TiO_2 POWDER PHOTOCATALYST FROM SOL-GEL ROUTE AND ITS IMMOBILISATION WITH CEMENT FOR PHOTOCATALYTIC PHENOL REMOVAL

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ABSTRACT

Two types of TiO_2 powders of water-to-TPT ratios (Powder 1: water/TPT = 1 and Powder 2: water/TPT= 2) were synthesized via sol-gel method. The effect of hydrolysis degree on the formation of TiO_2 powder particles was investigated using various physical-chemical characterization methods. The synthesized powders were then immobilised by mixing them with cement to be cement-bonded TiO_2 photocatalyst. For photocatalytic measurement, phenol solution was selected as a model of pollutant to be degraded by both cement-bonded TiO_2 photocatalysts to analyse their photocatalytic efficiency. The photodegradation of phenol test revealed cement-bonded TiO_2 Powder 2 was more efficient than Powder 1 due to its high crystallinity which can lead to faster charge separation and the increased number of phenol molecules adsorbed.

Keywords: *Cement-bonded TiO_2 Photocatalyst, Phenol Photodegradation, Sol-gel Method, Water-to-TPT Ratios*

1.0 INTRODUCTION

TiO_2 semiconductor has been discovered since 1970s and its outstanding properties in oxidising toxic and polluted water through photocatalytic oxidation have been widely studied since then [1]. It becomes one of the most promising photocatalysts to degrade organic and inorganic molecules either in liquid phase such as salicylic acid [2], toluene [3], sulfides [4], and methyl orange [5; 6] or gases phase such as methanol [7], carbon dioxide [8], and nitrogen oxide [9].

The photocatalytic process is initiated by UV irradiation that induces the TiO_2 band excitation to form electrons (e^-) at the lower conduction band and holes (h^+) at the upper valence band [10]. In order to excite the electron from the valence band to the conduction band, the amount of light energy needs to be absorbed by anatase TiO_2 has to exceed its band gap energy of 3.2 *eV* [11]. Thus, only light below 400 nm is absorbed and capable to form the e^-/h^+ pair. When separated, these two species can migrate to the catalyst surface and act as a reducer (oxygen reduction in superoxide ion) and oxidant (water oxidation in hydroxyl radical or direct oxidation of the reactant) as reported by Zahraa *et al*. (2003) [12]. The main reaction of photocatalysis is presented in equation (1)-(10).

Absorption:

$$TiO_2 + hv \text{ (bandgap energy)} \rightarrow TiO_2\,(e^-_{cb} + h^+_{vb}) \qquad (1)$$

Oxide-reduction:

$$h^+_{vb} + H_2O\text{ads} \rightarrow OH^{\cdot} + H^+ \qquad (2)$$

$$h^+_{vb} + OH^-_{ads} \rightarrow OH^{\cdot} \qquad (3)$$

$$e^-_{cb} + O_2 \rightarrow O_2^{-\cdot} \qquad (4)$$

Transfers:

$$O_2^{-\cdot} + H^+ \rightarrow HO_2^{\cdot} \qquad (5)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (6)$$

$$O_2^{-\cdot} + HO_2^{\cdot} \rightarrow HO_2^- + O_2 \qquad (7)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \qquad (8)$$

Degradation:

$$OH^{\cdot} + RH \rightarrow R^{\cdot} + H_2O \qquad (9)$$

$$R^{\cdot} + O_2 \rightarrow \text{….oxidation products} \qquad (10)$$

The photodegradation of any organic and inorganic molecules into carbon dioxide and water happens when an electron (e^-) and hole (h^+) pair is formed in the solid catalyst of TiO_2 when the wavelength of UV irradiation exceeds TiO_2 band gap energy of 3.2 *eV* as shown in equation (1). Total mineralisation of pollutant can be achieved directly when superoxide anion of $O_2^{-\cdot}$ and radical ion of $OH^{\cdot}$ react with water as described in equations (3) and (4). Photodegradation of pollutant process can also occur using the generated hydrogen peroxide of H_2O_2 in equation (6). This H_2O_2 is used in the reaction to produce more hydroxyl radicals for further oxidizing the organic and inorganic molecules. The participation of H_2O_2 is presented in equations (11) and (12).

Hydrogen peroxide formed can also participate in the reaction:

$$e^{-}_{cb} + H_2O_2 \rightarrow OH^{\cdot} + OH^{-} \quad (11)$$

$$H_2O_2 + O_2^{-\cdot} \rightarrow OH^{\cdot} + OH^{-} + O_2 \quad (12)$$

TiO_2 attracts the greatest attentions among researchers to treat the polluted environment due to its chemical stability, photostability, non-toxicity, inexpensive, and most importantly reusability as it can reduce the cost for cleaning process when being used for photocatalytic process [13-15].

Despite all the advantages in using TiO_2 for environmental applications, one main problem of using TiO_2 is the separation of the powder in the aqueous media after the photocatalytic process. Hence, many techniques of immobilisation have been developed to attach the TiO_2 powder to simplify the cleaning stage after photocatalytic process later on. Some of the developments are immobilisation of TiO_2 on perlite granules [1], silica sheets [16], thin film [17], bamboo charcoals [18], and activated carbon [19]. Wu *et al*. (2008) reported that immobilisation of TiO_2 on a substrate not only assisting the separation of TiO_2 powder from the aqueous but also to increase the powder distribution on the substrate to achieve higher surface area of the powder [18].

