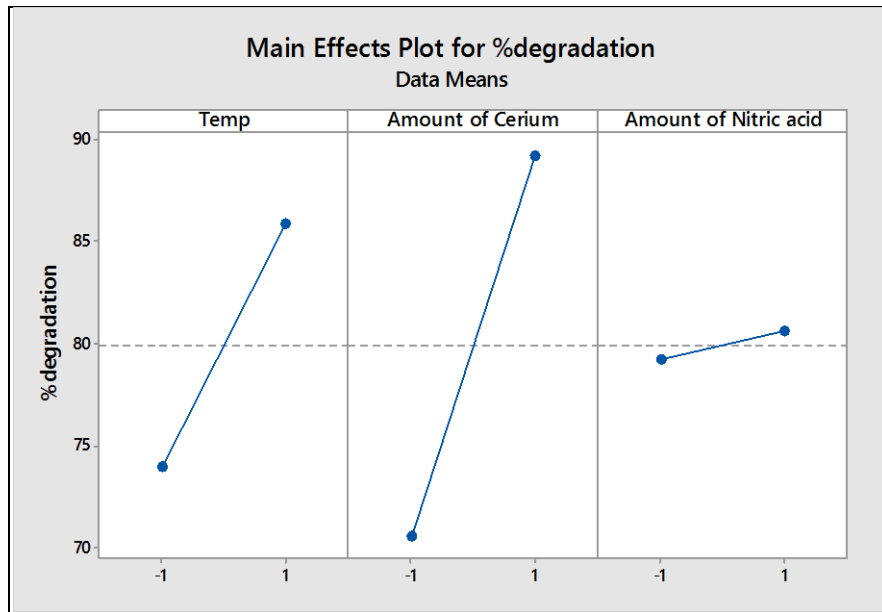
Table 4.3 Investigated variables for 2-chlorophenol removal

Variables	Levels	
	-1	+1
Calcine Temperature (A)	200 °C	600 °C
Amount of Cerium (B)	0.07 %mol	0.35 %mol
Amount of nitric acid (C)	0.05 V/V	0.15 V/V

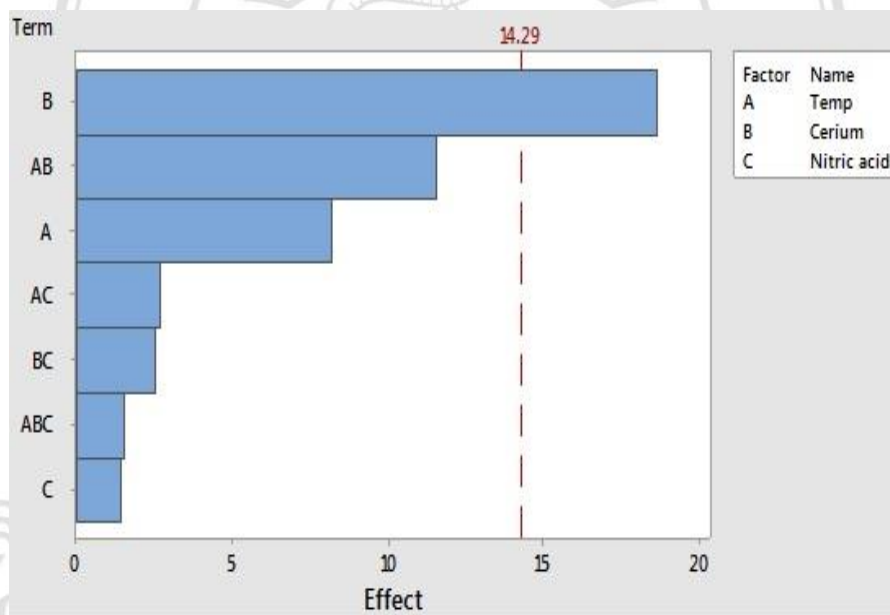
Table 4.4 Static batch experiments generated using 2^k factorial design

Run	Temperature (°C)	Cerium Dosage (Vol/Vol)	Amount of nitric acid (mL)	%Degradation
1	200	0.07	0.05	64.87
2	200	0.07	0.15	72.21
3	200	0.35	0.05	80.52
4	200	0.35	0.15	78.24
5	600	0.07	0.05	72.43
6	600	0.07	0.15	72.96
7	600	0.35	0.05	99.08
8	600	0.35	0.15	99.10

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(a)



(b)

Figure 4.6(a) Main effect plot for %degradation (b) Pareto chart of the effects for the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination

The static batch experiments studied three parameters consist of calcined temperature (A), amount of cerium (B) and amount of nitric acid (C) following 2^k factorial design designation. The formula used to calculate the percentage of 2-chlorophenol degradation is displayed in Equation 3-1. Static batch experiments generated using 2^k factorial design as shown in Table 4.4.

The results indicate that when the calcination temperature and the amount of nitric acid increase with increasing the percent degradation of 2-chlorophenol. The results also indicate that the amount of cerium increases while, increasing the percent degradation of 2-chlorophenol. At 0.35 %mol cerium, the percentage removal of 2-chlorophenol was higher than that at 0.07 %mol cerium as shown in Figure 4.6(a). Figure 4.6(b) displays the Pareto chart showing the effects of the variables. The data summarized that the amount of cerium greatly affects the percent removal of 2-chlorophenol rather than that of calcination temperature. On the other hand, the amount of nitric acid has a minimal effect on the removal of 2-chlorophenol. Thus, in this research the main effect focused on calcination temperature and the amount of cerium using the average value 0.1 v/v of nitric acid (Tsao & Patel, 2013).

4.4 Effect of synthesis parameters

4.4.1 Effect of amount of dopant

As shown in Figure 4.7, the effect of amount of dopant cerium was observed on the photocatalytic degradation of 100 mL with initial 2-chlorophenol concentration of 20 ppm, amount of HNO_3 0.10 vol $\text{HNO}_3/\text{Ti}(\text{OBU})_4$, operating temperature of 40 °C, light intensity of 16.85 mW/cm^2 .

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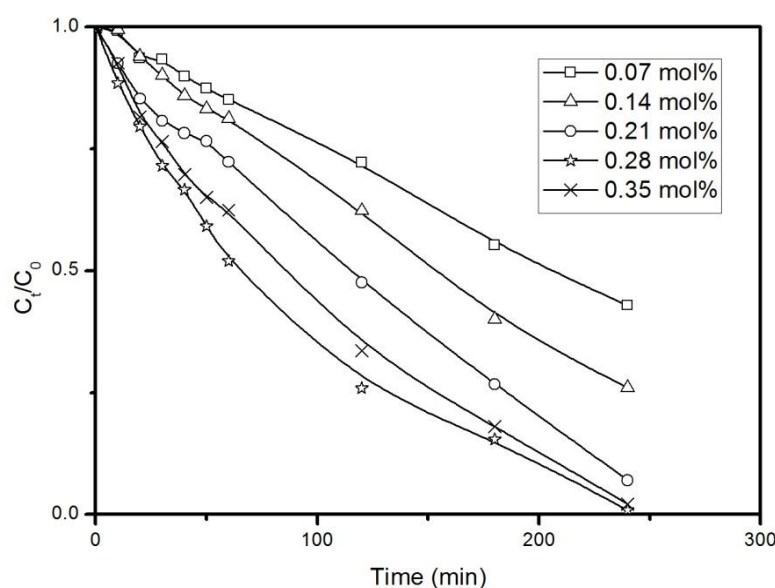


