

# **DEVELOPMENT OF SUPPORTED TiO<sub>2</sub> PHOTOCATALYST BASED ADSORBENT FOR PHOTOCATALYTIC DEGRADATION OF PHENOL**

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## **ABSTRACT**

The presence of harmful organic compounds such as phenols and their derivatives in water supplies and from industrial effluents is a topic of global concern. In recent years, it has received considerable attention as an alternative for treating industrial waste water. Photocatalysis is an emerging promising technology as it will completely oxidize harmful organic compounds present in the waste stream without leaving behind any hazardous residues. In the present study, photocatalytic degradation of phenol was investigated using supported TiO<sub>2</sub> photocatalyst based adsorbent as a semiconductor photocatalyst in a batch reactor. The synthesized photocatalyst composition was developed using TiO<sub>2</sub> as photoactive component and zeolite as the adsorbents, all supported on silica gel using colloidal silica gel binder. The project included the search for the optimum composition of the supported catalyst and to study the reusability of prepared catalyst. The optimum formulation of supported catalyst was found to be (TiO<sub>2</sub>:ZSM-5:silica gel:colloidal silica gel=5:3:5:3) which gave the highest efficiency with 98% degradation of 50 mg/L phenol solution in six hours. The supported TiO<sub>2</sub> was found to be stable for repeated use.

**Keywords:** Photocatalysis; Phenol; Supported TiO<sub>2</sub>; Adsorbent; Binder

## **INTRODUCTION**

The release of those phenols and their derivatives in the environment is an ever increasing problem for the global concern. Due to their high solubility and stability in water, it is an onerous process to treat phenolic water to innocuous levels for many biological and chemical processes. Conventional water treatment technologies such as solvent extraction, activated carbon adsorption, and chemical treatment process such as oxidation by ozone (O<sub>3</sub>) often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method [1,2]. Due to these reasons, considerable attention has been focused on complete oxidation of organic compounds to harmless products such as CO<sub>2</sub> and H<sub>2</sub>O by the advanced oxidation process (AOP) and appears as the most emerging promising technologies. A great deal of attention has been devoted to titanium dioxide (TiO<sub>2</sub>) for use as photocatalysts due to the stability of its chemical structure, biocompatibility, physical, nontoxicity, low cost and it possesses high oxidizing power [3,4]. However, from an engineering point of view the immobilization of TiO<sub>2</sub> onto support is preferable compare to the slurry system as to avoid costly and difficult separation and the recycling of the photocatalyst [5,6]. Among the various supports, silica gel is very promising as a support, since it has been used widely in the industry and it possesses good light transmission and adsorption of pollutants [7].

Nevertheless, there are problems that limit the TiO<sub>2</sub> photocatalysis potential as wastewater treatment. According to Haque *et. al.* [8], the requirement for near UV light and a high energy is required to drive lamps as the intrinsic quantum yields of titania are low. We attempt to solve these problems by dispersing TiO<sub>2</sub> onto a good adsorbent, since reactions predominantly occur on the surface. The adsorbents collect pollutants, even in the dark to the photocatalyst surface, which reducing the requirement of a high energy [9-11]. Among the various adsorbents, zeolite (ZSM-5) has been chosen for the several reasons: its unique Al-O units in zeolite framework are the photocatalytic active sites, it can delocalize band gap excited electrons of TiO<sub>2</sub>, thus reduce electron-hole recombination process on the surface and adsorption of intermediates [12,13].

With this goal in mind, special attention was given in this research in order to obtain the optimum composition of each component in this supported catalyst and to study the reusability of prepared catalyst. The prepared catalyst consists of the mixture of ZSM-5 and TiO<sub>2</sub> supported onto the silica gel using colloidal silica gel as binder.