Therefore, this paper discusses on the development of two types of TiO_2 powder via sol-gel method with the mol ratios of water-to-TPT were fixed at 1(Powder 1) and 2 (Powder 2). Both of calcined TiO_2 powders were then characterized physically and chemically using TG/DTA, XRD, FESEM, FTIR, BET surface area, and Nano-*S* particle sizer to investigate the effect of hydrolysis rate on the powders' properties and their photocatalytic efficiency. Then, the obtained powders were mixed with white plaster cement to immobilise the powder. White plaster cement is a polymer modified cement-based white finish coat skim plasters which formulated with special chemical additives to provide good workability, improved adhesion and gives a very fine surface compared to gypsum finish. Besides, white cement is an easily available material and cheap in price which can reduce the cost of production. This technique can also provide higher surface area for TiO_2 to increase the number of pollutants absorb on its surface. The developed cement-bonded TiO_2 photocatalyst was utilised for the photodegradation of phenol in solution. For TiO_2 Powder 1 and 2 photocatalytic evaluation, the phenol solution concentration was measured by UV-Vis spectrometer.

2.0 METHODOLOGY AND CHARACTERISATION

2.1 Raw Materials

Methanol used as organic solvent for synthesis of TiO_2 powder was purchased from Systerm. Titanium isopropoxide (TPT) from Sigma Aldrich was used as source of Ti- monomer. White plaster cement (spray plaster-white finish 221) was purchased from PYE Products (M) Sdn. Bhd. and used for immobilization of TiO_2 powder.

2.2 Synthesis of TiO_2 Powder via Sol-gel Method

TiO_2 Powder 1 (mol ratio of water/TPT = 1) and Powder 2 (mol ratio of water/TPT = 2) were synthesized via sol-gel method. To synthesize TiO_2 powders, the process was done through hydrolysis process of methanol with TPT. Organic solvent of methanol was used to carry out the hydrolysis process to form a formable solution (sol) and a loosely cross-link matrix (gel). Methanol and TPT were mixed at room temperature in a flask. The TPT was hydrolysed by water to produce the gel TiO_2 powder after reflux at 67°C. The reaction of TiO_2 synthesis process is presented in equation (13).

$$Ti\,\{OCH\,(CH_3)_2\}_4 + 2H_2O \xrightarrow{\text{reflux°C}} TiO_2 + 4\,(CH_3)\,2CHOH \quad (13)$$

The white solution was filtered to obtain the gel TiO_2 powder. The powder was dried at 200°C for one hour and finally calcined to 400°C for one hour.

2.3 Characterisation of TiO_2 Powder

The amorphous TiO_2 powders were characterised using Thermogravimetric and Differential Thermal Analyser) (TG/DTA) (PYRIS DIAMOND, Perkin Elmer). For physical characterisation and crystal structure of the powders, an XRD machine from Shimadzu "XRD 6000" was used with the scanning range started from 20 to 50 degree in 2θ. Fourier Transform Infra-Red (FTIR) (SPECTRUM 100, Perkin Elmer) was utilised to identify chemical bonds existed in the powders. A surface area analyser (BET-Autosorb-1, Quantachrome Instrument) was used to measure the surface area of both powders. Particle size of the powders in suspension was measured by utilising the Zetasizer (Nano *S*, Malvern Instrument). Field Emission Scanning Electron Microscope (FESEM) (JSM 6700F, JOEL) was used to characterise the powders' surface morphology. For phenol photodegradation measurement, the change in initial concentration of phenol solution after being irradiated by UV was measured by Uv-Vis Spectrometer (Lambda-35, Perkin Elmer).

2.4 Preparation of Immobilised TiO_2 Powder

30 *g* of TiO_2 powder was mixed with 70 *g* of white cement to obtain 30% of TiO_2 in white plaster cement for phenol photodegradation experiment. The TiO_2 powder and cement were mixed together and water was added as a binder. The mixture was stirred homogeneously before poured into the aluminum mould of width and length of 5 cm x 5 cm and depth of 2 cm. The mould containing the wet mixture was placed in the dryer for drying process before the cement-bonded TiO_2 photocatalyst could be used for the photocatalytic experiment.

2.5 Photodegradation of Phenol

Two parameters were varied to investigate their effect on photodegradation of phenol; (1) effect of initial concentration of phenol solution and (2) effect of UV intensity on photocatalytic performance using the cement-bonded TiO_2 photocatalyst of Powder 1 and Powder 2. This work was divided into two parts. In the first part of the photocatalytic experiment, a 250 *ml* of phenol solution with initial concentration of 0.01, 0.03, 0.05, 0.07, and 0.10 *mg/mL* were prepared and the rate of degradation was studied. In second part, UV intensity was varied from 0.5, 0.7, 1.0, and 2.6 mW/cm^2 with initial concentration of phenol solution was 0.01 *mg/mL.* The photodegradation of phenol was carried out for 7 hours under stirring condition with the cement-bonded TiO_2 photocatalyst was placed at the center. The water sampling was done for every one hour.

