CHAPTER 3

Materials and Methods

3.1 Optimization study of the modified TiO_2 catalyst

All experiments were done at Chia Nan University, Taiwan. The study of oxidation or degradation of the 2-chlorophenol was conducted using doped-titanium dioxide catalysts under visible light. The process flow for the methodology of the whole research is shown in Figure 3.1. The research was done according to the following sequence:

1. Synthesis of modified TiO_2 catalyst
2. 2^k factorial design was used to identify the main effects of this experiment.
3. Optimization study of the modified TiO_2 catalyst.
4. Preparation and optimization of modified TiO_2 catalyst.
    a. Test for the effect of the synthesis parameters of TiO_2 (amount of dopant, amount of acid and calcination temperature) after studying the main effects by 2^k factorial design.
    b. Test for the effect of the operating parameters that affects photocatalytic oxidation performance after studying the main effects by 2^k factorial design. The catalyst using the following conditions,
        - pH (2 – 9)
        - Initial 2-chlorophenol concentration (10 – 50 ppm)
        - Photocatalyst dosage (1.0 – 5.0 g/L)
    c. Analysis of residual chlorophenols concentration was carried out using high performance liquid chromatography (HPLC).
5. Comparison between various doped TiO_2 and control paramaters.

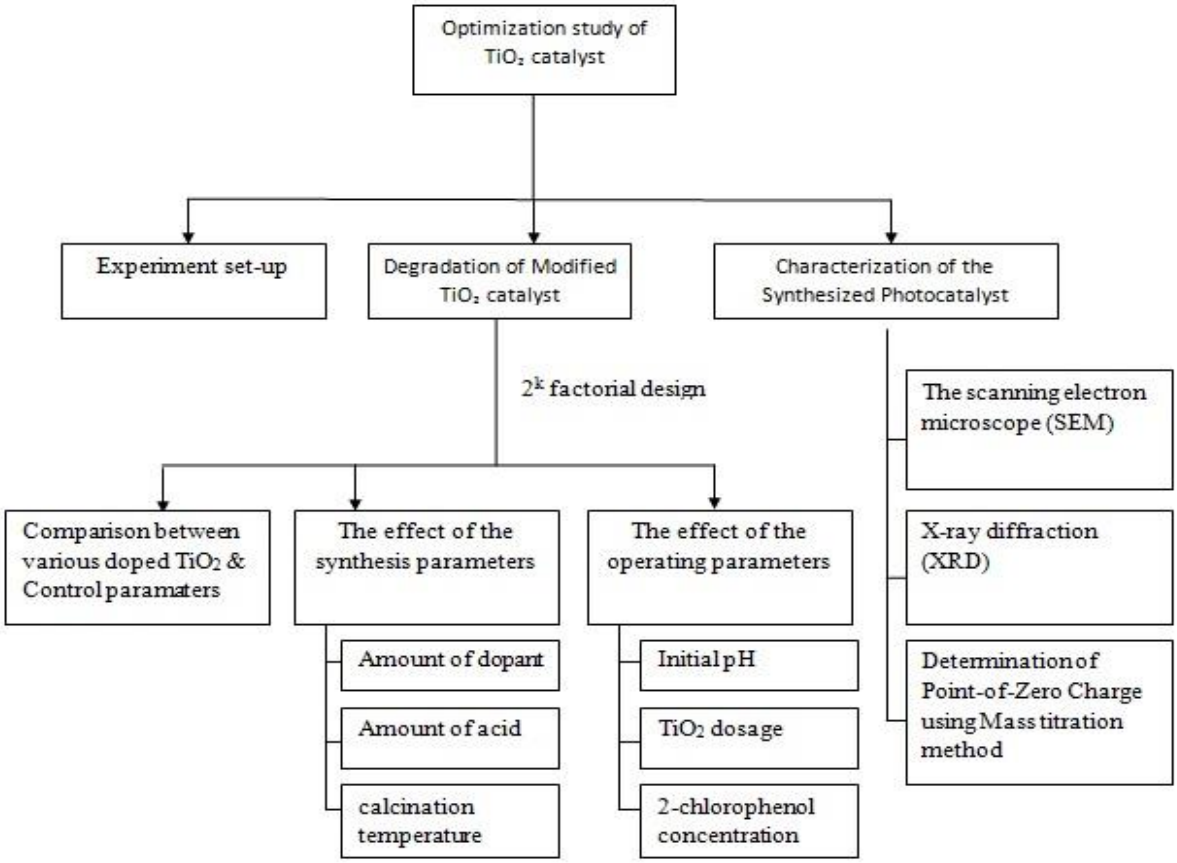

Figure 3.1 Process flow diagram of the methodology for the research study

3.2 Materials and Chemicals

3.2.1 Chemicals

- Titanium (iv) n-butoxide (99%) was used as the titanium precursor.
- Ethyl alcohol was used as a solvent to prepare the TiO_2 solution.
- Nitric acid (HNO_3) was used as the acid catalyst to control hydrolysis rate.
- All chemicals were analytical commercial.
- All reagents were prepared by using the deionized water.
- 2-chlorophenol (C_6H_5OCl) was used as the surrogate organic pollutant on phototocatalytic experiment.
- Cerium (iii) nitrate hexahydrate (99.5%) was used as the dopant for cerium doped TiO_2 (TiO_2/Ce).

3.2.2 Experiment set-up

The reactor system were composed of immobilized photocatalysts on glass tube reactor was sealed with an improvised septum made of polytetrafluoroethylene (PTFE) and parafilm tapes. The glass tubes were housed in a cubic, airtight box with dimensions of 60 cm X 60 cm X 60 cm. Blue lig

ht emitting diode (LED) ($\lambda \approx 440$ to 490 nm) was used as a light source. Temperature and humidity inside the controlled environment were monitored through a thermometer. The position of LED bulbs was upon the immobilized photocatalysts. A schematic diagram of the reactor system is shown in Figure 3.2.