Figure 4.7 Effect of amount of dopant on photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination; experimental conditions: initial pH 5.5, 20 ppm 2-chlorophenol, 3g/L TiO₂ and 0.1 v/v of nitric acid

The addition of different amount of dopant 0.07, 0.14, 0.21, 0.28 and 0.35 %mol. The increase in the amount of dopant results to the increase in the % 2 -chlorophenol degradation. The performance in 2-chlorophenol removal could be arrayed in order of 0.28%molTiO₂/Ce > 0.35%molTiO₂/Ce > 0.21%molTiO₂/Ce > 0.14 %molTiO₂/Ce > 0.07%molTiO₂/Ce with the efficiencies of 99, 97, 92, 74 and 57%, respectively. The % 2-chlorophenol degradation using photocatalyst dopants of 0.28 and 0.35%mol at 0 – 60 minutes were observed. The degradation rates all of ratio are sharply. The photocatalyst dopants of 0.28 and 0.35%mol, both of them, can decrease amount of 2-chlorophenol rapidly until they were removed 100% at 240 minutes after irradiation. However, 0.07 and 0.14%mol photocatalyst dosage, the removal efficiencies are very low at 0 – 240 minutes. Highest degradation efficiency of 100% was observed at 0.28 %mol of dopant during the synthesis. Photocatalytic oxidation efficiency increases as the concentration of TiO₂ was increased up to 0.28 %mol that was able to degrade 100% of 2-chlorophenol at 240 minutes. With the increasing amount of TiO₂, more electron and hole pairs are available, so the reaction rate increases. On the other hand, increasing the amount of TiO₂ to 0.35 %mol, the performance of the oxidation process was decreased because the concentration of cerium

dopant in TiO₂ is high. The finding is supported by Yamaji et al. (2012) who explained the performance of the oxidation process decreased because the concentration of cerium dopant by UV radiation cannot penetrate perfectly into the solution in the presence of cerium and the performance of the photocatalytic activity was decreased (Yamaji et al., 2012).

The scanning electron micrographs of sample of TiO₂-doped with 0.28 %mol of cerium calcined at 600 °C are shown in Figure 4.1 and Figure 4.2, respectively. All of particles have nanogranular and rough surface with diameters of 10 – 50 μm. The SEM are conformity from the study of Lenka Matějová et al. (2013) who used cerium ratio doped TiO₂ at 0.28%mol to explain these observations indicate that cerium in Ce-doped TiO₂ photocatalysts is probably present as the ceria amorphous phase and the titania crystallite-size depends on the cerium loading (Lenka Matějová et al., 2013).

4.4.2 Effect of calcination temperature

The effect of calcination temperature is an important parameter. This part aimed to study the effect of calcination temperature on TiO₂ photocatalytic property. It was measured by photocatalytically degrading 2-chlorophenol model compound. And it was calcined at 200, 300, 400, 500 and 600 °C, respectively. The degradation efficiency values for the photocatalysts calcined at different temperatures are shown in Figure 4.8. In this part, it represents the calcination temperature at 200 °C for 240 minutes which, can remove only 53% of 2-chlorophenol. While increasing the calcination temperature further to 300 °C, that the amount of 2-chlorophenol decreases. It also explained that increases the removal efficiency. On the other hand, the calcination temperature at 500 and 600 °C, the degradation reached 96% and 100% of 2-chlorophenol for 240 minutes s, respectively.

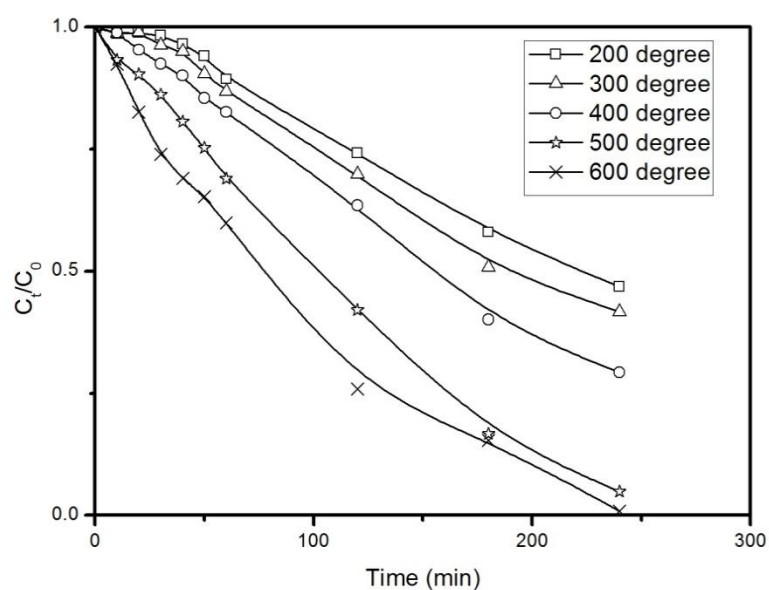


Figure 4.8 Effect of calcination temperature on the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination; experimental conditions: initial pH 5.5, 20 ppm 2-chlorophenol, 3g/L TiO₂ and 0.1 v/v of nitric acid

The performance was highest at 600 °C. Because, high calcination temperature is known to increase the crystallinity of TiO₂, increasing the photocatalytic activity of the titania by removing the bulk defect sites that could promote the electron-hole pair recombination. However, higher temperature of calcination will promote aggregation of particles or sintering effect which then increases the particle size of the photocatalyst (Chen et al. 2009). The initial decreased of photocatalytic activity when the calcination temperature was decreased from 600 °C to 200 °C could be due to the decreased in the calcination temperature as increasing in the amount of bulk defect sites and also decreasing in the crystallinity of the TiO₂. This would increase the rate of electron-hole pair recombination, and thus, decreased the photocatalytic activity of the TiO₂ (Hung, 2009; Nikolić et al., 2011; Yamaji et al., 2012). The XRD patterns observed high intensity peak formations and crystal growth after calcined of synthesized TiO₂. While increasing the calcined temperature, the intensity peak and crystal growth also increases, it also explained that increases the removal efficiency.

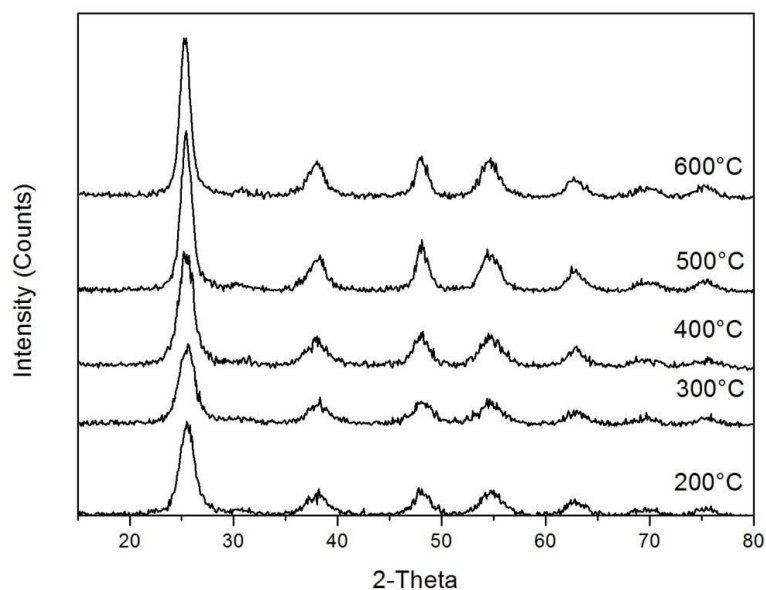


Figure 4.9 XRD spectra of synthesized TiO₂ catalyst calcined at various calcination temperatures