3.0 RESULTS AND DISCUSSION

3.1 TiO$_2$ Powder Characterisation

Figures 1 and 2 represent the TG/DTA of TiO$_2$ Powder 1 and 2 respectively. From TGA curves, both TiO$_2$ powders showed a drastic weight loss at temperature below *ca.* 150 °C. This is due to the evaporation of volatile species of water and methanol from the powders. A second weight loss at temperature of ca. 300 °C is attributed to the removal of inorganic compounds of TPT [20]. From the DTA curves, a sharp exothermic reaction peak is observed at 414 °C for Powder 1 and 337 °C for Powder 2. These peaks are attributed to the TiO$_2$ powders crystallization transition from amorphous to anatase titania.

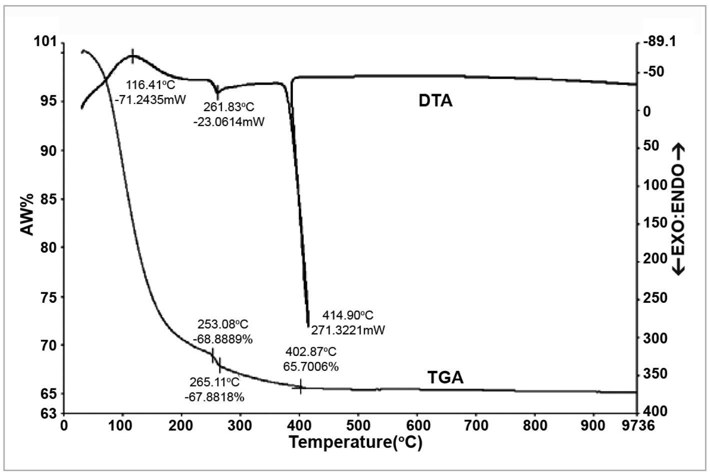

Figure 1: TG/DTA of TiO$_2$ Powder 1

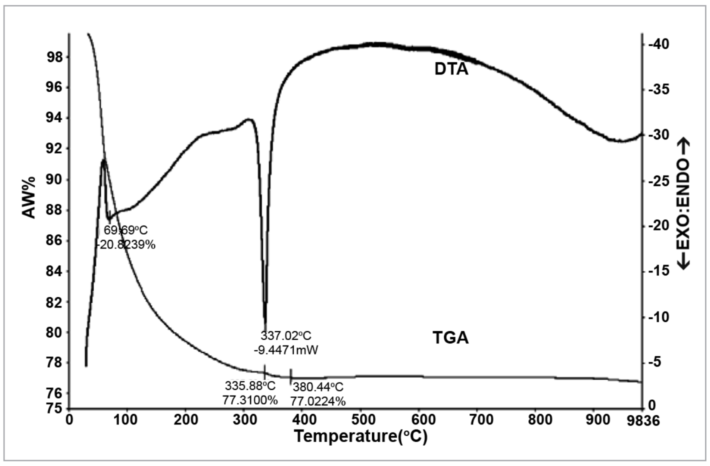

Figure 2: TG/DTA of TiO$_2$ Powder 2

From the analysis, the crystallisation temperature of TiO$_2$ Powder 1 was higher than TiO$_2$ Powder 2. This difference could be attributed to the effect of hydrolysis rate experienced by the powders during synthesis process. In this sol-gel method, the TPT was hydrolysed by water to form TiO$_2$ solution. The hydrolysis rate to form these particles is greatly affected by the amount of water. As the amount of water added to TPT increases, the hydrolysis rate for polymerisation process is also increased. Since the amount of water added to TPT solution for the synthesis of Powder 1 was less than Powder 2, Powder 1 experienced less progressive hydrolysis compared to Powder 2. It is expected that slow polymerisation process will result in formation of small particles. Due to the smaller particle of Powder 1, its transformation from amorphous to crystalline phase of anatase crystal structure happened at higher temperature as it needed more heat to crystallise than TiO$_2$ Powder 2 with larger particles.

Figure 3 shows the XRD pattern for TiO$_2$ Powder 1 and 2. From the analysis, both powders show the presence of the highest peak at 25° in 2θ. This peak indicates, both TiO$_2$ powders are purely in anatase crystal structure. Nonetheless, TiO$_2$ Powder 2's peak is higher than Powder 1 reflecting its higher crystallinity than Powder 1. The broader XRD pattern of Powder 1 reflecting its powder particles are smaller than Powder 2.

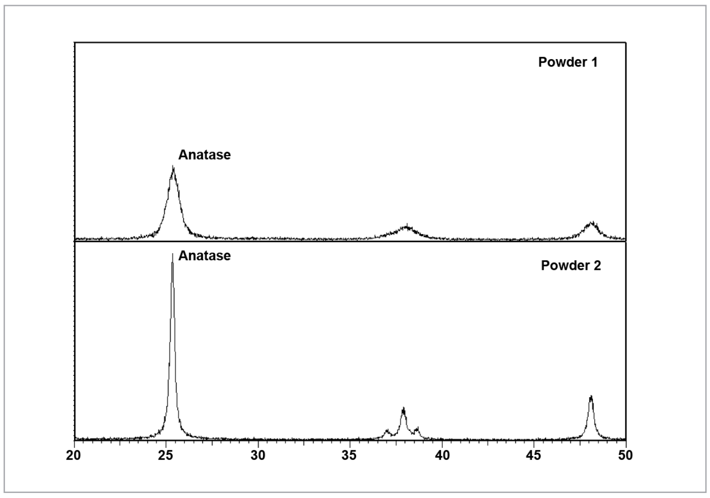

Figure 3: XRD patterns of TiO$_2$ Powder 1 and Powder 2

The difference in particle size between TiO$_2$ Powder 1 and 2 is confirmed by the calculation of the grain size using Scherrer's equation presented in Table 1.

