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## PERFORMANCE OF TUNGSTEN OXIDE DOPED TITANIA via SOL-GEL PROCESS FOR PHOTO-DEGRADATION OF TRANS-CINNAMIC ACID

**RINGKASAN:** Bahan-bahan berasaskan  $TiO_2$  selepas mengalami tindakbalas haba boleh wujud dalam tiga fasa kristal yang berbeza iaitu 'rutile' (tetragonal), 'anatase' (tetragonal) dan 'brookite' (orthorombic). 'Rutile' adalah bentuk yang paling stabil, manakala 'anatase' dan 'brookite' berada dalam metastabil dan mudah berubah kepada 'rutile' apabila dipanaskan. Untuk mengkaji kesan pendopan ke atas aktiviti foto pemangkinan pada suhu yang berbeza, tungsten oksida,  $WO_3$  telah dimasukkan ke dalam struktur  $TiO_2$  pada suhu yang berlainan. Analisis menunjukkan bahawa tungsten oksida menyumbang ke arah pembentukan struktur stabil nano kristal berbentuk bulat dan spektrum XRD juga membuktikan kehadiran pencampuran struktur kristal 'anatase-rutile' wujud pada suhu 600 °C. Pendopan  $WO_3$  dalam  $TiO_2$  menunjukkan tindakbalas yang aktif terhadap foto-pemangkinan ke atas penguraian asid trans-cinnamic dalam masa 90 minit. Pendopan  $WO_3$  dalam  $TiO_2$  pada suhu 500 dan 600 °C menunjukkan penguraian asid trans-cinnamic iaitu 100 % dalam tempoh 90 minit.

**ABSTRACT:** Generally,  $TiO_2$  based materials that undergo thermal treatment can exist in three different crystalline phases which are rutile (tetragonal), anatase (tetragonal) and brookite (orthorombic). Rutile is the most stable form, whereas anatase and brookite are in metastable and readily transformed to rutile when heated. In order to investigate the effects of dopant in photocatalytic activities towards changes of temperature treatment, tungsten oxide,  $WO_3$  was incorporated into  $TiO_2$  structure at different thermal temperatures. The results indicated that tungsten oxide was found to contribute towards the formation of stabilized rounded nanoparticles structure and the XRD spectra indicated mixture of nanocrystals composite anatase-rutile at 600 °C. The  $WO_3$ -doped  $TiO_2$  showed active photo-degradation in trans-cinnamic acid throughout 90 minutes of test duration. It exhibited better performance in decomposition of trans-cinnamic acid at 100 % within 90 minutes at 500 and 600 °C thermal treatment.

Keywords: trans-cinnamic acid, photo-degradation and tungsten oxide doped titania photocatalyst.

## INTRODUCTION

Realizing the importance of keeping our planet clean, researchers are actively working for eco-friendly alternative technologies for all areas of daily life. Sustainable energy production and pollutant destruction are two of the areas in which intense research is being carried out, (Manoj *et al.*, 2012). Photocatalytic technology evolves around the irradiations of photocatalysts to create powerful oxidation reactions is a well-known green technology for environmental remediation. However, the ability of the photocatalytic degradation to remove the organic pollutants is influenced by the photocatalyst materials.  $\text{TiO}_2$  is widely used as photocatalyst for oxidizing the organic and inorganic substrates in water through redox process (Fujishima and Zhang, 2006) but the ability of  $\text{TiO}_2$  has not emerged to be one of the most fascinating materials in both homogeneous and heterogeneous catalysis. This had engaged the attention of researchers in exploring the semiconductor materials to enhance the removal of ambient concentrations of organics from water or air for environmental cleaning, drinking water treatment, industrial and health applications. The efficient and successful application of photocatalysis correspond to the pollutant, photocatalyst and source of illumination that come into close contact with each other. Thus, investigations of photocatalytic performance of a photocatalyst including the mechanisms are usually carried out using model compounds prior to scaling-up. Model compounds are commonly applied to validate the photocatalytic degradation performance and efficiency of a material (Ibhadon and Fitzpatrick, 2013). The current work focuses on evaluation of the performance of various photocatalyst materials prepared using a standard reactor in decomposition of trans-cinnamic acid. The efficiencies of the photocatalyst powder prepared at different temperatures and different concentrations were assessed to determine the optimum loading for applications.