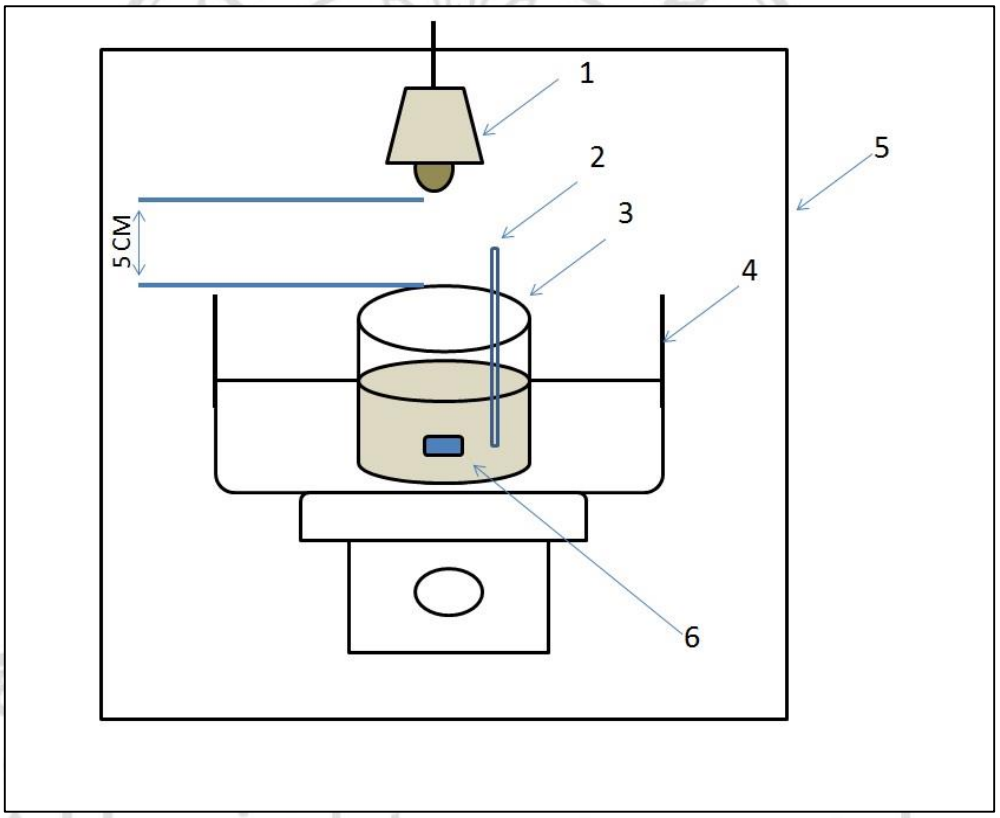

Figure 3.2 Schematic diagram of the photocatalytic reactor

1.	LEDs or UV lamp	2.	Thermometer
3.	Reactor	4.	Water bath
5.	Black box	6.	Magnetic stirrer bar

3.3 Experimental procedure

Experimental works were devided into two parts, which included TiO_2 photocatalyst synthesis and the determination of the degradation TiO_2-dopant. This experimental that used two-factor factorial design to find the main effect. Procedures are shown in Figure 3.3.

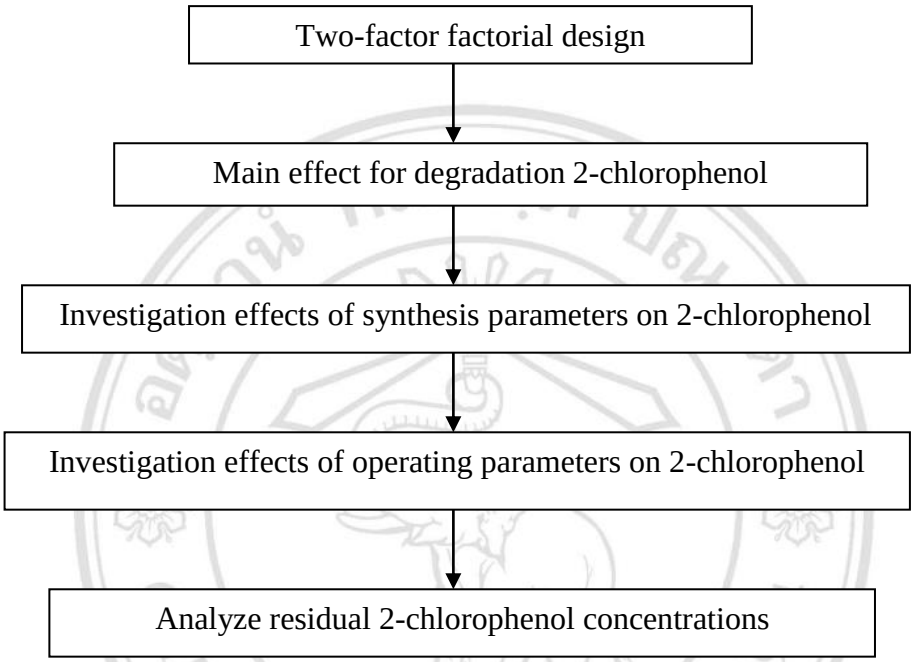

Figure 3.3 Experimental procedures

3.4 Synthesis of Titanium Dioxide

The hydrothermal process was used for the synthesis of the TiO_2 photocatalysts. For the study on the effect of synthesis parameters, 10 mL of the $Ti(OBu)_4$ was added to 40 mL ethanol at a constant stirring rate of 450 rpm. After 5 mins, different amounts of HNO_3 (0.05, 0.10, and 0.15 vol $HNO_3/Ti(OBu)_4$) were then added. After another 10 minutes, different volumes of Cerium (III) nitrate hexahydrate (0, 0.07, 0.14, 0.21, 0.28, and 0.35 %mol) and 5 mL of water were added to the mixture. The mixture was vigorously stirred until a gel was formed. The gel was aged for 24 hours and then was taken into an autoclave machine for hydrothermal process. After that, it was dried in an oven at 105 ^{0}C. The product was pulverized and then calcined at different temperatures (200, 300, 400, 500 and 600 ^{0}C) with a heating rate of 5 ^{0}C / min. In this study, the maximum condition was determined by 2^k factorial design. This part aimed to study the effect of hydrothermal method on the synthetic TiO_2 property. Optimum effect in this hydrothermal section; however, after the