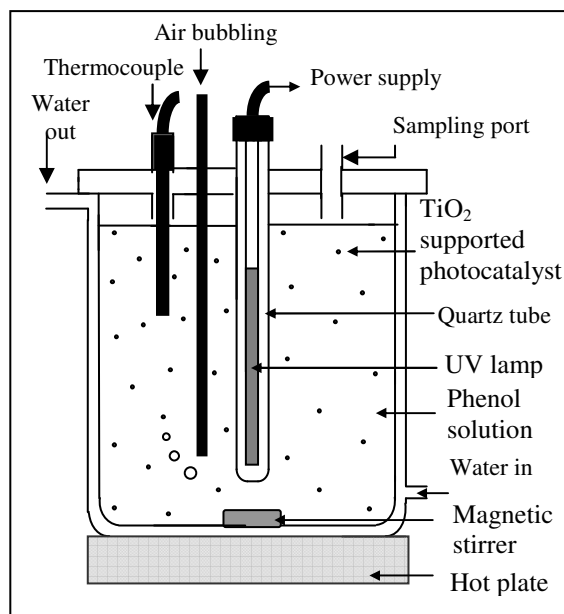
## MATERIALS AND METHODS

**Materials.** Phenol ( $\geq 99.5\%$ ) was selected as a model organic compound in the present study. It was purchased from Fisher Scientific and used as received. Powdered particles of Zeolite ZSM-5 (425 m<sup>2</sup>/g and Si/Al= 23) was purchased from Zeolyst International was treated by calcined at 500 °C for an hour. Silica gel with a particle size of 0.2-0.5 mm was purchased from Acros Organic. Colloidal silica gel (30 wt. % silica suspension in water) was purchased from Sigma Aldrich and used as received. For the preparation of the TiO<sub>2</sub>, Titanium (IV) Isopropoxide (TTIP, 98 %) and ethanol (C<sub>2</sub>H<sub>5</sub>OH 95 %) were purchased from Acros Organic and TiO<sub>2</sub> Degussa P25 powder (50 m<sup>2</sup>/g; 15-30 % rutile + 85-70% anatase) was purchased from Degussa, Germany. All the solutions were prepared using deionized water from Milli-Q system and controlled by its resistivity (18.2 MΩ).

**Preparation of Catalyst.** TiO<sub>2</sub> nanoparticle was synthesized using sol-gel method as reported [14]. A mixture of 1 TTIP:2 C<sub>2</sub>H<sub>5</sub>OH:5 H<sub>2</sub>O was prepared for the sol-gel solution. A solution of TTIP in ethanol was prepared with molar ratio TTIP/C<sub>2</sub>H<sub>5</sub>OH = 1/2. The solution was stirred at room temperature for an hour. Subsequently water was added drop by drop under vigorous stirring. A molar ratio of H<sub>2</sub>O/TTIP = 5 was used. The gel obtained was dried at 80°C for 24 hours. The modified sol-gel solution was prepared by addition of a calculated amount of TiO<sub>2</sub> Degussa P25 to the sol solution before dried in the oven at 80°C for 24 hours. The powder was added slowly with vigorous stirring to prevent the formation of agglomerates. The TiO<sub>2</sub> obtained then was immobilized according to literature method [8]. A known weight of TiO<sub>2</sub> and ZSM-5 were mixed in the appropriate amount of colloidal silica gel. A known weight of silica gel then magnetically stirred into the mixture for about 30 minutes. The mixture was dried at ambient conditions and then dried in the oven at 100°C. The granules obtained were gently crushed and screened, followed by washing with deionized water for several times. After the impregnation process have finished, the catalyst was calcined in the furnace at 600°C for three hours.

**Experimental set up.** Figure 1 shows the schematic diagram of the experimental set up. The batch photocatalytic reactor consists of a pyrex glass jacketed reactor with dimensions of 23 x 10 cm x 8 cm (height x outside diameter x inside diameter) and at the top portion has ports for sampling, gas purging, thermocouple and UV lamp. The lamp and reactor were placed inside a wooden box painted black so that no stray light can enter the reactor. The reactor was placed on a magnetic stirrer for thorough mixing. A 15 W low pressure mercury lamp (PCQ lamp,

UVP, Inc) was located in the center of the reactor. A 1 cm diameter of quartz tube protected the lamp from solution contact. In order to conduct experiments at the controlled temperature and protect the lamp from overheating, the reactor was surrounded with a cooling jacket and a fan.