Table 1: Particle size of TiO$_2$ powders using Scherrer's equation

TiO$_2$ Powder	Degree in 2θ	Particle size (*nm*)
1	25.3	10.8
2	25.3	30.2

Figure 4 shows the FTIR spectra for methanol (a), titanium tetraisopropoxide (b), TiO$_2$ gel powder (c), TiO$_2$ powder after drying at 200°C (d), and TiO$_2$ powder after calcination (e).

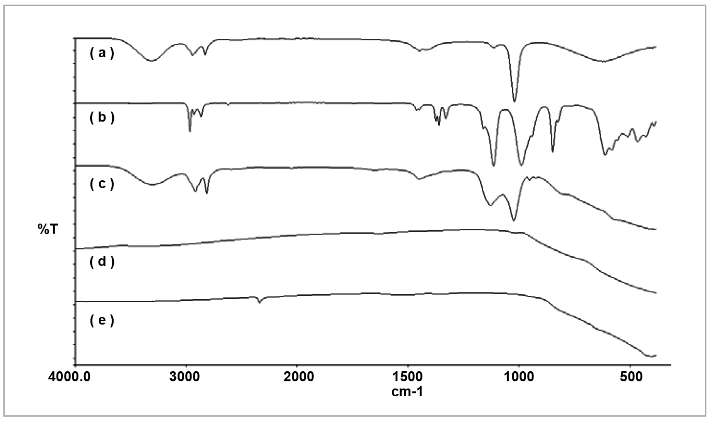

Figure 4: FTIR spectra of (a) methanol solution, (b) titanium (IV) isopropoxide, (c) TiO$_2$ powder after filtration process, (d) TiO$_2$ powder after drying at 200°C process and (e) TiO$_2$ powder after calcination treatment at 400°C

In Figure 4(a) absorption peaks of methanol appears at 3314 cm^{-1} which is attributed to O-H stretching band and at 1113 cm^{-1} attributed to C-O stretching band. Figure 4(b) shows the FTIR spectra of titanium (IV) isopropoxide with absorbance peaks at 2942 cm^{-1} and 987 cm^{-1} that belongs to aliphatic C-H stretching band and C-H alkene bending band respectively. From Figure 4(c), it is clearly shown that the gel powder after filtration process resembled mixture spectra of both chemicals of methanol and titanium tetraisopropoxide. After drying at 200°C, all the bands disappears and only inorganic Ti-O bond's weak stretching band at 394 cm^{-1} is observed as shown in Figure 4(d). This peak of inorganic phase of TiO_2 becomes stronger and densified after the powder was calcined at 400°C (Figure 4(e)).

It is important to notify that in FTIR analysis, Ti-O does not always present at lower wavenumber. Hong'en *et al*. (2008) [21] reported that they managed to obtain TiO_2 submicrospheres that showed Ti-O stretching mode at higher wavenumber of about 568 cm^{-1}. Wang *et al*. (2005) [22] also found out that strong absorption bands in the range of 400-850 cm^{-1} was corresponding to Ti-O-Ti network.

TiO_2 Powder 1 and 2 surface area analysed by BET surface area analyzer are shown in Figures 5 and 6.