Figure 4.9 shows the phase of the synthesized TiO₂ at different calcinations temperature. There is a high transformation from amorphous to crystal phase TiO₂ as calcination temperature was increased. The XRD patterns represent only the principal crystal phase of anatase. Rutile was not observed in the catalysts indicating that the synthesized TiO₂ were pure anatase and no rutile phase formed. The advantages of anatase are the most photoactive and are the easiest to produce. Anatase is better than rutile because the conduction band of anatase is more favorable for photoexcited electrons reaction. Moreover, at the surface of anatase phase titania, peroxide groups can become stable, but not in rutile phase titania (Zhao and Yang 2003).

These experiments are supported by the results of Sikong et al. (2008) who explain about SiO₂-doped TiO₂ and used calcinations temperature at various temperatures (300-700°C). The SiO₂-doped TiO₂ powder showed a phase transformation from amorphous to anatase phase at 300-600°C. But the rutile phase only appeared when the photocatalyst was calcined at 700°C (Sikong, et al., 2008). Park et al. (2009) also investigated the effects of calcination temperature on carbon self-doped TiO₂ and used calcination temperature at 200-500°C. Consistent with the current study, they also found increased crystallinity with increasing calcination temperature. Their XRD peaks only revealed anatase phase of TiO₂

for samples calcined at 200-400°C. However, rutile phase TiO₂ already appeared for samples calcined at 500°C, which was different from this current study (Park, et al., 2009).

4.5 Control parameters

This part aimed to study the effect of removal of 2-chlorophenol by different processes. The removal efficiency of 2-chlorophenol was observed through the synthesized Ce-doped TiO₂ without blue LED light and the synthesized Ce-doped TiO₂ using blue LED light. However, both of them, the removal efficiency of 2-chlorophenol were degraded very low. Control parameters on the photocatalytic degradation of 2-chlorophenol is presented in Figure 4.10.

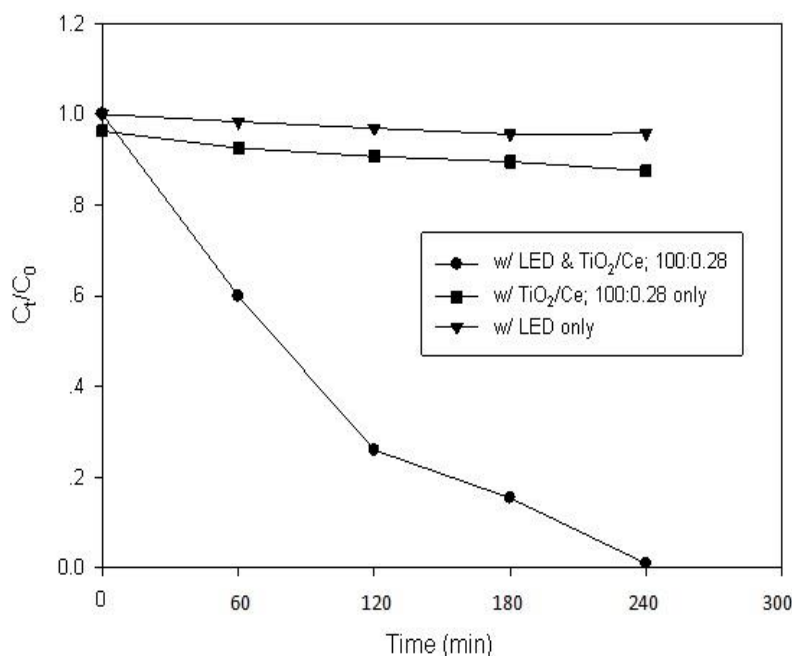


Figure 4.10 Control parameters on the photocatalytic degradation of 2-chlorophenol under blue light illumination; experimental conditions: initial pH 5.5, 20 ppm 2-chlorophenol, 3g/L TiO₂ and 0.1 v/v of nitric acid

The performance in 2-chlorophenol removal could be arrayed in order of synthesized Ce-doped TiO₂ using blue LED light > synthesized Ce-doped TiO₂ without blue LED light > The blue LED light only with the efficiencies of 99, 9 and 4% respectively. However, percentage removal is significant achieved when the solution is applied with the synthesized TiO₂ and illuminated with blue light. 100% 2-chlorophenol removal was observed at 240 minutes of irradiation. This suggests that the photocatalysis indeed happened and caused the removal of 2-chlorophenol from the solution.

4.6 Effect of operating parameters

4.6.1 Effect of initial pH

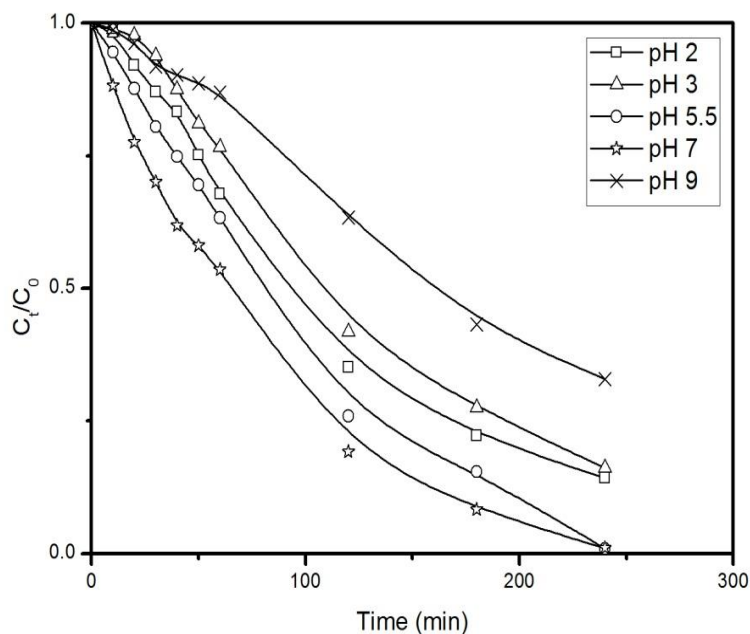


Figure 4.11 Effect initial pH on the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination; experimental conditions: 20 ppm 2-chlorophenol, 3g/L TiO₂

Initial pH is an important parameter that affects the rate of photocatalysis because it affects the adsorption of the substrate on the surface of TiO₂. Improving the adsorption of the pollutant can result to an increase in the photocatalytic activity (Kim, et al. 2008). Initial pH changed the surface charge of TiO₂ particles and shifted the potentials of catalytic reactions (Chen et al., 2012; Li et al., 2015b).