hydrolytic condensation, the hydrolyzed solution was sealed and then autoclaved at 121°C and 103.4 kPa for selected time before placing into the oven to dry at 105°C. A forementioned procedure of TiO_2 is called hydrothermal treatment.

The synthesis of titanium dioxide procedures and Diagram for TiO_2 are illustrated in Figure 3.4 and 3.5, respectively.

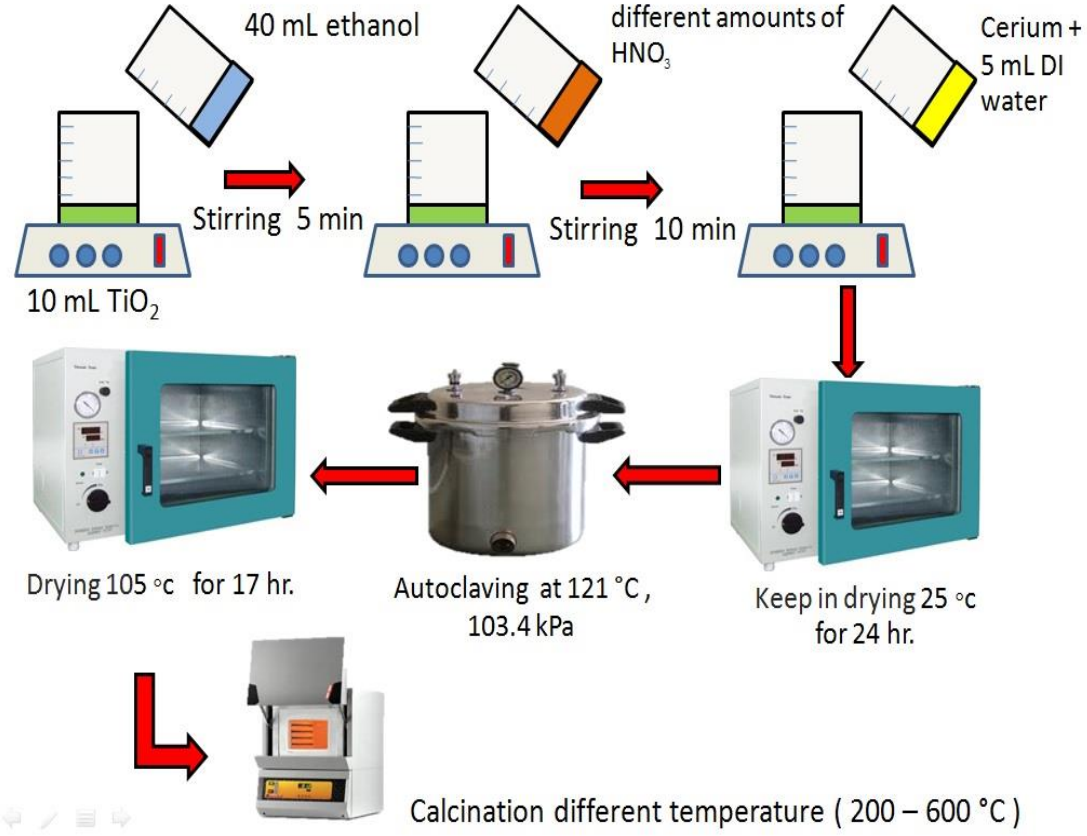

Figure 3.4 Synthesis of titanium dioxide procedures

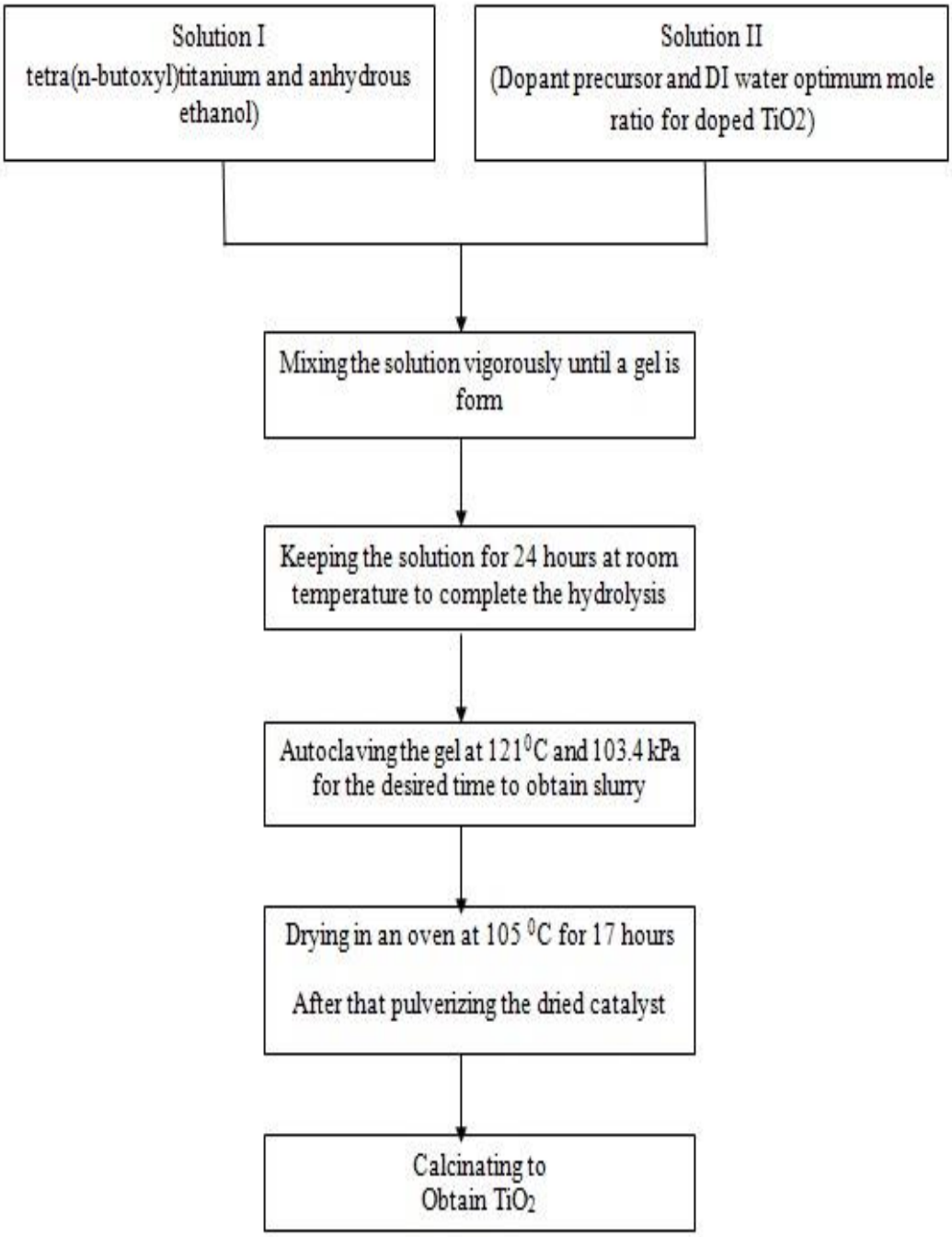

Figure 3.5 Schematic for TiO_2 synthesis by hydrothermal method

3.5 Comparison between various doped TiO_2

The experiment was conducted to find out the efficiency of the hydrothermal process and to compare with that of sol-gel process. It could be arrayed in order by cerium 0.28%mol doped TiO_2 with hydrothermal process, undoped TiO_2 with hydrothermal process, undoped TiO_2 with the sol-gel process and P25 with the sol-gel process to find performance in 2-chlorophenol removal at 7 hours.

