Effect Of Calcination Temperature Of Zinc Oxide Catalyst In Photocatalytic Degradation Of 2,4,6-Trichlorophenols Using UV Light

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***Abstract*—2,4,6-Trichlorophenols (2,4,6-TCP) is one of the chlorophenols compound that have a highest toxicity. It carcinogen to human could cause blood and liver cancer throughout the drinking water and foods. Thus, the photocatalytic degradation of 2,4,6-TCP by using UV light and enhance by using Zinc Oxide are needed. The effect of different concentration of 2,4,6-TCP which are 10 ppm and 40 ppm and calcination temperature of catalyst i.e 400°C, 500°C and 600°C were investigated. The characterization of ZnO at different calcination temperature were performed by using Thermogravimetric (TGA) and Brunauer-Emmett-Teller (BET) analysis. The percentage degradation was measured by using HPLC instrument after exposed the 2,4,6-TCP at concentration of 10 ppm and 40ppm with ZnO catalyst under UV light for 6 hours. Therefore, the results show the weight loss and BET surface area decreased as the calcination temperature increased which is from 400°C to 600°C attribute to high thermal stability and have agglomerated particles in ZnO. The optimum degradation of 2,4,6-TCP for 10 ppm is 97.54% at 4 hours while for 40 ppm is 96.83% at 6 hours exposed to UV light at 600°C of calcination temperature of Zinc Oxide. It shows that ZnO catalyst at high calcination temperature lead to more effective in photocatalytic degradation of 2,4,6-TCP under UV light.**

***Keywords*— 2,4,6-Trichlorophenol, Photocatalytic Degradation, ZnO, BET, TGA.**

1. INTRODUCTION

2,4,6-Trichlorphenols (2,4,6-TCP) is one of the chlorophenols compound which is resistant to biodegradation and continue in the environment for long duration of time [1]. They are one of the largest numbers of group of industrial toxic compound and usually found in industrial wastewaters like pulp and paper, dye and pigment, pharmaceuticals and municipal waste incineration [2]. The uses of 2,4,6-TCP usually in many type of pesticide formulations and as a wood preservative. For example, the used of 2,4,6-TCP in pesticide is like fungicides, bactericide, herbicides and as glue preservative while in textile as anti-mildew agent but most of the uses of this compound was terminated in United State [3]. Besides that, they could be separated by wind and water. They could grow and released from one species to the next through the food chain. Therefore, chlorophenols were recognized as environmental pollutants owing to their high potential of phytotoxicity and zootoxicity [4]. According to the Environmental Protection Agency, 2,4,6-TCP is the environmental pollutant and reported as priority pollutants [5]. It will give a bad effect in a short term and long terms effects like inhalation or oral exposure in humans and chronic cancer [2]. Therefore, the degradation of 2,4,6-TCP is necessary due to the high toxicity, carcinogen properties, structural stabilization and persistence in the environment [6].

In 1980, Advanced Oxidation Processes (AOPs) is the first suggested process for treatment of clean water and tertiary of waste water which has a contaminant of toxic organic compound and non-biodegradable [7]. AOPs is created to generate hydroxyl radical (OH•) that give high efficiency for eliminating the contaminant compound [8]. OH• able to oxidize mostly all the organic compounds and produced a water (H_2O) and carbon dioxide (CO_2) [9]. In this process, there are many ways of production of OH• and one of it is Heterogenous AOPs [7]. This process involve a multi-phase system which is usually use a catalyst in degradation of compound [10]. The principle of the process is by the appearance of electron-hole pairs that give the oxidation and reduction processes occur [11]. Zinc Oxide (ZnO) is a semiconductor material that used as a catalyst for these AOPs because it is the most effective photocatalyst for the degradation of contaminants compound [12]. It can absorb a large fraction of the UV range and has 387nm of equivalent threshold wavelength [13]. Besides that, it has band gap of 3.2 eV and the exciton binding energy is high that is 60 meV. Furthermore, it is high electron mobility in range of 10 to 100 times more than Titanium Dioxide (TiO_2) and has higher quantum yield and can be an alternative for TiO_2 [14].