This part aimed to characterize the photocatalytic activity of synthetic TiO₂ under different pH under blue light irradiation. The effect of initial pH in the solution is shown in Figure 4.11. The performance in 2-chlorophenol removal could be arrayed in order of initial pH 7 > initial pH 5.5 > initial pH 2 > initial pH 3 > initial pH 9 with the efficiencies of 99, 98, 85, 83 and 67%, respectively. The highest % 2-chlorophenol degradation observed at pH 7 and pH 5.5, the degradation observed 100% and 99% respectively. However, at low pH 2 and 3, the degradation was reduced to 85 and 83 % respectively. On the other hand, increasing the pH of the solution to 9 the result was decreased to 67 % degradation.

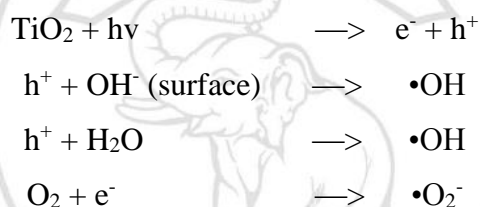
The effects of pH can be explained by part of the point of zero charge (pzc) or surface charge. The studies of 2-chlorophenol degradation using Ce-doped TiO₂ revealed that for TiO₂ catalyst with a p_{H_{pzc}} of 2.83 and operated condition on initial pH of 5 and 7, the degradation rate increases when increasing the initial pH up to 7, but decreasing significantly at a pH more than 8.53, which is a pK_a of 2-chlorophenol. Even if, the pK_a of 2-chlorophenol onto TiO₂ surface is more than 8.53 causes 2-chlorophenol ions transform to 2-chlorophenol anion. Then 2-chlorophenol anion becomes a negative charge at alkaline condition and the oxidation process was slows down. That exhibit was some studies reported that at alkaline condition, which have chlorinated organic compounds hydrolyze. Thus, to minimize hydrolysis of the organic compounds, the working pH of Ce-doped TiO₂ catalyst during the oxidation process should be in acidic condition or standard condition. So the condition of TiO₂/Ce 100:0.28 %mol catalyst was in acidic condition more than pure TiO₂ catalyst, which have advantage was the solution have not chlorinated organic compounds hydrolyzed that make removal effective of 2-chlorophenol decrease. According to the details of the point of zero charge (pzc), this can suggests that the charge of the surface of TiO₂ can be changed by adjusting the pH. The surface of TiO₂ is positively charged at acedic condition while it is negatively charged at alkaline condition and the negatively charged substrates have better adsorption in low pH. The formation of these radicals is more efficient at lower pH or acidic conditions (Reymond and Kolenda, 1999; Lu et. al., 1993). The experiment comfimity with Tolosa, et al., (2011a) used modified TiO₂ with p_{H_{pzc}} of 3.39 suggested that because of the negative charge at the photocatalyst surface at pH conditions higher than p_{H_{pzc}} the adsorption reaction slows down with the chance of forming some intermediates (Tolosa, et al., 2011a).

4.6.2 Effect of photocatalyst dosage

As shown in Figure 4.12, the concentration of the catalyst that should be considered in the photocatalytic process were ranging from 1 g/L to 5 g/L and were added to the 2-chlorophenol solution. The degradation rate of 2-chlorophenol using 1 g/L photocatalyst dosage at 0 – 60 minutes was observed the amount of 2-chlorophenol rapidly decreases until it was removed 100% at 240 minutes after irradiation. However, 5 g/L photocatalyst dosage, the removal efficiency is very low at 0 – 60 minutes. The performance in 2-chlorophenol removal could be arrayed in order 3 g/L > 4 g/L > 2 g/L > 5 g/L > 1 g/L with the efficiencies of 98, 96, 85, 69 and 66%, respectively. The increased in photocatalyst dosage

from 1 g/L to 3 g/L as increasing the number of active sites available for surface reaction. This experiment was supported by Wang et al., (2012) they explained that the amount of dosage increases with increasing in the surface area for the photocatalysis and the number of active sites. In addition to, the amount of hydroxyl radicals can increase cause increasing in the degradation rate (Wang et al., 2012). Thus, the degradation efficiency increases with increasing photocatalyst dosage.

The h^+ of TiO_2 could pull an electron from OH^- or water molecule to form $\bullet OH$. The e^- reacts with oxygen molecule to form super oxide anion ($\bullet O_2^-$). The structure of organic pollutants are separated and rearranged by $\bullet O_2^-$ powerful oxidizing agents. Then, The structure of organic pollutants transform into CO_2 and H_2O . The photocatalysis of electron and hole pairs can recombine as e^- returns to its original state. Therefore, it should have electron acceptor, for example O_2 to block the recombination. Thus, the radicals of $\bullet OH$ and $\bullet O_2^-$ increase cause increasing the performance of the photocatalytic activity.



The highest % degradation of 2-chlorophenol was found at a photocatalyst dosage of 3 g/L for 240 minutes. However, the photocatalyst activity decreases with increasing dosage from 3 g/L to 5 g/L. This can be explained by the TiO_2 particles near the light source that blocked the light for the other particles thus, decreasing the photocatalytic activity. This can be caused by ‘shielding effect’ in which the suspended TiO_2 near the light source blocks light for the remaining TiO_2 . This results to the reduction of light penetration, and thus, the formation of the hydroxyl radicals (Kiriakidou et al. 1999). Furthermore, an increase in photocatalyst dosage above an optimal amount causes a loss of surface area. Because of, agglomeration and sedimentation decrease the available photocatalyst surface for photon absorption resulting to decreasing in degradation (Yang, et al., 2008).

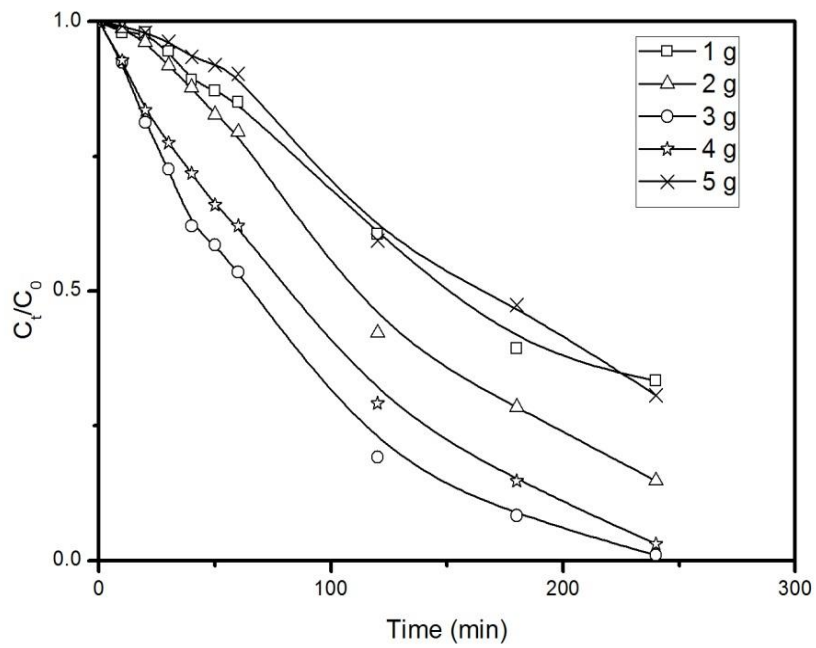


Figure 4.12 Effect photocatalyst dosage on the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination; experimental conditions: 20 ppm 2-chlorophenol, 3g/L TiO₂, initial pH at 7

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4.6.3 Effect of initial 2-chlorophenol concentration