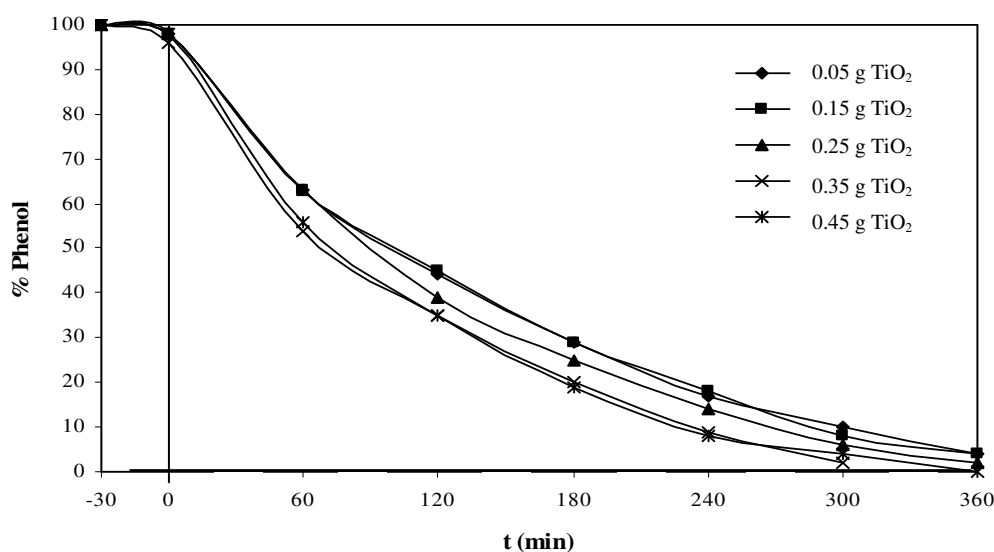
**Figure 1: Schematic Diagram of Batch Photocatalytic Reactor (cross section view).**

**Photocatalytic Degradation of Phenol.** An aqueous suspension of phenol (50 mg/l, 500 ml) containing the required quantity of supported photocatalyst was stirred for about 30 min in the dark to reach the adsorption/desorption equilibrium, followed by UV lamp illumination for degradation of phenol. During experiments, air was bubbled into the phenol solutions at a constant flow rate of 2 ml/min. This is the cheapest and simplest way to supply a sufficient amount of oxygen (O<sub>2</sub>) into the photocatalytic reactor. All reaction was carried out at atmospheric pressure and at room temperature. A base supported catalyst composition consisting of mixture of TiO<sub>2</sub> and ZSM-5 supported on silica gel using colloidal silica gel as binder (TiO<sub>2</sub>:ZSM-5:silica gel:colloidal silica gel=1:1:1:2) was used as reference point in order to evaluate the optimum loading for each of the catalyst component. Samples of the suspension were removed at specific time intervals for analysis. The residual phenol concentration was monitored using a high-performance liquid chromatography (HPLC). The HPLC system used in the experiment comprised of Perkin-Elmer UV/VIS 200 HPLC Detector, a Luna 5 μm C18 (2) 100A column and a Perkin-Elmer 200 HPLC pump with an injector port. The mobile phase in this HPLC system consisted of 40 % acetonitrile and 60 % deionized water. The flow rate was adjusted to 1 ml/min. Full loop injection at 20 μL was conducted and the retention time of phenol was 3.81 min. Before HPLC analysis, all samples were filtered using WHATMAN filter (PTFE-membrane, 0.45 μm).

## RESULTS AND DISCUSSION

**Optimum Composition of Supported Photocatalyst.** Selection of optimum catalyst composition is important in order to minimize excess of catalyst and for economic effect. Thus, each component loading in the supported photocatalyst were investigated.

**TiO<sub>2</sub> Loading.** Experiment was carried out with different TiO<sub>2</sub> loading; 0.05 g, 0.15 g, 0.25 g, 0.35 g and 0.45 g, at fixed phenol concentration (50 mg/L). It was believed that increased in TiO<sub>2</sub> loading, the photodegradation rate should be increased as well, owing to the higher holes and hydroxyl radicals were generated. However, it remains almost constant beyond certain level as shown in Figure 2. This performance is due to the fact that number of photons absorbed and the number of phenol molecules adsorbed were increased as the amount of TiO<sub>2</sub> loading increased. After above a certain level, excess of TiO<sub>2</sub> particles occur. Thus, the UV light penetration was hindering by photocatalyst itself [15,16]. Besides, as the TiO<sub>2</sub> loading increase, it could cause greater aggregation of TiO<sub>2</sub> particles on the catalyst surface. Hence, reducing the specific surface area, consequently reduces the photodegradation efficiency.