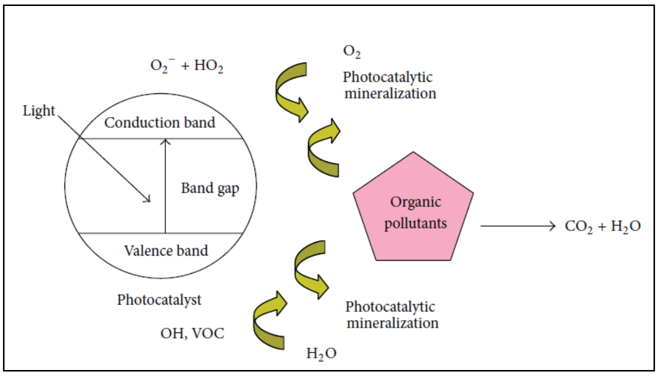


Fig. 1 Schematic diagram of photocatalytic degradation of organic Contaminant byusing semiconductor as a catalyst [15]

Fig. 1 shows the schematic diagram of photocatalytic degradation of organic contaminant by using semiconductor as a catalyst. The electron will be move upwards which is from the valence band to the conduction band with the simultaneous creation of holes (h^+) in the valence band [16]. The electron can be excited when the irradiation happen on the photocatalyst with exists of light which is the photons of energy to or more than the band gap energy of photocatalyst.

Then, absorption of oxygen (O_2) occurred on the surface of photocatalyst that make the electron in a trap. The production of superoxide radicals ($O_2{•}^-$) is from desorption of O_2. By reacting $O_2{•}^-$ with H_2O it can generate the hydroperoxy radical ($HO_2{•}$) and OH radical. Both radicals can eliminate the organic pollutants because both are known as strong oxidizing agents. Lastly, the oxidation of organic pollutants will produce product with CO_2 and H_2O [15]. According to Herrmann (1999), the photocatalytic degradation which is used a catalyst in the reaction is the future of water treatment [11].

In this study, the ZnO was synthesized by using sol gel method and characterized by Thermo Gravimetric Analysis (TGA) and Brauneur Emmett Teller (BET) analysis [17]. Both analyses were detected the weight loss and surface area of ZnO nanoparticles. Then, the ZnO catalyst will be applied to the photocatalytic degradation of 2,4,6-TCP under UV light with different calcination temperature i.e. 400°C, 500°C and 600°C. The results are analyzed by the High Performance Liquid Chromatogram (HPLC) instrument to see the percentage of degradation.

2. METHODOLOGY

2.1. Materials

2,4,6-Trichlorophenol (98%) from Merck. Zinc Acetate Dihydrate ($Zn(CH_3COO)_2.2H_2O$) (≥99%) and Ethanol (95%) are purchased from HmbG Chemicals. Sodium Hydroxide (NaOH) (≥98%) from Sigma Aldrich. Methanol from ChemAR Systerm.

2.2 Apparatus

The apparatus that have been used in this study are beaker, quartz tube, conical flask, volumetric flask, measuring cylinder, funnel, filter paper, magnetic stirrer, analytical balance, furnace, UV lamp in Airstream Horizontal Laminar Flow Cabinet (ACH-4A1), HPLC instrument with brand of Perkin Elmer (Series 200), Mettler Toledo TGA/DSC 1 Star e System and 3Flex Version 3.02.

2.3 Preparation of 2,4,6-TCP stock solution

In this study, a 0.25 g of 2,4,6-TCP was diluted in 500 mL of Methanol which is to prepare a stock solution. The stock solution was placed in the dark room [18].

2.4 Preparation of ZnO nanoparticles

A sol gel method was used to synthesize the ZnO nanoparticles. There have two solutions that are Solution A and B. Solution A was prepared by adding 2 g of $Zn(CH_3COO)_2.2H_2O$ dissolved in 15 mL of water. Solution B was prepared by adding 8 g of NaOH dissolved in 10 mL of water. Both solutions letting it dissolved for 15 minutes. Then, Solution A and B were mixed together. The titration of ethanol was done until the white precipitate was formed. Filter the residue and dry it in oven at 80°C for 60 minutes. The dried residue was placed in the furnace for calcination at three temperatures i.e. 400°C, 500°C and 600°C for 5 hours [19].

2.5 Characterization of ZnO nanoparticles

The thermal-decomposition of solid catalyst was performed by using a Mettler Toledo TGA/DSC 1 Star e System which is for TGA analysis. The catalyst was heated from 50°C to 800°C with the heating rate of 10°C/min in the flow of nitrogen 1 L/min. 20 mg of ZnO was used in TGA analysis [20]. For the BET analysis was performed by 3Flex Version 3.02 instrument. The catalyst was conducted under 290°C for 3 hours with nitrogen (N_2) at a constant temperature of 77.358 K [21].