## MATERIALS AND METHODS

### Synthesis of $\text{TiO}_2$ Sol-gel Derived Based Materials

Titanium tetrabutoxide (Sigma-Aldrich) was reacted with acetylacetone (acac, *Fluka*) in a molar ratio of 1:4. The change from transparent solution to slightly yellowish indicates the formation of titanium octahedral complex which acac acts as ligand. The Ti complex was diluted in equivalent volume ratio with ethanol (EtOH, *Fisher*). 1N hydrochloric acid (HCl) aqueous solution was initially prepared from the concentrated

HCl with deionized H<sub>2</sub>O. 1N ammonium hydroxide, NH<sub>4</sub>OH was also prepared in the same manner as 1N HCl. The dissolved WO<sub>3</sub> solution was also prepared in a beaker. The WO<sub>3</sub>-doped TiO<sub>2</sub> was prepared by reacting the Ti-acac complexes with the dissolved WO<sub>3</sub> solution and 1N HCl followed by an equivalent molar of 1N NH<sub>4</sub>OH. The developed precipitate was separated from the supernatant solution and dried at room temperature. The resulted particles were washed 3 times with deionized water before oven drying at 80 °C for 24 h. The prepared particles were then thermal treated at various temperatures of 400 °C, 500 °C and 600 °C for 1 h.

The morphological and structural changes of WO<sub>3</sub> doped TiO<sub>2</sub> particles were investigated using LEO1525 Field Emission Scanning Electron Microscope and the elongation on the structural phases under various treated temperatures was inspected using Bruker X-ray diffractometer.

### Performance Evaluation of Photocatalyst Materials

Investigations of photocatalytic performance have usually been carried out using model compound. The selected compound can strongly influence the photocatalytic performance due to the effect of the structure of model compounds and other factors on the degradation process (Ibhadon and Fitzpatrick, 2013). In this work, trans-cinnamic acid was chosen as a model compound for testing the reactivity of the synthesized photocatalyst and validating the photocatalytic degradation efficiency of the organic pollutant. The experimental set-up of the standard reactor is shown in Figure 1.



*Figure 1. Experimental set-up of the photocatalytic degradation of trans-Cinnamic acid using standard reactor*

The standard reactor consists of a flat bottom flask to allow for UV-Visible radiation with wavelength  $\lambda$  of 358 nm. The system is equipped with a jacketed envelope facilitating the flow of a temperature-constant fluid to maintain constant temperature throughout the experiment. The photocatalytic activity of the photocatalyst materials was evaluated by photodegradation of 50 ppm trans-Cinnamic acid. The 50 ppm trans-cinnamic acid solution was prepared by dissolving 50 mg of trans-cinnamic acid  $C_6H_5CH=CHCOOH$  (ChemCruz) in 1 L of distilled water. The solution's pH was  $3.0 \pm 0.1$ .