3.6 2^k factorial design

The performance of the synthesized modified photocatalyst was compared with a commercial TiO_2 photocatalyst Degussa P-25 in terms of the extent and rate of 2-chlorophenol degradation at optimum operating conditions. Using the optimum conditions for the photocatalytic degradation of chlorophenols, residual chlorophenol concentration was measured at specific time intervals. Results were fitted in a first order rate equation based on the Langmuir-Hinshelwood model. The procedures of this experimental that use two-factor factorial to find the main effect are according to the following sequence;

1. The experiments studied three variables parameters consisting of calcined temperature, amount of cerium and amount of nitric acid. Using 100 mL of 20 ppm initial concentrations of 2-chlorophenol, amount of HNO_3 was 0.10 vol HNO_3 / $Ti(OBu)_4$, operating temperature of 40 °C, light intensity of 16.85 mW/cm^2 are shown in Table 3.1

Table 3.1 Investigated variables for 2-chlorophenol removal

Variables	Levels	
	-1	+1
Calcine Temperature (A)	200 ^{0}C	600 ^{0}C
Amount of Cerium (B)	0.07 %mol	0.35 %mol
Amount of nitric acid (C)	0.05 V/V	0.15 V/V

2. Design of experiment using 2^k factorial design to find the percentage of degradation (%Degradation) following the formula used to calculate the percentage of 2 -chlorophenol. The response values are the percent 2-CP degradation (%Degradation) is shown in equation (eq.3-1).

$$Y = (C_0-C_t)/C_0 \times 100 \qquad \text{(eq.3-1)}$$

When Y is percentage of 2-chlorophenol degradation
C_0 is initial 2-chlorophenol concentration (ppm)
C_t is residual 2-chlorophenol concentration (ppm)

The experiment used two-factor factorial design to find the main effect with every two replicates. Then it was particulary varied the main effect and Pareto chart of the effects for the photocatalytic degradation to find the best conditions which affect degradation of chlorophenol. Design of experiment is shown in Table 3.2.

Table 3.2 Design of static batch experiments generated using 2^k factorial design

Treatment	**Type of catalyst Ratio TiO_2 : Ce (%mol)**	**Amount of Nitric acid (vol HNO_3/vol $Ti(OBu)_4$)**	**Calcination temperature (◦C)**
1	100 : 0.07	0.05	200
2	100 : 0.07	0.05	600
3	100 : 0.07	0.15	200
4	100 : 0.07	0.15	600
5	100 : 0.35	0.05	200
6	100 : 0.35	0.05	600
7	100 : 0.35	0.15	200
8	100 : 0.35	0.15	600

(*Two replicates)

3.7 Photocatalytic activity measurement

The photocatalytic activity of the synthesized photocatalysts was tested using 2 -chlorophenol as the model pollutant. 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. The mixture was adsorbed for 30 minutes, then illuminated with blue LED lamp (λ = 450 nm) for 30 min. 4 -mL of mixture were sampled out every 1 hour. The collected samples were filtered with 0.2 μm syringe filter and then analyzed for 2-chlorophenol using HPLC. The effect of operating parameters on the photocatalytic degradation of 2-chlorophenol was studied by adjusting the parameters mentioned above. The pH was adjusted by adding 0.1 M NaOH or 0.1 M HNO_3 solution. This experiment of the case of photocatalytic oxidation was the focus after 30 minutes of dark adsorption to allow the 2-chlorophenol equilibrated among solid surface and aqueous phase.

3.8 Synthesis parameters in photocatalytic experiments

2^k Factorial Design was used to investigate effects of synthesis parameters and to find the optimum ratio in synthesis parameter part**.** The Experimental ranges for synthesis parameters are summarized in Table 3.3.