2.6 Photocatalytic Degradation Procedures

In this experiment, two different concentrations which are 10 ppm and 40 ppm were prepared from a stock solution of 2,4,6-TCP and placed it into a glass bottles. 1 g of ZnO catalyst with different calcination temperature i.e. 400°C, 500°C and 600°C were added in each of the glass bottle. All the glass bottles were exposed under UV lamp with distance of 15 cm. The samples that have been exposed were taken for every 1 hour to 6 hours and were analyzed by HPLC instrument. The following information was the condition in HPLC system [22].

HPLC system : Hewlett-Packard HP 1050 Liquid Chromatography with Ultraviolet Absorbance Detector
Column : 15 cm x 150 mm
Mobile phase : Solvent A- Deionized Water
Solvent B- Methanol and Water (7:3%,v/v)
Flow Rate : 1.0 mL/min
Injection Volume : 20 µL
Stop/Post Time : 5 minutes
Detection Wavelength : 290 nm

The percentage degradation will be obtained by using the following equation [22].

$$\text{Percentage of Degradation (\%)} = \frac{(C_0 - C)}{C_0} \times 100\%$$

Where, Co is the initial concentration and C is the final concentration of 2,4,6-TCP solution.

3 RESULTS AND DISCUSSION

3.1 Characterization of ZnO nanoparticles

3.1.1 TGA Analysis

Table 1 shows the data of weight of ZnO nanoparticles in percentage were obtained from TGA analysis. The weight loss of the catalyst was decreased when heated from 50°C to 800°C. It can be said that the moisture content and other impurities were eliminated when heated at high temperature [23]. The total weight loss of ZnO as-prepared was the highest compared to ZnO calcined at 400°C to 600°C. This is because it does not undergo drying process. So, ZnO as-prepared had high moisture content and other impurities. For the ZnO calcined at 400°C to 600°C, it shows that the total weight loss decreased as the calcination temperature of ZnO increased. Thus, ZnO calcined at 600°C contain less moisture content and other impurities compared to temperature at 400°C and 500°C. For the residual weight of catalyst, it should be increased when the total weight loss decreased [24]. Unfortunately, catalyst of ZnO calcined at 400°C had highest percentage of residual weight. This is because there must be experimental error. Therefore, ZnO calcined at 600°C had highest residual weight which is means that at 600°C was more thermally stable than others catalyst.

Table 1: Percentage of weight in TGA analysis

Catalyst	Percentage of Weight (%)	
	Total Weight Loss	Residual Weight
ZnO as-prepared	10.30	89.66
ZnO calcined at 400°C	0.36	99.82
ZnO calcined at 500°C	0.32	99.34
ZnO calcined at 600°C	0.25	99.72

3.1.2 BET Analysis

The BET surface area of the catalyst was investigated from the measurements of N_2 adsorption-desorption isotherm [25]. Based on Fig. 2, BET surface areas for calcination temperature of ZnO nanoparticles from 400°C to 600°C were decreased. The BET surface areas values for 400°C, 500°C and 600°C were 6.4 m^2/g, 2.9 m^2/g and 2.0 m^2/g respectively. It can be said that at highest calcination temperature had a smaller BET surface area because the particles of ZnO become agglomerated when heating ZnO at high temperature [26].

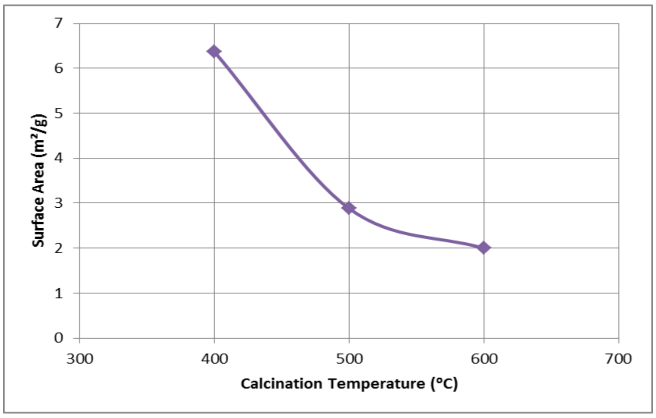


Fig. 2 : Graph of Surface Area against Calcination Temperature of ZnO nanoparticles