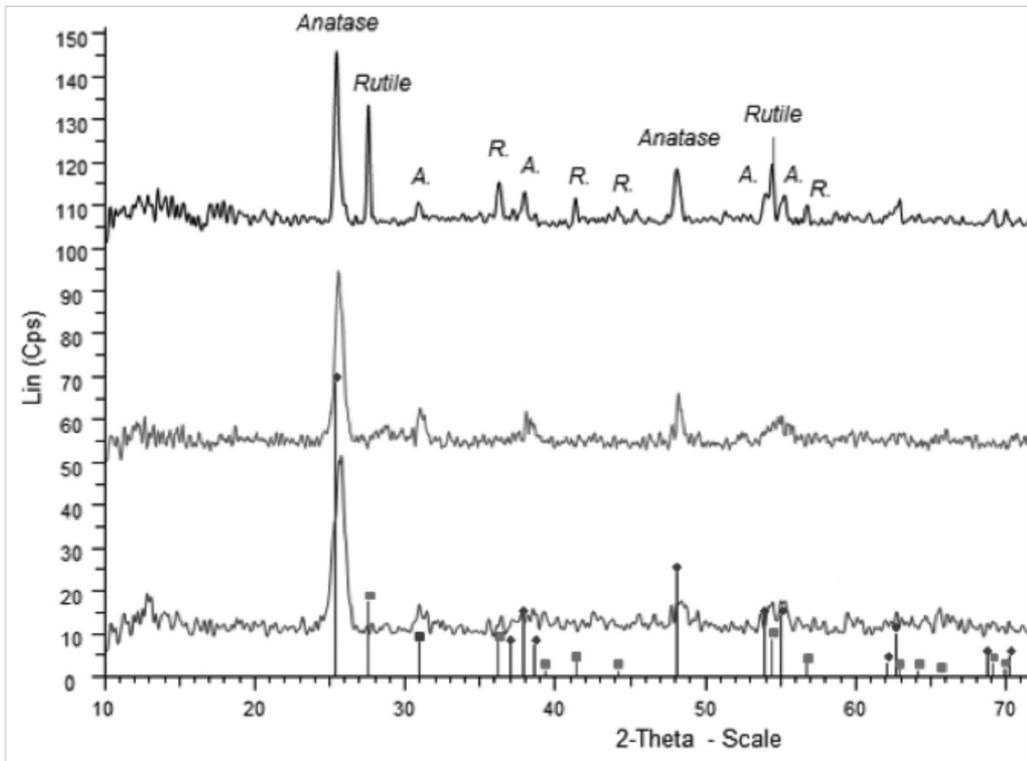
100 mg of the photocatalyst material was added into 250 ml of 50 ppm trans-cinnamic acid to form suspension under vigorous stirring in the dark to reach the adsorption-desorption equilibrium. The photocatalytic reaction was started by turning on the LED lamps. 1 ml of the aliquot was withdrawn from the flask at the following time intervals: 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 75 and 90 minutes. The solution was then diluted with distilled water to make up to 10 mL prior to UV-Vis spectrophotometer analysis.

Analysis of trans-cinnamic acid was carried out using UV-Vis spectrophotometer (Perkin Elmer model Lambda 35) at the specific wavelength of 273.9 nm. The spectrometer was calibrated using a series of trans -cinnamic acid at different concentrations ranging from 1 ppm to 10 ppm prior to analysis. A blank run was also carried out under the conditions described above without the photocatalyst material as control. The experiment was also repeated with different photocatalyst dosage to assess the optimum photocatalyst concentration for degrading 50 ppm of trans-cinnamic acid in order to avoid excessive catalyst being used in the photocatalysis reaction.