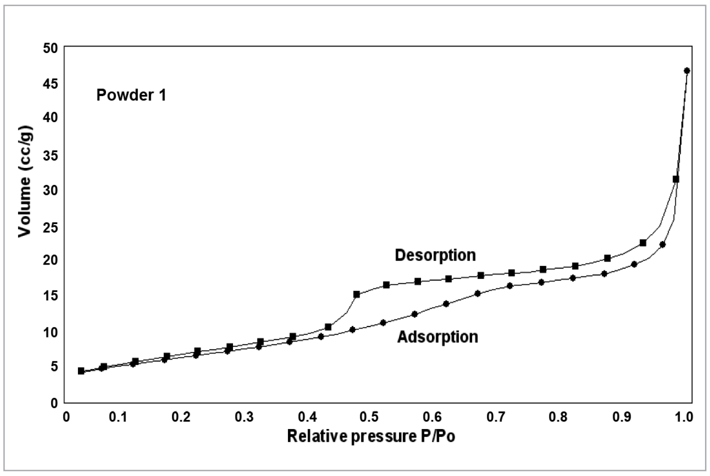

Figure 5: N_2 adsorption-desorption isothermal analysis of TiO_2 Powder 1

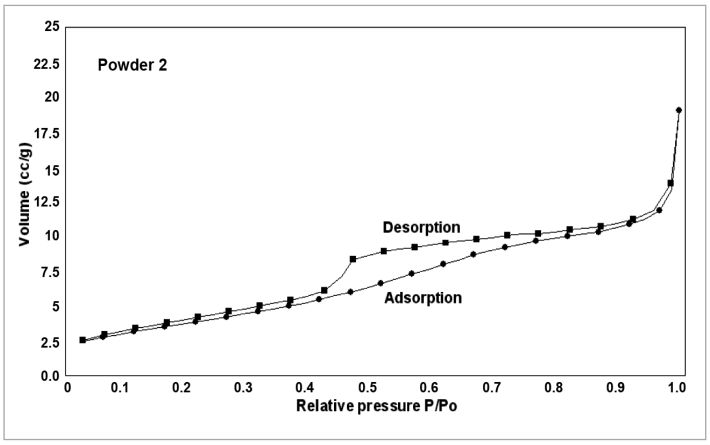

Figure 6: N_2 adsorption-desorption isothermal analysis of TiO_2 Powder 2

The N_2 adsorption-desorption isotherms of TiO_2 Powder 1 and 2 can be attributed to their pore connectivity effects. BET surface area analysis shows that both of sol-gel TiO_2 powders have Isotherm type II which was evaluated from the adsorption curve shown in Figures 5 and 6. Type II isotherms are normal form of isotherms obtained with a nonporous and macroporous adsorbent. From BET surface area analysis, Powder 1 and Powder 2 have surface area of 24.8 m^2/g and 14.6 m^2/g respectively. The hysteresis loop formed by the adsorption-desorption curve indicates that both powders have type *E* hysteresis loop that can be attributed to "ink-bottle" pores.

The particle size of TiO_2 Powder 1 and 2 measured by the particle size analyser are shown in Figures 7 and 8. From the analysis, Powder 1's mean particle size is 118 nm with particle size distribution range from 50 to 300 *nm*. The particle size of Powder 2 is recorded to range from 80 to 400 *nm* with mean particle size of 167 *nm*. However, the powder particle size measured from this analysis was quite big in size due to the possibility that powder's agglomerate was measured instead of the individual particles. This argument is supported by Imasu and Sakka (2007) [23] that most particles were dispersed into a primary size in aqueous suspension. In addition, small particles tend to agglomerate due to its high surface energy to attract other particles to combine together and form large primary particles. Hence, it is presumed that particles are aggregated into agglomerates in this suspension.

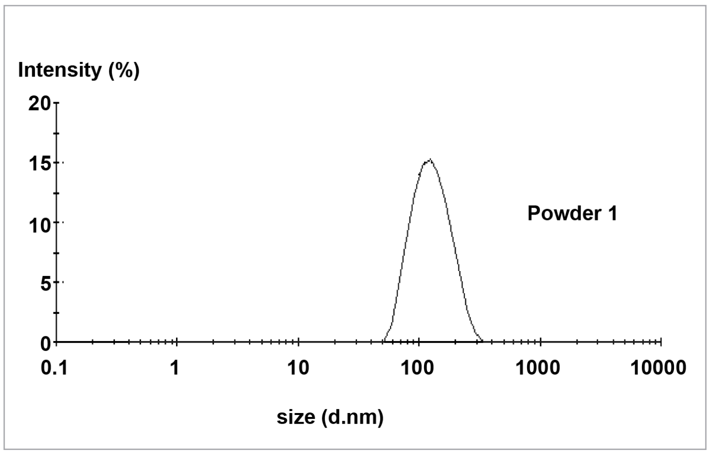

Figure 7: Particle size distribution of TiO_2 Powder 1

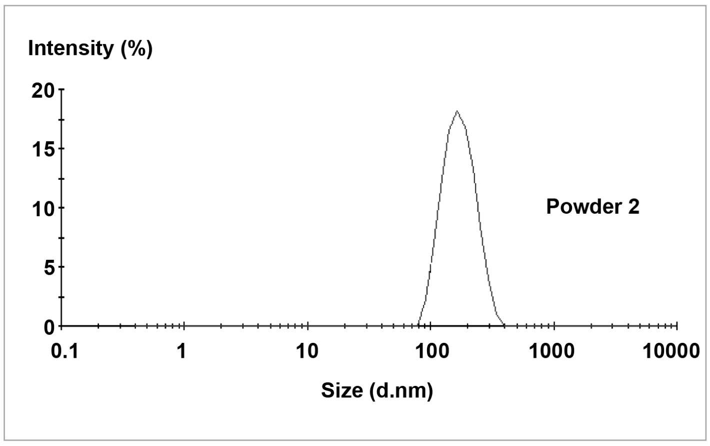

Figure 8. Particle size distribution of TiO_2 Powder 2

Figures 9 and 10 show the FESEM results of TiO_2 Powder 1 and 2. From the images, both TiO_2 powders have spherical shape with TiO_2 Powder 1 has smaller particle size than Powder 2. The formation of small particles of Powder 1 was due to its less progressive hydrolysis rate and polymerisation process during the synthesis. Hence, the powder particles could form slowly in the solution and produced small size particles. Meanwhile