3.2 Photocatalytic Degradation of 2,4,6-TCP

3.2.1 Effect of the concentration of 2,4,6-TCP

The effect of concentration of 2,4,6-TCP was studied for the percentage degradation of 2,4,6-TCP with two different concentration which are 10 ppm and 40 ppm as shown in Table 2. From Fig. 3 shows that the concentration of 2,4,6-TCP decreased as the time of exposed under UV light increased. 10 ppm of concentration of 2,4,6-TCP has highest percentage degradation of 2,4,6-TCP which is 97.54% at 600°C compared to 40 ppm. Therefore, from this result show that the lower the concentration of contaminant will give a highest percentage of degradation of 2,4,6-TCP. Furthermore, at 10 ppm of 2,4,6-TCP need a short period of time of exposure under UV light to achieved high percentage of degradation 2,4,6-TCP. While, at 40 ppm of 2,4,6-TCP need long period of irradiation time to achieved higher removal of 2,4,6-TCP. This is because when the concentration of 2,4,6-TCP decreased, less reactant molecules were absorbed on the surface of ZnO catalyst and the removal of 2,4,6-TCP take a short period of time [27].

Table 2: Percentage of Degradation TCP for different initial concentration

Time (hr)	Percentage Degradation of TCP (%)					
	10ppm			40ppm		
	400°C	500°C	600°C	400°C	500°C	600°C
1	89.38	81.44	87.89	79.03	62.01	75.04
2	97.41	92.71	94.32	88.19	71.64	85.86
3	97.44	96.82	97.44	88.86	83.12	91.59
4	97.51	96.86	97.54	88.95	91.91	94.99
5	97.52	97.52	97.54	89.81	92.69	95.29
6	97.53	97.53	97.54	93.12	95.26	96.83