Table 3.3 Experimental ranges for synthesis parameters

Synthesis Parameter	Experimental Values
Dopant Amount	0, 0.07, 0.14, 0.21, 0.28, and 0.35 %mol
Acid Amount	0.05, 0.10 and 0.15 vol HNO_3/ $Ti(OBu)_4$
Calcination Temperature	200, 300, 400, 500 and 600 ^{0}C

3.9 Operating parameters in photocatalytic experiments

After studying the effect of synthesized parameters, 2^k Factorial Design was used to find the optimum ratio in operating parameter part. The Experimental ranges for operating parameters are summarized in Table 3.4.

Table 3.4: Experimental values for operating parameters in photodegradation experiments

Operating parameters	**Experimental values**
Initial 2-chlorophenol concentration	10, 20, 30, 40 and 50 ppm
Initial of pH	2, 3, 5.5, 7, 9
Photocatalyst dosage	1.0, 2.0, 3.0, 4.0, 5.0 g/L

3.10 Comparison between various doped TiO_2

The experiment was conducted to find out the efficiency of the hydrothermal process and to compare it with that of sol-gel process and it could be arrayed in order by cerium 0.28%mol doped TiO_2 with hydrothermal process, undoped TiO_2 with hydrothermal process, undoped TiO_2 with the sol-gel process and P25 with the sol-gel process to find performance in 2-chlorophenol removal at 7 hours.

3.11 Control parameters

In this study, the photocatalytic activity of the synthesized ce-doped TiO_2, in this study investigated under the blue light irradiation and without blue light irradiation using operating temperature of 40 °C with light intensity of 16.85mW/cm^2 for 7 hours.

3.12 Analytical methods

The concentration of 2-chlorophenol on the collected samples were determined by High Performance Liquid Chromatography (HPLC). The wavelength used for detection was 280 nm. The mobile phase was acetonitrile and water with a volume-to-volume ratio of 60:40. The temperature of the column was set at 30 ^{0}C and the flow rate was adjusted to 1.0 mL/min. 2 mL of the sample was injected for every reading. The retention time of 2-chlorophenol was observed for approximately 15 minutes.

3.12.1 X-ray diffraction (XRD)

XRD uses single or multiphase specimens comprising a random orientation of small crystallites, each of the order of 1–50μm in diameter. Each crystallite in turn is made up of a regular, ordered array of atoms. An ordered arrangement of atoms (the crystal lattice) contains planes of high atomic density which in turn means planes of high electron density. A monochromatic beam of X-ray photons were scattered by these atomic electrons and if the scattered photons interfere with each other, diffraction maxima may occur. In general, one diffracted line was occured for each unique set of planes in the lattice. A diffraction pattern is typically in the form of a graph of diffraction angle (or interplanar spacing) against diffracted line intensity. The pattern is made up of a series of superimposed diffractograms, one for each unique phase in the specimen.

Crystal structure of the synthetic TiO_2 was characterized by the X-ray diffraction spectroscopy (XRD) (D8 Discovery, Bruker-AXS) with Cu Kα radiation (λ = 0.15406 nm) in a 2θ range of 20-80° and a scanning speed of 3°/min.

3.12.2 The scanning electron microscope (SEM)

The scanning electron microscope (SEM) was used and focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm

to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 1000X to approximately 10,000X, spatial resolution of 10 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure, and crystal orientations.

The SEM column and sample chamber are at a moderate vacuum to allow the electrons to travel freely from the electron beam source to the sample and then to the detectors. High-resolution imaging is done with the chamber at higher vacuum, typically from 10-5 to 10-7 Torr. Imaging of nonconductive, volatile, and vacuum-sensitive samples can be performed at higher pressures.

3.12.3 Point of zero charge (pzc) analysis

Point of zero charge of each as - synthesized TiO_2 was analyzed by using the dynamic light scattering (Malvern ZS90) and used mass titration method to determine the point of zero charge. The mass titration is the one method of determining the point of zero charge (pzc) of TiO_2 catalyst using amounts of the synthesized TiO_2 0.01%, 0.10%, 1%, 5%, 10%, 20%, 30%, and 40% by weight added to DI water and pH of the equilibrated diffusion.