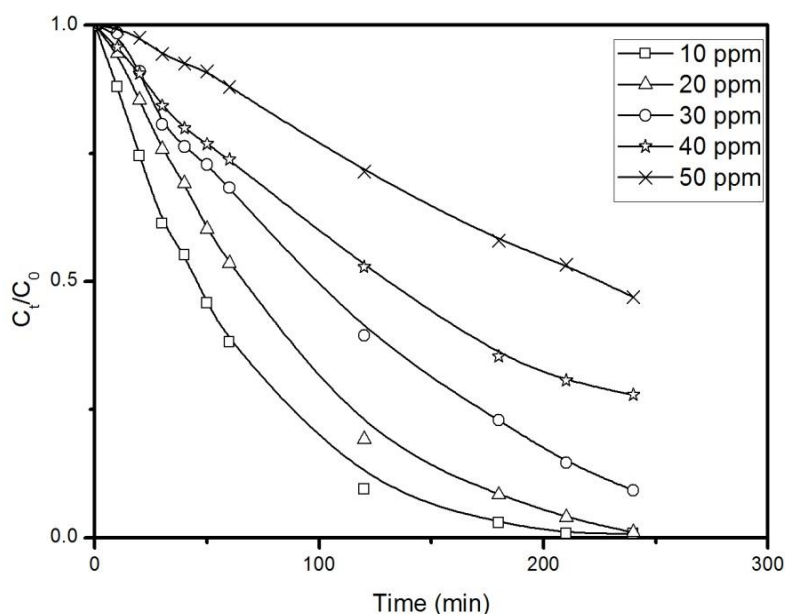


Figure 4.13 Effect of Initial 2-chlorophenol concentration on the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂ under blue light illumination; experimental conditions: 20 ppm 2-chlorophenol, 3g/L TiO₂, initial pH at 7

The effect of initial concentration on the photocatalytic degradation of 2-chlorophenol is shown in Figure 4.13. The performance in 2-chlorophenol removal could be arrayed in order 10 ppm > 20 ppm > 30 ppm > 40 ppm > 50 ppm with the efficiencies of 99, 98, 90, 72 and 53%, respectively. At 240 minutes reaction time, the lowest % 2-chlorophenol degradation was observed to be 53% at an initial concentration of 50 ppm, which is highest initial concentration used in this study. The experiment was supported by Borji et al., (2014). The initial 2-chlorophenol concentration increases, with increasing the amount of the adsorbed reactants and intermediates on the surface of the photocatalys. This would reduce the number of active sites for the generation of the hydroxyl radicals, which would result to a reduction of the photocatalytic activity of the TiO₂ (Borji et al., 2014). The % degradation increases from 72% to 100% when the initial concentration was lowered from 40 ppm to 20 ppm, respectively. The highest degradation rate was observed at the lowest initial concentration of 10 ppm, which degraded 100% of 2-chlorophenol at 240 minutes reaction time. The effect of initial 2-chlorophenol concentration on photocatalytic

degradation is shown in Figure 4.13. Table 4.5 lists the apparent first-order rate constant and it also can estimate half-lives $t_{1/2}$ and $t_{1/2}^*$ on the initial concentration of 2-chlorophenol at different initial concentrations.

Table 4.5 Apparent first-order rate constants K_{obs} , $t_{1/2}$ and $t_{1/2}^*$ of the photodegradation of 2-chlorophenol at different initial concentrations

Initial concentration (ppm)	C_0 (mol)	K_{obs}	$t_{1/2}$	$t_{1/2}^*$
10	0.08	1.3521	0.72	0.51
20	0.16	0.9170	1.18	0.89
30	0.23	0.5866	1.65	1.26
40	0.31	0.3329	2.26	1.63
50	0.39	0.1855	3.89	2.00

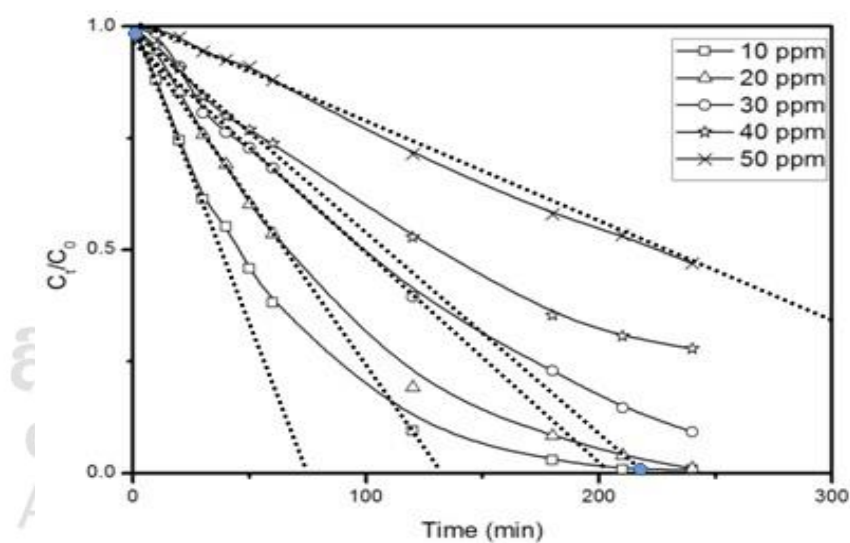


Figure 4.14 Effect of the initial 2-chlorophenol concentration on photocatalytic degradation

4.7 Kinetic model

The kinetics of 2-chlorophenol oxidation by photocatalytic oxidation using TiO_2 , this is important to eliminate the competitive reaction from several intermediates being formed from 2-chlorophenol oxidation (Lu et al., 1993). This study decided obvious on the

linearized plot of $-\ln C/C_0$ versus irradiation time to determine the oxidation rate of 2-chlorophenol is shown in Figure 4.15. The y-intercept and slope which represent “ $1/kr$ ” and “ $1/krK$ ” were summarized in Table 4.6. The degradation rates of 10 and 20 ppm 2-chlorophenol under blue light radiation using TiO_2/Ce . Both of concentrations were completely removed in 200 minutes after irradiation.

Higher r^2 values for the first graph suggest that the pseudo-first-order reaction kinetics can better describe the photocatalytic degradation process. It was found that the degradation data in Table 4.6 at the initial stage of 240 minutes. It can be obviously explained by pseudo-1st order reaction.