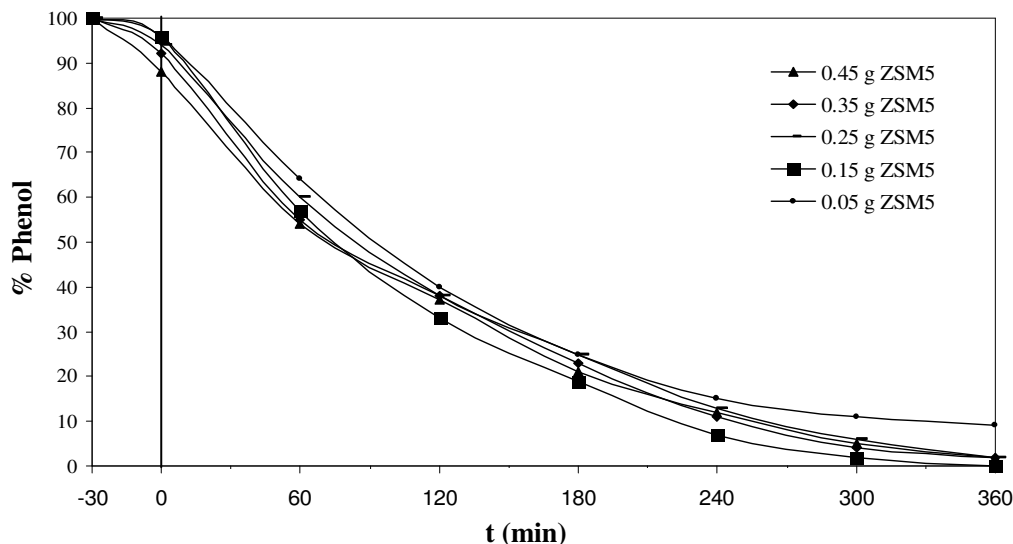


**Figure 2: Degradation of Phenol at different TiO<sub>2</sub> Loading. Conditions: Air Flow Rate=2 L/min, Initial Concentration=50 mg/L).**

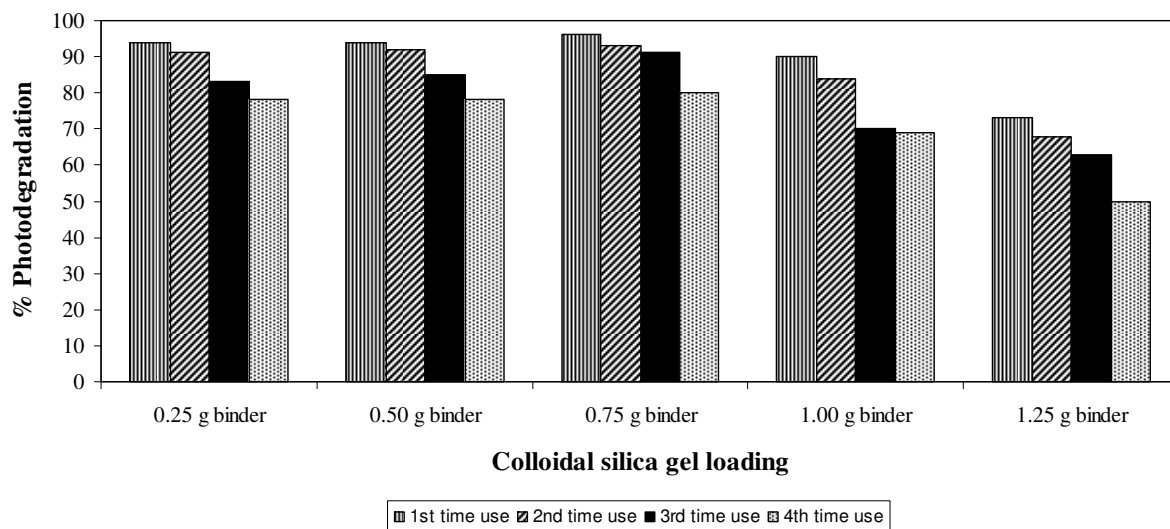
**Adsorbent Loading.** The composition of adsorbent loading were varied from 0.05 g, 0.15 g, 0.25 g, 0.35 g to 0.45 g of ZSM-5. Figure 3 shows that 0.15 g of ZSM-5 exhibits the optimum adsorbent loading. At first 30 min in the dark, increase in the ZSM-5 loading will lead to increase in phenol degradation. After the illumination of UV lamp, the photodegradation take place which indicates that increase the addition of ZSM-5 over 0.25 g will reduce the degradation of phenol. Degradation of phenol become slower since the surface of ZSM-5 increase, thus increase the diffusion pathway for phenol molecules [17].