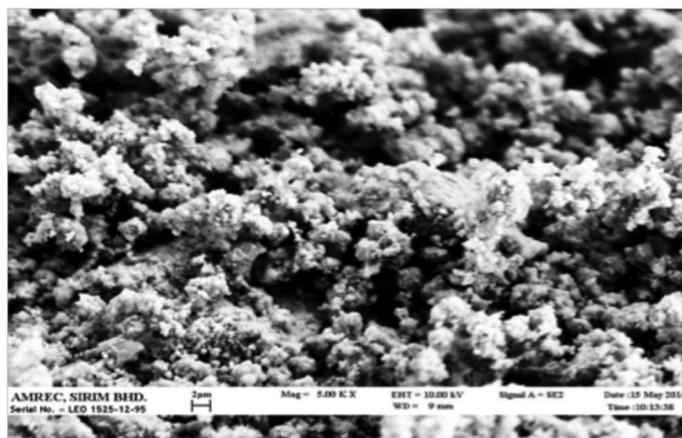
## RESULTS AND DISCUSSION

All  $WO_3$ -doped  $TiO_2$  samples which based on the different thermal treatment temperatures of 400, 500 and 600 °C obtained similar clear white powder form. Observation on the crystallography by X-ray diffractometry on the evolution of phase crystallinity towards different temperature treatment was presented in Figure 2 which indicated formation of 2 types of polymorphs for  $TiO_2$  namely anatase and rutile. Anatase can be easily observed by the presence of strong peak at  $25.3^\circ$  for all subjected thermal treatments whereas emission peaks for rutile with major  $K\alpha$  emission line at  $27.5^\circ$  only emerged whenever the materials undergo treatment at 600 °C (Kuznetsova, 2007). Another significant observation throughout the temperature evolution was the peak intensities become narrower and few other emission peaks for both crystals were revealed especially after thermal treatment at 600 °C. In addition, signal over noise ratio for overall diffraction angle,  $2\theta$  were also improved. These conditions indicated the crystalline quality has been enhanced

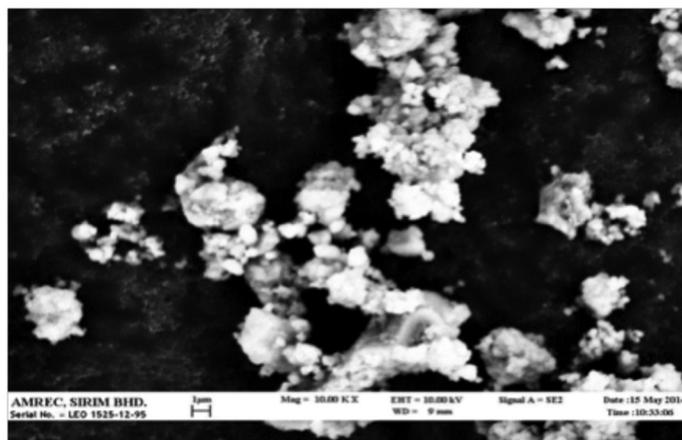
which sequentially can be staged as change of disorder phase into crystal-anatase phase and followed by conversion of anatase to rutile phase for the latter stage (Raj, 2009). The other observation that strengthen our judgement on the crystal quality confinement with increase of thermal treatment was on the splitting of major  $K\alpha$  peak for anatase into  $K\alpha_1$  and  $K\alpha_2$  which were positioned at  $25.3^\circ$  and  $26.0^\circ$ , respectively (Niwa, 2008). Apart from the narrowness in peak intensity, one can also noticed that the intensity of anatase peak has been reduced gradually throughout the increased of thermal treatment stating that the particles experienced reduction in size (Kumar, 1993).



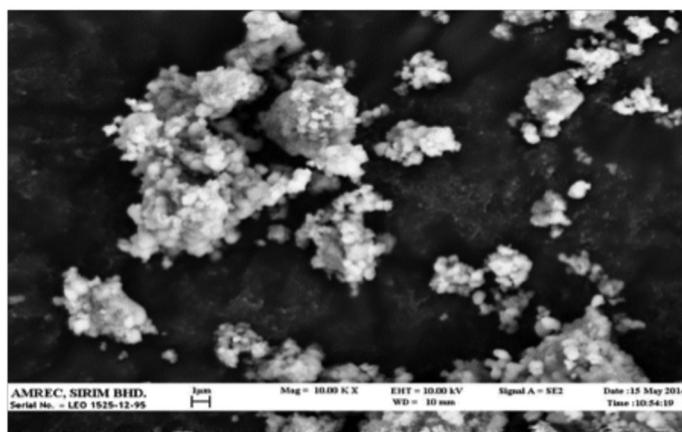
**Figure 2.** XRD spectra of  $WO_3$ -doped  $TiO_2$  prepared from sol-gel process at  $400^\circ C$ ,  $500^\circ C$  and  $600^\circ C$ , which showed the presence of brookite phase at  $2\theta = 30.81^\circ$ .