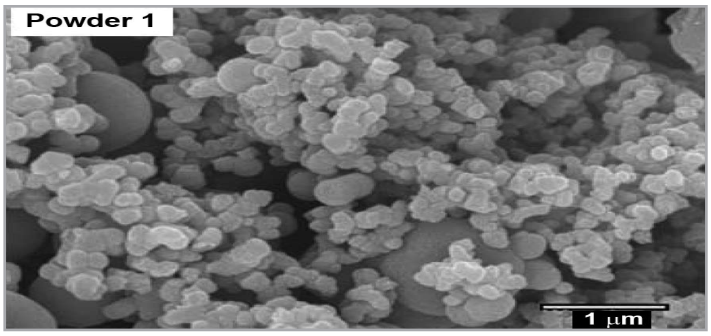

Figure 9: FESEM picture of TiO$_2$ Powder 1

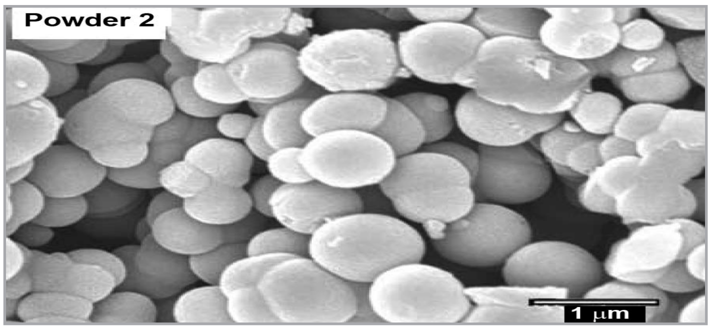

Figure 10: FESEM picture of TiO$_2$ Powder 2

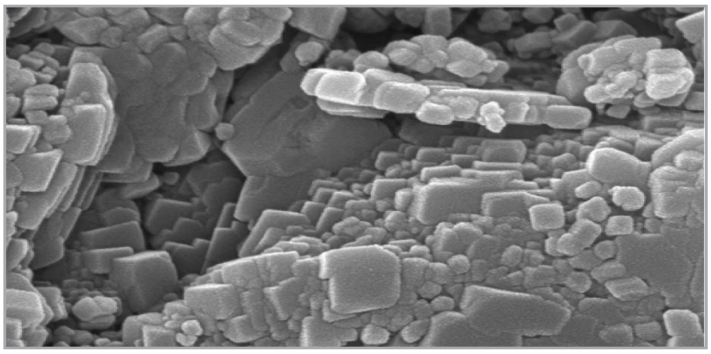

Figure 11: FESEM picture of white plaster cement

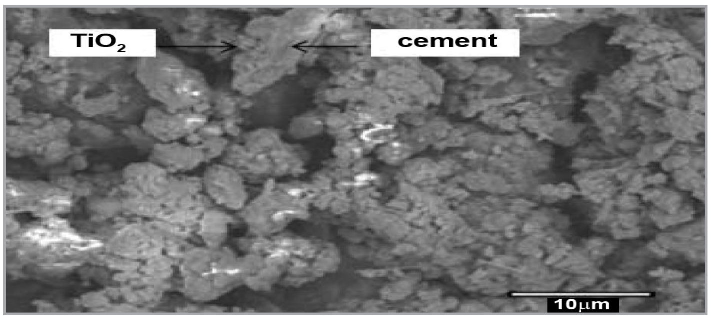

Figure 12: FESEM surface morphology of 30% of TiO$_2$ Powder 1 in cement

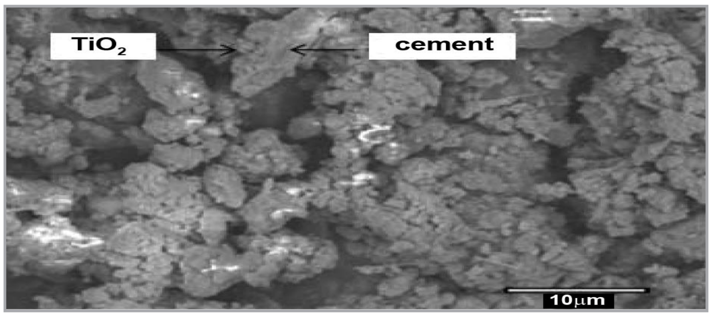

Figure 13: FESEM surface morphology of 30% of TiO$_2$ Powder 2 in cement

Powder 2 has large particles because of the rapid hydrolysis rate resulting from the large addition amount of water. The addition of water to the solution has accelerated the formation of powder particles without giving it enough time to produce the particles slowly.

Figure 11 shows the FESEM picture of pure cement. From the figure, the individual particle of white cement is in rectangular shape with flat surface. Figures 12 and 13 show the FESEM pictures of TiO$_2$ powders when mixed with white plaster cement. From the pictures, the TiO$_2$ powders were well-adhered to the cement's surface. This observation is important to make sure the TiO$_2$ powders are immobilised and distributed homogeneously on the cement surface to make sure the maximum amount of TiO$_2$ can take place in the photocatalytic process.

3.2 Photodegradation of Phenol using the Immobilised TiO$_2$ Powder

3.2.1 *Effect of Initial Concentration on Phenol Solution Degradation*

The photocatalytic of cement-bonded TiO$_2$ photocatalyst on phenol degradation was investigated for 7 hours by varying the initial concentration from 0.01, 0.03, 0.05, 0.07, and 0.10 *mg/mL*. Figures 14 and 15 show the graph of concentration *vs*. time on phenol degradation at various concentrations using the cement-bonded TiO$_2$ photocatalyst after being irradiated to UV light of intensity of 2.6 *mW/cm*^{2}.