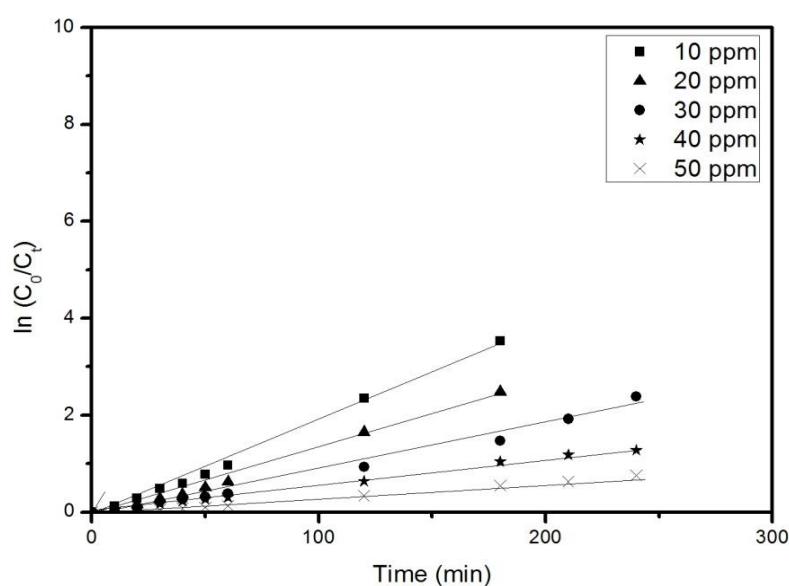


Figure 4.15 Linearized pseudo-first order kinetics plot for the photocatalytic degradation at different concentration of 2-chlorophenol using TiO_2/Ce

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Table 4.6 Apparent first-order rate constant and correlation coefficient on the photocatalytic oxidation of 2- chlorophenol at different initial concentration

Initial 2-CP Concentration (ppm)	K _{obs}	1/K _{obs}	Correlation coefficient,r ²	
			1 st order	2 nd order
10	1.3521	0.73959	0.9775	0.6211
20	0.9170	1.09027	0.9876	0.7731
30	0.5866	1.70473	0.9792	0.8053
40	0.3329	3.00390	0.9958	0.9765
50	0.1855	5.39083	0.9691	0.9189

The integrated form of equation (eq.4 - 4) is

$$t = \frac{1}{k_r K} \ln \left(\frac{C}{C_0} \right) + \frac{1}{k_r} (C_0 - C) \quad (\text{eq.4 - 4})$$

Where; C₀ is the initial concentration of 2-chlorophenol. The following equation indicates that a plot of t_{1/2}* vs. the initial concentration should be linear:

$$t_{1/2} * = \frac{0.5C_0}{k_r} + \frac{\ln 2}{k_r K} \quad (\text{eq.4 - 5})$$

Plotting between “t_{1/2}*” and initial concentration of organic pollutant should be a linear line as in the following Equation (eq.4-4). By substituting k_r = 1.75×10⁻³ mM/min and K is 45.71 mM⁻¹ into equation (eq.4 - 5), the estimate half-life are obtained and listed in Table 4.5. Figure 4.16 shows the dependence of t_{1/2} and t_{1/2}* on the initial concentration of 2-chlorophenol. The results revealed values between t_{1/2} and t_{1/2}*. Both of them are very different. The value of t_{1/2}* increase with increasing initial 2-chlorophenol concentration (40 – 50 ppm). However, the value of t_{1/2} is practically steady. The difference between t_{1/2} and t_{1/2}* becomes larger with increasing initial concentration. It was suggest that the reaction byproducts may compete with 2-chlorophenol so as to interruption the half-life of these reactions (Lu et al., 1993).

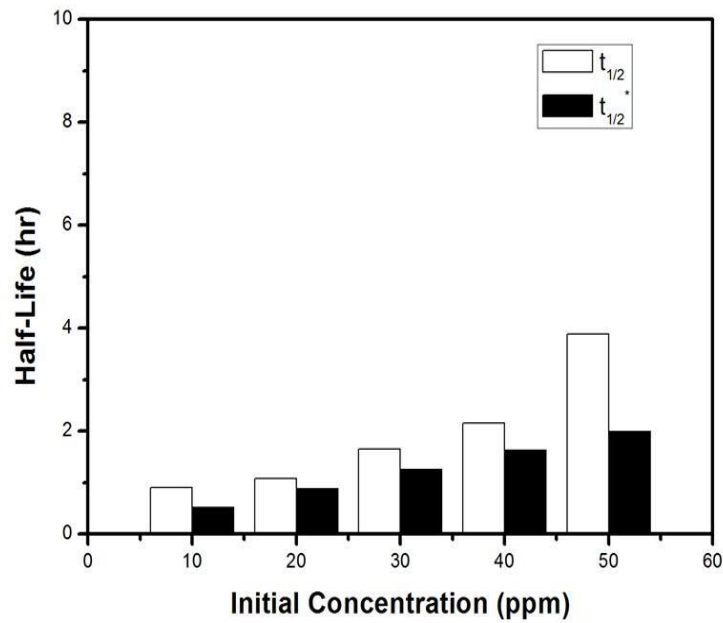


Figure 4.16 Dependence of observed and estimated half-life on the initial, concentration of 2-chlorophenol

4.7.1 Langmuir-Hinshelwood model

The kinetic reaction follows Langmuir-Hinshelwood expression for analysis of heterogeneous photocatalytic oxidation (Lu et al., 1993; Ku et al., 1996). Assuming no competition on the reaction by-products, the simplest form of the oxidation rate for the Langmuir-Hinshelwood model is given by

$$r = \frac{k_r K C_t}{1 + K C_t} \quad (eq. 4 - 6)$$

Where: r is the rate of degradation or oxidation

k_r is the specific rate constant

K is the equilibrium adsorption constant for 2-chlorophenol

C_t is the concentration of the 2-chlorophenol

This equation is a linear line when plotted between inverse initial rate and inverse concentration was shown in Equation (4-7):

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r K C} \quad (eq. 4 - 7)$$

Slope ($1/k_r K$) and interception ($1/k_r$) are positive. The constants, k_r and K , can be obtained from the intercept and slope of the line formed when “ $1/r$ ” is plotted against “ $1/C$ ”.

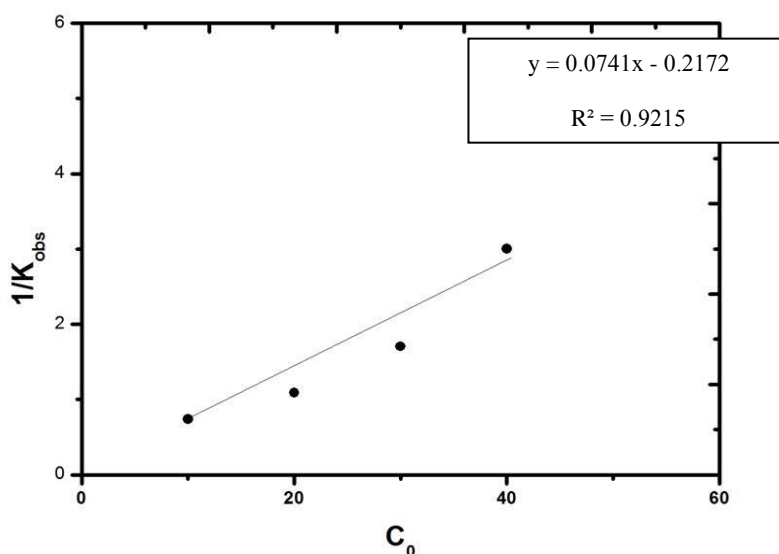


Figure 4.17 Linearized reciprocal kinetic plot of K_{obs}^{-1} as a function of initial concentration on the photocatalytic oxidation of 2-chlorophenol

The estimating of the linear regression between the two variables, the inverse K_{obs} , K_{obs}^{-1} as a function of the reciprocal of initial concentration C_0^{-1} and finding the coefficient, r^2 . Linearized kinetic plot and the relationship between these two variables are using data from Table 4.7. The linearized kinetic plot for the photocatalytic degradation of phenol by $CuSO_4$ -doped TiO_2 is shown in Fig 4.17. The calculated r^2 value of 0.9215 suggests that the Langmuir-Hinshelwood kinetics is a good model describing the specific photocatalysis process. That Calculated values of Correlation coefficient (r^2), specific rate constant (k_r) and equilibrium adsorption constant (K) were 0.9215, $3.13 \times 10^{-3} \text{ mM}\cdot\text{min}^{-1}$ and 16.92 mM^{-1} respectively.