(a) 400 °C



(b) 500 °C



(c) 600 °C

**Figure 3.** FESEM images of prepared  $\text{WO}_3$ -doped  $\text{TiO}_2$  showed rounded nanoparticles structure throughout various processing temperature at 400 °C, 500 °C and 600 °C

FESEM has been carried out in order to obtain a comprehensive view on fabricated nanoparticles for the samples. As noticed in Figure 2, developed nanoparticles obtained 'grain-like' rounded shaped particle structures for all subjected curing temperature. Thermal treatment at 400 °C indicated the nanoparticles were well distributed throughout the surface with variety of particles sizes. On the other hand, treatment at higher temperatures of 500 and 600 °C provide smaller range in sizes distribution and exhibited high degree of agglomeration than the one with 400 °C treatment. Formation of agglomeration for these kind of samples (metal oxide) may come from the presence of high surface energy after experiencing thermal treatment. In principle, smaller particle size provides higher relative surface area over volume thus produce higher surface energy (Yao, 2015). From the perspective of thermodynamic, the increased of surface energy makes this material unstable which requires it to transform to more stable structures in every possible way (Nielsen, 1964) which in this experiment was the transformation from amorphous to crystals of anatase and rutile. Agglomeration, from one side, leads to decrease in entropy of the thermal treatment system (Stambolova, 2011) but from another side it leads to facilitate a negative enthalpy changes that promote stabilization by bond formation. As long as the enthalpy factor outweighs the entropy factor, agglomeration can take place (Cao, 2004). Based on this understanding, we suggested that thermal treatment at higher temperature especially 600 °C provides higher reduction in particle size which produces higher surface energy and in the stabilization progress, exhibited higher degree of agglomeration with more confined crystal quality compared to lower thermal treatment of 400 °C. This observation was concomitant with the result on the crystallography stating higher temperature provides finer crystal quality.

All sample with different thermal treated temperature were further investigated on the photocatalytic efficiencies by photo-irradiation setup as mentioned in the previous section. Details on decomposition of trans-cinnamic acid concentration was tabulated in Table 1 and sequential on the performance evaluation of the decomposition was depicted in Figure 3.

**Table 1.** Performance evaluation of photocatalyst materials with loading of 100 mg in 250 mL of 50 ppm trans-cinnamic acid solution.

Concentration of Trans-Cinnamic acid (mg/L)										
Time (min)	Control	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (400 °C)	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (500 °C)	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (600 °C)	Removal efficiency y (%)	*P25 Powder	Removal efficiency (%)
0	50.73	0.00	44.37	0.00	41.91	0.00	43.19	0.00	47.86	0.00
5	50.73	0.00	21.07	52.52	24.36	41.87	30.61	29.13	20.74	56.67
10	49.11	7.58	14.21	67.99	17.95	57.17	28.04	33.08	14.35	70.02
15	48.27	9.18	12.61	71.58	13.54	67.69	22.84	45.51	8.87	81.48
20	47.34	10.92	11.57	73.92	11.62	72.28	18.19	56.60	9.69	78.75
25	45.57	14.26	7.18	83.81	7.69	81.64	13.30	68.26	8.72	81.79
30	44.64	16.00	5.99	86.51	5.93	85.85	10.10	75.91	5.26	89.01
40	41.56	21.80	4.15	90.65	4.41	89.48	5.53	86.81	4.21	91.21
50	39.86	24.99	4.31	90.29	3.29	92.16	3.93	90.63	3.98	91.68
60	36.62	31.09	3.59	91.91	2.48	94.07	3.37	91.97	3.01	93.72
75	31.69	40.37	2.71	93.88	0.96	97.71	2.08	95.03	2.25	95.29
90	28.45	46.47	1.84	95.86	0.16	99.62	0.40	99.04	0.98	97.96

Note: \*P25 powder is commercial photocatalytic materials product from Degussa.

It was also noticed that the increase of thermal treatment from 400 °C to 600 °C contributed to higher degradation of trans-cinnamic acid. Both WO<sub>3</sub>-doped TiO<sub>2</sub> at 500 °C and 600 °C showed higher photo-degradation efficiency at greater than 99 % after 90 minutes of photocatalytic performance test as compared to WO<sub>3</sub>-doped TiO<sub>2</sub> at 400 °C which only achieved 96 % of trans-cinnamic acid degradation.