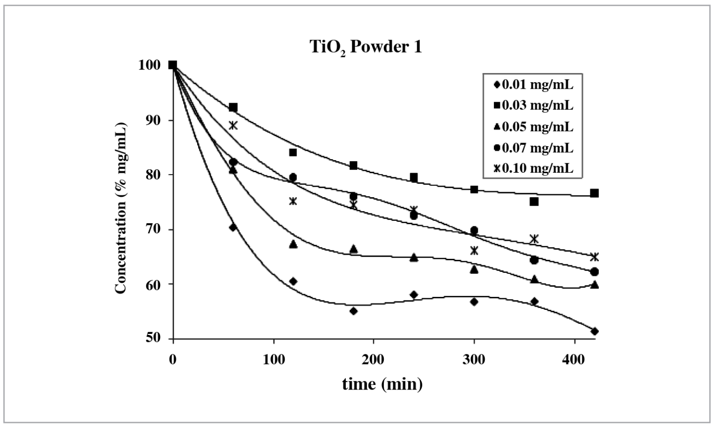

Figure 14: Effect of initial concentrations on phenol degradation using TiO$_2$ Powder 1

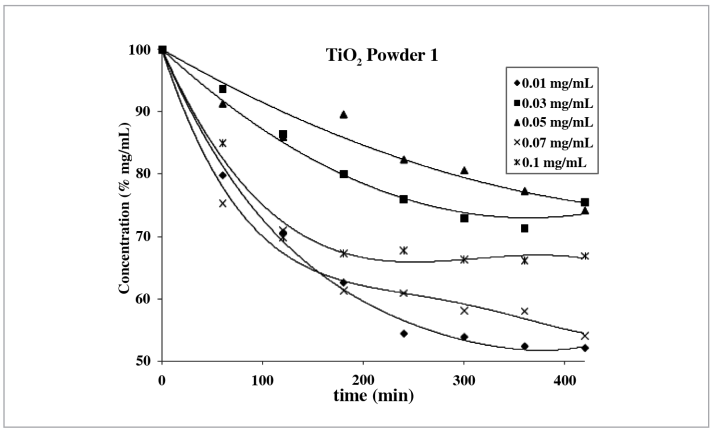

Figure 15: Effect of initial concentrations on phenol degradation using TiO$_2$ Powder 2

From the graphs, a decreased in the phenol photodegradation initial rate was observed with further increased in phenol initial concentration. As the initial concentration increased, more organic substance adsorbed on the catalyst's surface but the UV intensity and amount of catalyst loading were maintained constant. Therefore, due to the increased of the quantity of phenol solution, the generation of hydroxyl radicals would be lesser since there were fewer active sites for the adsorption of hydroxyl ions and the generation of hydroxyl radicals. Besides, when the phenol solution concentration increased, the photons would be able to be intercepted before they could reach the catalyst surface. Consequently, the photons absorption by the catalyst was reduced and led to the reduction of phenol degradation rate [24]. Therefore, 30% of TiO_2 Powder 1 and 2 in cement performed the fastest photodegradation rate when phenol in solution initial concentration was 0.01 *mg/mL.*

3.2.2 Effect of UV Intensity on Phenol Solution Concentration

The effect of UV intensity on phenol photodegradation was investigated for 7 hours with the initial concentration of phenol solution was selected as 0.01 *mg/mL*. The UV intensity was varied from 0.5, 0.7, 1.0, and 2.6 *mW/cm*^{2}.

Figures 16 and 17 represent the graphs of the effect of light intensity on phenol degradation using cement-bonded TiO_2 photocatalyst of Powder 1 and 2. As the amount of light intensity increased, the rate of phenol degradation was also increased with time. The increased of phenol degradation rate with the increased of UV light intensity was due to the amount of photons in the system. At low intensity, the amounts of photons were lesser and as the UV intensity increased, photons would be generated more in the system leading to higher reactive species generation and contributed to more destruction of phenol. Laoufi *et al*. (2008) [25] also proved that higher catalyst activity occurred under high light incident intensity.

Another experiment was carried out to compare which cement-bonded TiO_2 photocatalyst gives better photocatalytic performance under all the optimum conditions evaluated from the previous experiments. The initial concentration of phenol solution and UV intensity were fixed at 0.01 *mg/mL* and 2.6 *mW/cm*^{2} respectively. From Figure 18, it can be observed that Powder 1 has higher degradation rate than Powder 2 for the first 3 hours. This is due to the small particle size of Powder 1 that capable of adsorbing more pollutants on its surface compared at the early stage of degradation. Then, the degradation rate started to become constant for TiO_2 Powder 1. As for TiO_2 Powder 2, initially, it has slower photocatalytic rate compared to Powder 1. After several hours, its photoactivity started to accelerate and performed better photocatalytic activity than Powder 1. The higher crystallinity possessed by Powder 2 has led to faster charge separation and producing more photons to generate more hydroxyl radicals and accelerate the degradation of phenol molecules.

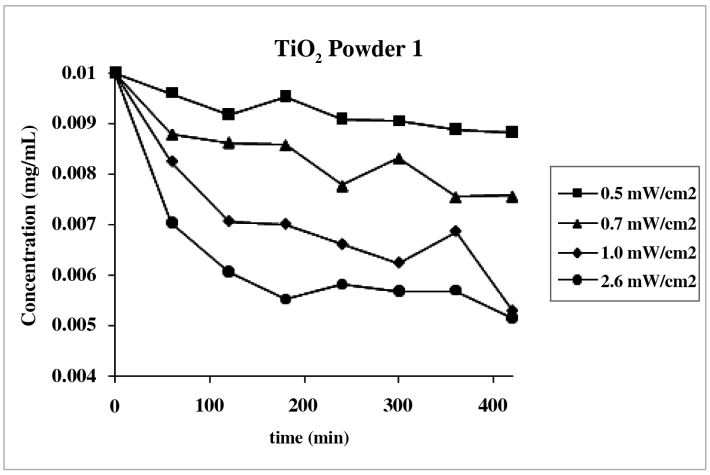

Figure 16: Effect of UV intensity on phenol degradation using TiO_2 ***Powder 1***