Table 4.7 Calculated values of specific rate constant, equilibrium adsorption constant and correlation coefficient of 2-chlorophenol

k_r ($\times 10^{-3} \text{ mM}\cdot\text{min}^{-1}$)	K (mM^{-1})	Correlation coefficient, r^2
3.13	16.92	0.9215

4.8 Cost effective

4.8.1 Calculation electricity cost for synthesized photocatalyst

The purpose of this study was to estimate the cost of experiment. The study summarized cost of chemicals for synthesized TiO_2 , cost of electricity for synthesized catalysts and electricity cost for operating experiment. All of costs are based on the prices during experimental period. The values of equipments were derived from the data giving the best results of this experiment.

The basic cost assessments for synthesis TiO_2 catalysts to degradation 2-chlorophenol as shown in Table 4.8 were calculated by the cost of electricity in Taiwan (1 kW = 2.10 BAHT).

Table 4.8 Basic cost assessment for synthesis TiO_2 catalysts to degradation 2-chlorophenol

Chemicals	Quantity	Price (BAHT)
Titanium(iv) n-butoxide	250 mL	1600
Cerium	100 g	3600
Nitric acid	2.5 L	2150
Ethyl Alcohol	2.5 L	2500

The cost effective for synthesized TiO_2 was calculated by using 10 mL Titanium(iv) n-butoxid, Ethanol 40 mL and Nitric acid 0.5 mL for each batches. The costs of chemicals are 64, 40 and 0.43 baht, respectively. The costs of chemicals are following from amount of each chemicals. Thus, the total expenses is 104.43 baht/10g.

The cost assessment for a range of cerium dopant is shown in Table 4.9. This experiment used 0.28% mol TiO_2/Ce ratio. For synthesized 0.28% mol TiO_2/Ce . Calculation of cost effective was used by Titanium(iv) n-butoxide 10 mL, Ethanol 40 mL, Nitric acid 0.5 mL and 0.28% mol cerium for each batch.

Table 4.9 The cost assessment for cerium doped TiO₂ catalyst

Cerium ratio	Weight (g)	Price (BAHT)
0.07 %mol	0.01	0.36
0.14 %mol	0.02	0.72
0.21 %mol	0.03	1.08
0.28 %mol	0.04	1.44
0.35 %mol	0.05	1.80

This experiment was focused on TiO₂ with 0.28 %mol cerium due to this ratio is the highest performance degradation. The price of synthesized TiO₂ included with 0.28 %mol cerium for 1 gram is 1.0443 baht. According to the study TiO₂ with dopants can reused perfectly as 10 times (Andrew et al., 2006).

4.8.2 Calculation electricity cost to synthesized TiO₂ catalysts

Calculation electricity cost assessment for synthesis TiO₂ catalysts was expressed in the following equations;

$$Unit = \frac{(Power (W) \times time (hr))}{1000} \quad (\text{eq.4 - 8})$$

Table 4.10 The power and electricity of equipment for synthesis TiO₂ catalysts

Equipment	Power (W)	Operating time(hr)	Unit (kW)	Sample Contain (g)
Magnetic stirrer	73	0.5	0.0365	10
Furnace	2310	1	2.31	90
Drying Oven	880	40	35.2	240
Autoclave	2300	0.5	1.15	50

Table 4.10 shows the power (W), operating time (hr) and electricity (kW) of equipment for synthesized TiO₂ catalysts. The electricity of magnetic stirrer, furnace, drying oven and autoclave were calculated by equal. (4-8) and divided by amount of sample that the equipment can contained. The electricity (kW) of equipments for 1 gram are 0.0365, 2.31, 35.2 and 1.15 kW respectively. The cost effective was calculated by electricity (kW) of all equipments. The cost effective divided by sample contain and the results of all

equipments are 0.0076, 0.054, 0.31 and 0.023, respectively. The total cost for 1 gram is 0.3946 baht.

4.8.3 Calculation of electricity costs for operating experiment

Table 4.11 the intensity and power of equipment for operating experiment

Equipment	Power (W)	Operating time (hr)	Unit(kW)
Magnetic stirrer	73	4	0.292
Blue LED light	16.82	4	0.06728

In the part of operating, 2-chlorophenol was degraded by reactor (Magnetic stirrer, Blue LED light) as 240 minutes. As shown in Table 4.11, shows the summarized the Power (W), operating time (hr) and electricity (kW) of equipment for removed 2-chlorophenol. The power of reactor both of them can be calculated were calculated by equal (4-7) and divided by amount of sample that the equipment can contained as 0.3592 kW that is equal to 0.75432 baht. Thus, all of the cost assessments of synthesized TiO₂ catalysts to remove 2-chlorophenol are 3.898baht/L or 1,068 baht/m³.

4.9. Comparison the performance of degradation in 2-chlorophenol between Ce-doped TiO₂, CuSO₄ and V-doped TiO₂

This part aimed to compare the effects of photodegradation of 2-chlorophenol and to characterize the photocatalysis of synthesized TiO₂ between two experiments (Ce-doped TiO₂ using Hydrothermal method and CuSO₄, V-doped TiO₂ using Sol-gel method). In both of experiments, titanium (iv) n-butoxide (99%) was used as the titanium precursor. 2-chlorophenol (C₆H₅OCl) was used as the surrogate organic pollutant on photocatalytic experiment. The photocatalytic oxidation activity was investigated were focused after 30 minutes of dark adsorption to allow the 2-chlorophenol equilibrated among solid surface and aqueous phase. For the study on the effect of synthesis parameters, the following procedure has been done: 100 mL of 20 ppm 2-chlorophenol solution was mixed with the photocatalyst with the dosage of 3.0 g/L operating temperature of 40 °C, light intensity of 16.85 mW/cm². The best condition and characteristic of synthesized TiO₂ are shown in Table 4.12.

Table 4.12 the best condition and characterize of synthesized TiO₂

Condition and the best parameter	Performance of catalysts in 2-chlorophenol		
	Ce-doped TiO ₂	CuSO ₄ -doped TiO ₂	V-doped TiO ₂
Catalyst	Ce-doped TiO ₂	CuSO ₄ -doped TiO ₂	V-doped TiO ₂
Synthesis Method	Hydrothermal	Sol-gel	Sol-gel
Operating time	240 minutes	360 minutes	420 minutes
Amount of dopant	0.28%mol Cerium	0.21 %mol CuSO ₄	0.07 %mol Vanadium
Amount of acid	0.10	0.10	0.10
Calcination temperature	600 °C	300 °C	300 °C
Calcined temperature for anatase transform Rutile	>600 °C	> 400 °C	-
Initial pH	5.5 and 7	5.5	5.5
pH _{pzc}	2.83	3.84	-
Catalyst Dosage	3 g/L	2 and 3 g/L	3 g/L
Initial 2-CP Concentration	10 ppm	10 ppm	-
Crystallite Size	9.93 – 11.66 nm	9.77 – 11.98	-
pH _{pzc}	2.83	3.84	-
Correlation coefficient (R ²)	0.9215	0.9563	-
specific rate constant (k _r)	3.13 x 10 ⁻³ mM.min ⁻¹	2.47 x 10 ⁻³ mM.min ⁻¹	-
equilibrium adsorption constant (K)	16.92 mM ⁻¹	17.42 mM ⁻¹	-
Cost	1068 baht/m ³	1643 baht/m ³	

4.9.1. Comparison of synthesis method

The Sol-gel and Hydrothermal methods were used to synthesize photocatalyst. Sol-gel is a successful method that involved in synthesis of nanoparticles, This technique does not require complicated instruments and provides simple and easy means for preparing nano-size particles. Hydrothermal method was applied by autoclaving the hydrolyzed mixture before dehydration and calcination to modify TiO₂ structure rather than sol-gel method. Because, the calcination process frequently lead to serious particle agglomeration, small surface area and easily to transform anatase to rutile phase, which all decrease the photocatalytic activity of titanium.