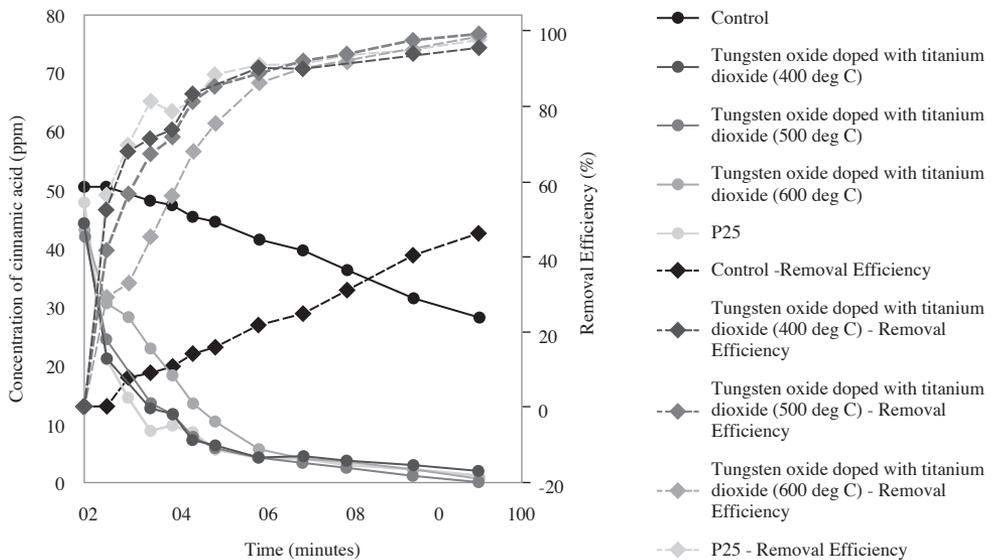


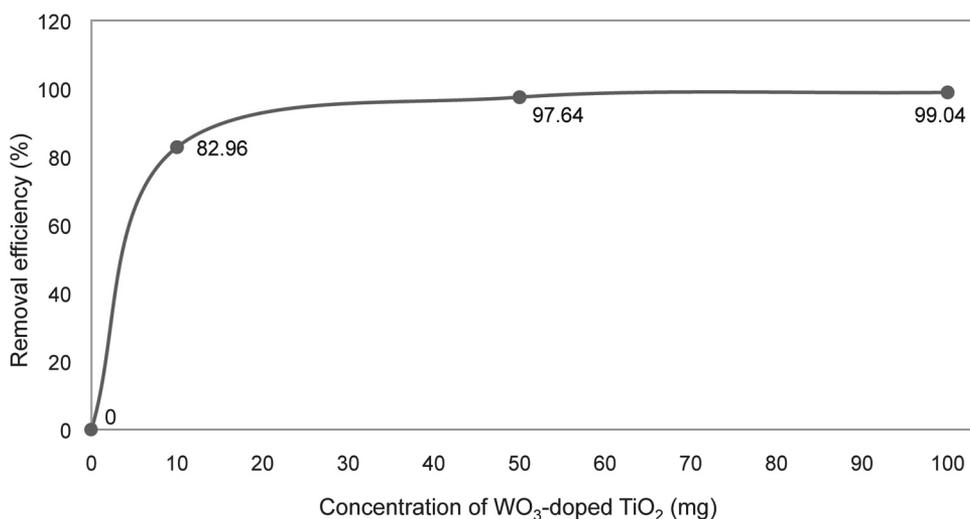
Figure 4. Performance of photocatalyst materials in decomposition of 50 ppm Trans-Cinnamic acid under UV radiation