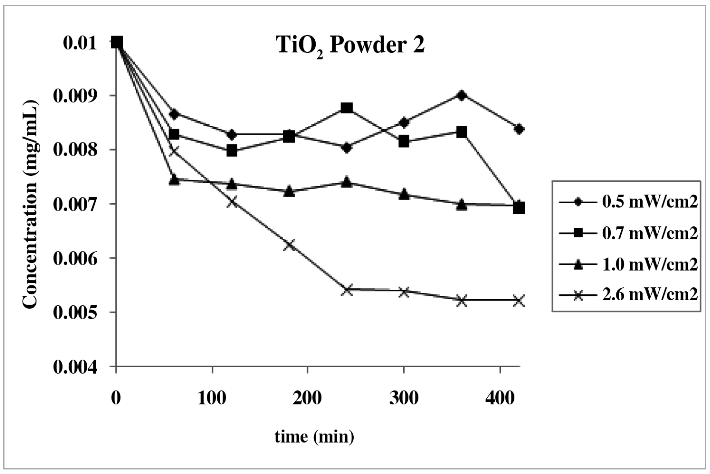

Figure 17: Effect of UV intensity on phenol degradation using TiO_2 ***Powder 2***

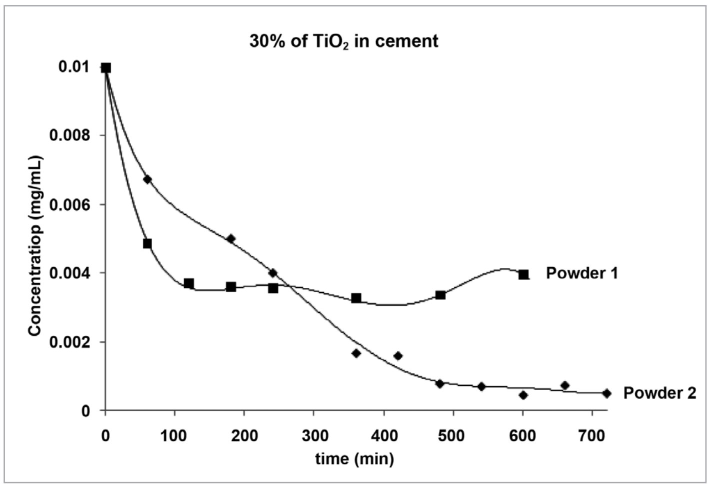

Figure 18: Graph of Concentration vs. time on phenol degradation using cement-bonded TiO_2 ***Powder 1 and 2***

TiO_2 Powder 2 managed to degrade 97% of phenol solution in 12 hours while TiO_2 Powder 1 degraded only 60% phenol molecules in the solution. Theoretically, TiO_2 powder with smaller particle size is favorable as it can enhance the photodegradation rate of the organic molecules due to its higher surface area. More pollutant molecules can be adsorbed on its surface to be converted into carbon dioxide and water. However, in this work TiO_2 Powder 2 performed better photocatalytic performance even though it has bigger particles than Powder 1. It can be concluded that TiO_2 Powder 2 higher crystallinity has played major role in the photocatalytic process which compensated its bigger particles. Hence, this work has proven that higher crystallinity TiO_2 powder is also desirable as it can produce more charge carriers at the photocatalyst's surface to accelerate the degradation of phenol molecules.

6.0 CONCLUSIONS

Two types of TiO_2 powder photocatalyst with water/TPT mol ratios of 1 (Powder 1) and 2 (Powder 2) have been synthesized via sol-gel method. TG/DTA results revealed TiO_2 Powder 1 crystallised at higher temperature than Powder 2 due to its smaller particles size that needed higher temperature to crystalline compared to TiO_2 Powder 2. XRD results showed that both TiO_2 powders are purely anatase crystal structure with TiO_2 Powder 2 has higher crystallinity than Powder 1. FTIR spectra confirmed that the Ti-O bond for the synthesized powder existed at the band of 394 cm^{-1}. Surface area of TiO_2 Powder 1 and 2 was recorded as 24.8 m^2/g and 14.6 m^2/g respectively. Particle size of each powder when measured with particle sizer was 118 *nm* for Powder 1 and 167 *nm* for Powder 2. From the FESEM analysis, both TiO_2 powders have spherical shape. TiO_2 Powder 2 has bigger particles than Powder 1 due to a very progressive hydrolysis rate during the synthesis process. Surface morphology analysis on cement-bonded TiO_2 photocatalyst showed that the TiO_2 powder particles were well-adhered to the white plaster cement's surface. From the 12 hours test of the phenol photocatalytic degradation, cement-bonded TiO_2 Powder 2 managed to reduce phenol concentration by 97% compared to only 67% by TiO_2 Powder 1. TiO_2 Powder 2 high crystallinity compensated its bigger particles to produce more charge carriers at the catalyst's surface to accelerate the phenol degradation.

ACKNOWLEDGEMENT

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