4.9.2. Comparison of amount of dopant

The optimum amount of Ce used for Ce-doped TiO₂ in hydrothermal process was 0.28%mol, which can remove 100% of 2-CP at 240 min. However, the CuSO₄-doped TiO₂ and V-doped TiO₂ was used sol-gel method. % 2-chlorophenol removed were about 100% for 0.21 %mol CuSO₄ at 360 minutes and 0.07 %mol Vanadium at 420 minutes.

Both of 0.28%mol Ce-doped TiO₂ and 0.21%mol CuSO₄-doped TiO₂ can decrease amount of 2-chlorophenol rapidly. However, the removal efficiencies of 0.07%mol of Ce-doped TiO₂ photocatalyst dosage and CuSO₄-doped TiO₂ were low. Moreover, as 0.07%mol vanadium-doped TiO₂ can decrease amount of 2-chlorophenol rapidly. The reasons of the result are explained by the amount of Ce-doped TiO₂ and CuSO₄-doped TiO₂ increase with increasing surface area that causes high performance. But, increasing amount of V-doped TiO₂, anatase phase was decreased and transforms to rutile phase.

4.9.3. Comparison of calcination temperature

The effect of calcinations temperature is an important factor in the performance of a sol-gel and hydrothermal method, because they influence to form crystal structure, particle size and surface area. The highest performance of calcinations temperature for Ce-doped TiO₂ using hydrothermal was 600 °C. Because, high calcination temperature is known to increase the crystallinity of TiO₂, increasing the photocatalytic activity of the titania by removing the bulk defect sites that could promote the electron-hole pair recombination. However, CuSO₄ and V-doped TiO₂ using Sol-gel method, the performances were highest at 300 °C. Because, the calcination temperature more than 300 °C causes the major

crystallize phase was transformed (anatase to rutile). Therefore, the anatase to rutile transformation takes place in this case at temperature higher than 500°C.

4.9.4. Comparison of initial pH

The best performance of all of experiments is initial pH of 5.5. On the other hand, increasing the pH of the solution to 9 the photocatalyst performance was decreased. The pKa of 2-chlorophenol was investigated at 8.53. Both of experiments, the performance decreases significantly at a pH more than 8.53 (pH 9). That can be explained the pKa of 2-chlorophenol onto TiO₂ surface is more than 8.53 causes 2-chlorophenol ions transform to 2-chlorophenol anion. Then 2-chlorophenol anion becomes a negative charge at alkaline condition and the oxidation process was slows down. The point of zero charge (pzc). The studies of 2-chlorophenol degradation using Ce-doped TiO₂ and CuSO₄-doped TiO₂ revealed that for TiO₂ catalyst with a pH_{pzc} of 2.83 and 3.84, respectively.

4.9.5. Comparison of catalyst dosage

Comparison of catalyst dosage between Ce-doped TiO₂, CuSO₄-doped TiO₂ and V-doped TiO₂ using different synthesized method revealed the highest % degradation of 2-chlorophenol was found at a photocatalyst dosage of 3 g/L for all of experiments. The percent degradation efficiencies of Ce-doped TiO₂, CuSO₄-doped TiO₂ and V-doped TiO₂ were 98% at 240 minutes, 99% at 360 minutes and 99 % at 420 minutes, respectively. The reason is photocatalyst dosage of experiments increase as increasing the number of active sites available for surface reaction. Moreover, the amount of hydroxyl radicals can increase cause increasing in the degradation rate.

4.9.6. Comparison of initial 2-chlorophenol concentration

The highest performance of initial concentration on the photocatalytic degradation of 2-chlorophenol using Ce-doped TiO₂, CuSO₄-doped TiO₂ and V-doped TiO₂ were 100% at 240 minutes, 99% at 360 minutes and 99 % at 420 minutes, respectively. The lowest % 2-chlorophenol degradation of Ce-doped TiO₂, CuSO₄-doped TiO₂ and V-doped TiO₂ were observed to be 53, 42 and 40% at an initial concentration of 50 ppm. The reason of experiments is the initial 2-chlorophenol concentration increases, with increasing the amount of the adsorbed reactants and intermediates on the surface of the photocatalys. This

would reduce the number of active sites for the generation of the hydroxyl radicals, which would result to a reduction of the photocatalytic activity of the TiO₂.

4.9.7. Comparison of characterized photocatalyst TiO₂

In this study, Ce-doped TiO₂ and CuSO₄-doped TiO₂ were used to compare the characterizing of morphology and structural properties of the synthesized photocatalysts. Both of experiments used scanning electron microscopy (SEM), X-ray diffraction (XRD) and mass titration method. The scanning electron micrographs of both experiments, they illustrate are a lot of shape particles formed from the synthesized TiO₂ catalysts. All of the synthesized TiO₂ samples agglomerate into smaller particles. All of particles have nanogranular and rough surface with diameters of 10 – 50 μm. The both results explained the crystallite-size depends on the cerium loading. The X-ray diffraction (XRD) for both Ce-doped TiO₂ and CuSO₄-doped TiO₂ with different amounts of dopant, the characteristic plane diffraction peak (1 0 1) for anatase phase of TiO₂ were observed. Besides, rutile phase was observed in Ce-doped TiO₂ at calcination temperature more than 600 °C but, the rutile phase of CuSO₄-doped TiO₂ was observed at calcination temperature more than 400 °C.

4.9.8. Comparison of cost effective between Ce-doped TiO₂ and CuSO₄-doped TiO₂

The cost effective of Ce-doped TiO₂ and CuSO₄-doped TiO₂ were estimated by cost of chemicals for synthesized TiO₂, cost of electricity for synthesized catalysts and electricity cost for operating experiment. The cost of Ce-doped TiO₂ with hydrothermal method is 3.898 baht/L or 1,068 baht/m³ and the cost of CuSO₄-doped TiO₂ with Sol-gel method is 4.531 baht/L or 1,643 baht/m³. Thus, the cost experiment of Ce-doped TiO₂ cheaper than CuSO₄-doped TiO₂. Even though, Ce-doped TiO₂ using hydrothermal method that used autoclave for synthesis. In addition to, the performance of Ce-doped TiO₂ is higher than CuSO₄-doped TiO₂. The best result of Ce-doped TiO₂ is 100% degradation in 2-chlorophenol at 4 hours after irradiation. However, the best result of CuSO₄-doped TiO₂ is 100% degradation in 2-chlorophenol at 7 hours after irradiation. Thus, the performance and all of the cost assessments of Ce-doped TiO₂ catalysts is better than CuSO₄-doped TiO₂.