The photo-degradation efficiency of WO<sub>3</sub>-doped TiO<sub>2</sub> at 600 °C was between WO<sub>3</sub>-doped TiO<sub>2</sub> at 400 °C and 500 °C. The WO<sub>3</sub>-doped TiO<sub>2</sub> at 600 °C was selected for further investigating the relationship between concentration of photocatalyst materials and photo-degradation reaction. Table 2 shows the performance of degradation of trans-cinnamic acid for 90 minutes photocatalytic testing at different loading of WO<sub>3</sub>-doped TiO<sub>2</sub> (600 °C) photocatalyst. The photodegradation rate of 50 ppm trans-cinnamic acid in different loading of WO<sub>3</sub>-doped TiO<sub>2</sub> (600 °C) decreased as the concentration of the cinnamic acid in the solution was reduced. It was noticed that photo-degradation occurred at lower photocatalyst loading of 10 mg. Figure 4 shows the relationship between WO<sub>3</sub>-doped TiO<sub>2</sub> (600 °C) loading and removal efficiencies. It could be observed that 10 mg of photocatalyst managed to degrade 80 % of trans-cinnamic acid. The results also revealed the optimum photocatalyst loading which is 60 mg, enables the degradation of more than 98 % of 50 ppm trans-cinnamic acid.

**Table 2.** Degradation efficiency of 50 ppm trans cinnamic acid at different loading of WO<sub>3</sub>-doped TiO<sub>2</sub> (600oC) photocatalyst.

Time (min)	Concentration of Trans-Cinnamic acid (mg/L)									
	Control	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (400 °C)	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (500 °C)	Removal efficiency y (%)	TiO <sub>2</sub> +WO <sub>3</sub> (600 °C)	Removal efficiency y (%)	*P25 Powder	Removal efficiency (%)
0	50.73	0.00	44.37	0.00	41.91	0.00	43.19	0.00	47.86	0.00
5	50.73	0.00	21.07	52.52	24.36	41.87	30.61	29.13	20.74	56.67
10	49.11	7.58	14.21	67.99	17.95	57.17	28.04	33.08	14.35	70.02
15	48.27	9.18	12.61	71.58	13.54	67.69	22.84	45.51	8.87	81.48
20	47.34	10.92	11.57	73.92	11.62	72.28	18.19	56.60	9.69	78.75
25	45.57	14.26	7.18	83.81	7.69	81.64	13.30	68.26	8.72	81.79
30	44.64	16.00	5.99	86.51	5.93	85.85	10.10	75.91	5.26	89.01
40	41.56	21.80	4.15	90.65	4.41	89.48	5.53	86.81	4.21	91.21
50	39.86	24.99	4.31	90.29	3.29	92.16	3.93	90.63	3.98	91.68
60	36.62	31.09	3.59	91.91	2.48	94.07	3.37	91.97	3.01	93.72
75	31.69	40.37	2.71	93.88	0.96	97.71	2.08	95.03	2.25	95.29
90	28.45	46.47	1.84	95.86	0.16	99.62	0.40	99.04	0.98	97.96

Note: \*P25 powder is commercial photocatalytic materials product from Degussa.



**Figure 5.** Relationship between WO<sub>3</sub>-doped TiO<sub>2</sub> photocatalyst loading and removal efficiency (%) at 90 minutes of photo degradation reaction

## CONCLUSION

Temperature treatment mainly governed the types, sizes and quality of fabricated titania crystal which has contributed to photo-degradation of trans-cinnamic acid. Treatment at lower temperature of 400 and 500 °C resulted on the formation anatase crystal, however more harmonized anatase-rutile crystal phases with confined crystal quality and smaller particles was successfully developed at high temperature of 600 °C. Minimum loading of 10 mg WO<sub>3</sub>-doped TiO<sub>2</sub> (600 °C) photocatalyst is required to achieve more than 80 % removal of 50 ppm trans-cinnamic acid. Continued adding up to 100 mg weight of WO<sub>3</sub>-doped TiO<sub>2</sub> (600 °C) in 50 ppm trans-cinnamic acid slightly enhanced the photo degradation reaction performance.

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