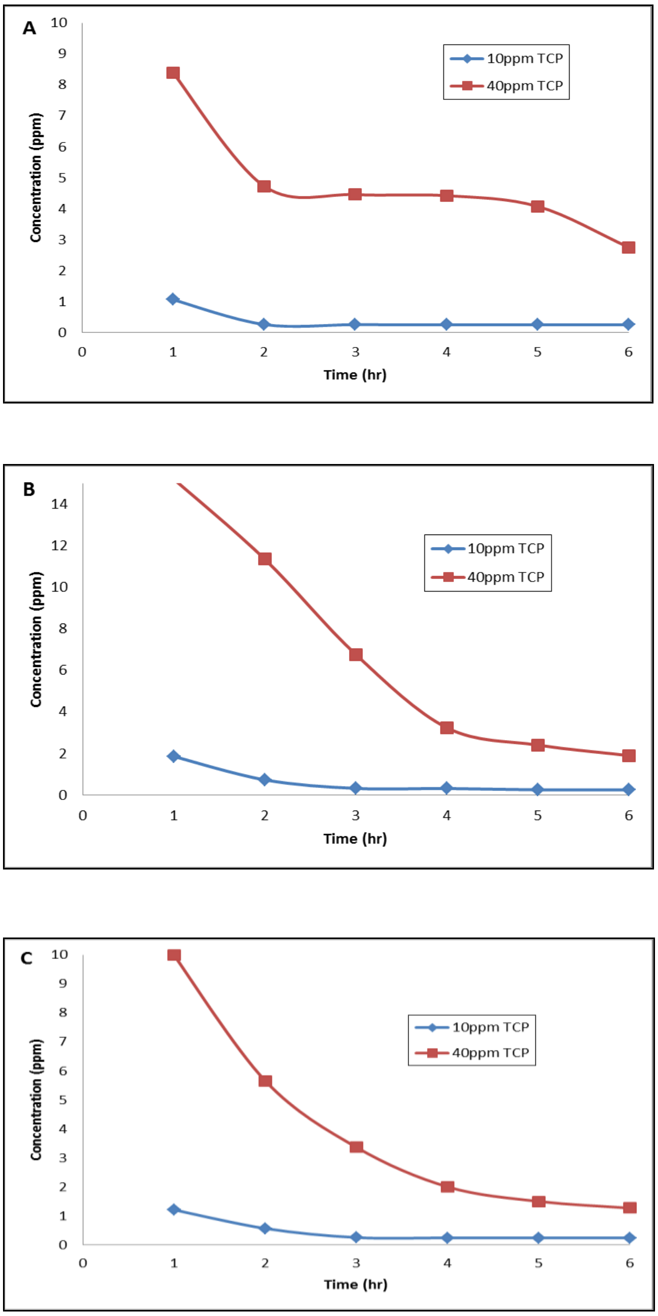


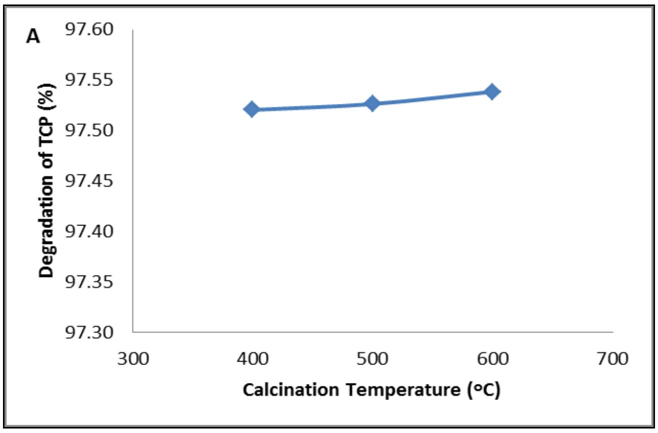
Fig. 3. Graph on effect of concentration for ZnO calcined at 400°C (A), ZnO calcined at 500°C (B), ZnO calcined at 600°C (C)

3.2.2 Effect of the calcination temperature of ZnO nanoparticles

The calcination temperature of catalyst is one of important factor to studied on the degradation of 2,4,6-TCP which are influence on the surface area and thermal stability. In Table 3 shows the percentage of degradation 2,4,6-TCP for differences calcination temperature of ZnO i.e. 400°C, 500°C and 600°C. The percentage of removal 2,4,6-TCP increased as the calcination temperature increased. Fig. 3 show that the highest percentage degradation is at 600°C for both concentration of 2,4,6-TCP. At high temperature, the catalyst tends to be well crystal structure with decreasing in surface area and have good thermal stability attribute to increase the percentage of degradation [28]. Therefore, calcination at 600°C for 6hr is the optimum temperature.

Table 3: Percentage of 2,4,6-TCP at differences calcination temperature of ZnO nanoparticles

Calcination Temperature (°C)	Percentage of Degradation 2,4,6-TCP (%)	
	10ppm	40ppm
400	97.53	93.12
500	97.53	95.26
600	97.54	96.83



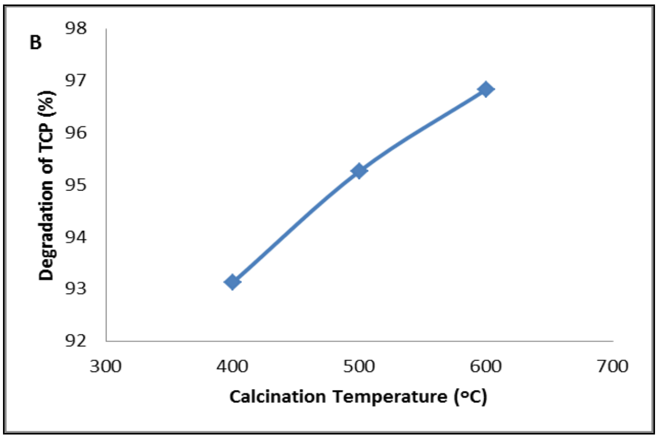


Fig. 3 : The percentage of 2,4,6-TCP on effect of calcination temperature of ZnO for 10 ppm concentration (A), 40 ppm (B)

In this study, it can be seen that to get highest degradation of 2,4,6-TCP need to increase the calcination temperature of ZnO. The time of exposed the sample under UV light may be affected the efficiency of degradation of 2,4,6-TCP. Other than that, when placed the sample to far from the UV light make the reaction is not completed. While synthesized ZnO nanoparticle must use ethanol instead of water to get a better performance of photocatalyst. Lastly, using HPLC instrument must use a suitable mobile phase to ensure that will get a better result.

4 CONCLUSION

As a conclusion, in TGA analysis at calcination temperature of 600°C have high thermal stability attribute the total weight loss is lowest which is 0.25% compared to others. The surface area is decreases as the temperature increases attribute to have agglomerated particles in ZnO. It can be seen that at 10 ppm, the exposed 2,4,6-TCP under UV light had optimum degradation percentage of 97.54% for 4 hours while on the other hand, for 40 ppm, the degradation percentage is 96.83% for 6 hours. Thus, the efficiency of degradation 2,4,6-TCP is highest at lowest concentration of 2,4,6-TCP in short period of time to be exposed to UV light. Both concentration of 2,4,6-TCP give highest percentage degradation of TCP at 600°C. Therefore, the optimum calcination temperature of ZnO is at 600°C

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