**Binder Loading.** One approach to immobilize the photocatalyst is by a binding method. The important needs for binder is it possess a good adherence between the catalyst and support over a prolonged period of time without losing its photocatalytic activity. According to the result studied by Haque *et.al.* [8], colloidal silica gel binder exhibits the best contaminant degradation efficiency. Figure 4 demonstrates the reusability of the prepared catalyst on the different amount of colloidal silica gel binder obtained after four experimental runs. After each run, it was observed that the color of the supported catalyst turned to dark brown. The change in color of photocatalyst is due to the accumulation of intermediates on the active sites of TiO<sub>2</sub> surface [18]. Hence, attribute to the reducing of photocatalytic activity in reuse catalyst. The result in Figure 4 indicates that the reusability of the supported catalyst with 0.25 and 0.50 g colloidal silica gel can almost execute as well as that with 0.75 g colloidal

silica gel. Nevertheless, increase the amount binder beyond that limit cause the decreasing in the photocatalytic activity. Since the result revealed that the photocatalytic activity among 0.25 to 0.75 g of colloidal silica gel are slightly differ each other, 0.25 g amount has been chosen as an essential aspect of the cost effectiveness.



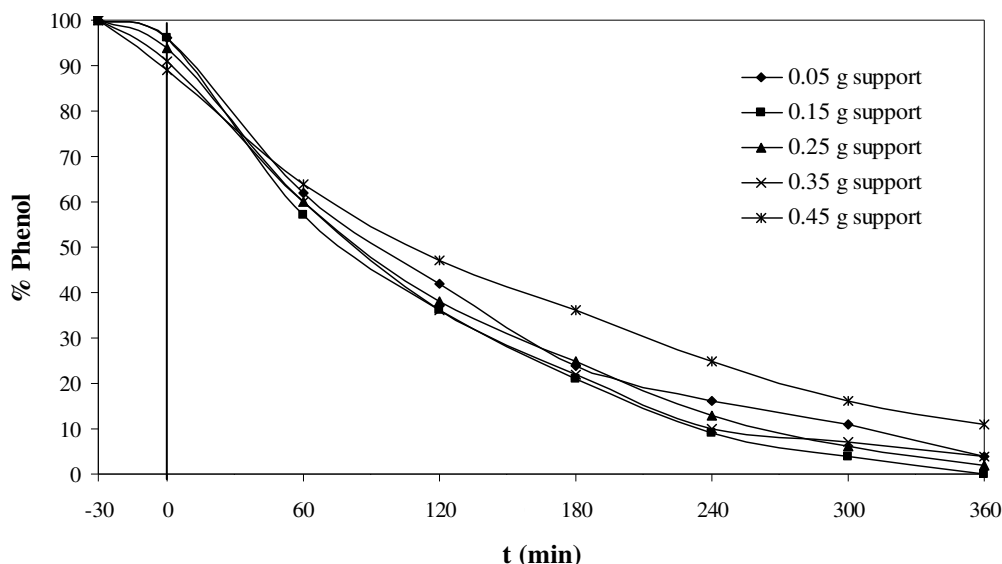
**Figure 3: Degradation of Phenol at different Adsorbent Loading. Conditions: Air flow rate=2 L/min, Initial concentration=50 mg/L).**



**Figure 4: Comparison of Photocatalytic Activity of Supported Catalyst at different Loading of Binder for four times used. Conditions: Air Flow Rate= 2 L/min, Initial Concentration=50 mg/L)**

**Support Loading.** To evaluate the effect of support loading on the degradation of phenol, several kinds of catalyst were prepared; 0.05 g, 0.15 g, 0.25 g, 0.35 g and 0.45 g silica gel was used. The other compositions were fixed with the base supported catalyst composition. According to the Figure 5, the adsorption of phenol on the catalyst in the dark increased with the increase of silica gel content in the catalyst. However, under the illumination, increase the

silica gel loading lead to the improvement in of the phenol degradation until it reaches an optimum level at 0.15 g silica gel. Further addition of silica gel decreases the phenol degradation. Silica gel also possesses the adsorption ability of the contaminant [7]. This is also consistent with our earlier report in the adsorbent loading section that increase in the adsorption will lead to the decrease in the photocatalytic degradation.



**Figure 5: Degradation of Phenol at different Support Loading. Conditions: Air Flow Rate=2 L/min, Initial Concentration=50 mg/L)**

## CONCLUSIONS

TiO<sub>2</sub> supported photocatalyst was successfully synthesized using the sol-gel method. The performance study of the synthesized photocatalyst under UV irradiation was performed in a batch reactor for the degradation of phenol. A series of experiments were conducted to investigate the optimum composition for each component in this catalyst. The optimum formulation for the synthesized photocatalyst which consist the mixture of TiO<sub>2</sub> and ZSM-5 supported on silica gel using colloidal silica gel as binder was found to be (TiO<sub>2</sub>:ZSM-5:silica gel:colloidal silica gel=5:3:5:3). After four times of repeated use, the system showed only a slight decrease in activity. Therefore, the supported photocatalyst synthesized in this study have been proven to be stable for repeated usage.

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