

The Comparison of Toluene Removal Rate in Two Photocatalytic Oxidation Systems of ZnO and TiO₂ Nanoparticles on SiO₂ bed

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ABSTRACT

Volatile organic compounds (VOCs) are one of the main group of air pollutants. Photocatalytic oxidation is one of the destructive methods for gaseous pollutants and has been received more attention in the past years. In this study investigated the comparison of the toluene removal efficiency by Photocatalytic Oxidation of Toluene by ZnO/SiO₂ and TiO₂/SiO₂. In this study, the effect of parameters such as the amount of relative humidity, initial concentration of pollutant, the apparent speed of gas and the minimum speed of fluidizing of bed on the process of photocatalytic oxidation of Toluene is examined by comparison between TiO₂/SiO₂ and ZnO/SiO₂ catalysts in a fluidized bed reactor. as it was explained, by absorption of water molecules on the surface of the catalyst and converting them to hydroxyl active radicals, these radicals act as a pushing factor in the reaction. The study also showed that an increase in the relative humidity in the 15–45% range would increase the efficacy of toluene oxidation. Conversion percentages between TiO₂/SiO₂ and ZnO/SiO₂ catalysts were not significantly different ($p > 0.05$), while the reaction rate of ZnO/SiO₂ catalyst was higher than TiO₂/SiO₂ catalyst ($p < 0.05$). In the study of the interaction between the apparent velocity variables, initial concentration of toluene and loading of zinc oxide and titanium dioxide, only the interaction between two gas velocity variables and initial concentration of toluene was significant. The results showed that ZnO/SiO₂ catalysts generally have a larger efficacy than TiO₂/SiO₂, presumably because ZnO/SiO₂ has more active sites. Additionally, the ZnO/SiO₂ catalysts offer better fluidity than TiO₂/SiO₂. The photo catalytic transformation rate of the pollutant is relatively low, as the optimum humidity level for appears to be 45%.

Keywords: Photocatalysis; Toluene; ZnO/ TiO₂; TiO₂/SiO₂; Fluidized bed Reactor

INTRODUCTION

Today, volatile organic compounds have become abundant in industrial and household sectors, harming the environment and causing air pollution. Volatile organic compounds released from industrial activities, such as petrochemical processing and refining, food processing, dyeing, and printing, could be a hazard to human health and the environment. Toluene, one of the volatile aromatic Compounds that are in the BTEX group mainly used as a reaction solvent and a paint thinner, is controlled under the stringent exhaust emission regulations [1]. People can be exposed to toluene in workplaces via inhaling, ingesting, or skin contact. Therefore, control of such volatile organic compound release to the environment is imperative for public safety [2].

Absorption of gaseous air pollutants by activated charcoal is one of the most common methods used in controlling air pollution. However, this method has shortcomings; namely, absorbent saturation and difficulty in reactivation [3,4]. The photocatalytic oxidation process can be used as an alternative to the absorption by activated charcoal, but the lack of

adequate studies on the efficiency of photocatalytic oxidation has prevented its widespread industrial application [5].

In previous photocatalytic oxidation studies, TiO₂ and SiO₂ were abundantly used because of their high photocatalytic efficiency, low cost, and non-toxicity [6]. In TiO₂-based photocatalysts, ultraviolet light (>388 nm) is used to overcome the energy difference between the capacity and conductivity and form electron-hole pairs [7]. The resulting electron-hole pairs participate in the reduction and oxidation reactions by forming hyperactive free radicals, e.g., hydroxyl radicals, which oxidize the volatile organic compounds into CO₂ and H₂O. Various factors, such as humidity and temperature, significantly influence the efficacy of the catalyst [8]. These factors are controllable reaction parameters in the bed reactors used [9].

In the study of Prieto and *et al.* showed that the photocatalytic particles used were prepared by mixing TiO₂ (Degussa P25) and starch in a methanol solution. The XRD and SEM results of these aggregates confirm the titanium dioxide (Degussa P25)

characteristics, such as the presence of anatase on the particle surface and spongy and wrinkled morphology. Toluene concentrations varied from 0.9 to 199ppm, and all the experiments were carried out with a flow rate of 300NL/h. Toluene conversions from 77% to 100% were obtained in the range studied. In this work, the regeneration processes of deactivated TiO_2 photocatalysts have been investigated using FT-IR and GC/MS techniques [10].

In contrast to the commonly used fixed bed reactors that require the photocatalyst particles to be placed on the reactor wall [11], we utilize a fluidized bed reactor in which catalysts are embedded in the silica gel support. The application of titania on Silica gel bed could combine pollutants' adsorption and their photocatalytic degradation [12].

Alumina gel or activated charcoal has also been used as an alternative to the silica gel support [12].

In the current study, we explore the photocatalytic oxidation of toluene by TiO_2 and ZnO and compare the efficacy of toluene removal by these two photocatalysts.

MATERIALS AND METHODS

TiO_2 (P25) and ZnO powders (Degussa; Germany) were used for photocatalytic oxidation reactions. Silica gel particles and toluene with the purity of 99.99% were used as the photocatalyst substrate (Merck; Germany). The immersion method was used to prepare ZnO/SiO_2 and $\text{TiO}_2/\text{SiO}_2$ catalysts [13]. ZnO and TiO_2 powders (Degussa; Germany) were dissolved in distilled water using the ultrasonic bath for 20 min. Then, the silica gel substrate was added to the containers with TiO_2 and ZnO solution and kept in the ultrasonic bath for 45 additional min. The rate of activation was a function of exposure time with pure air and UV radiation. The maximum activation achieved at 100°C after 24-hour exposure. An electric oven was used to calcify the catalysts by applying a thermal gradient of $10^\circ\text{C}/\text{min}$, maintaining the temperature at 400°C for 2 h. we used 0.2g TiO_2 or ZnO for every gram of silica to ensure 20 wt% of the photocatalyst.

In the photocatalytic oxidation of volatile organic compounds in a fluidized bed reactor, variables such as the relative humidity (5 level including: %15, %30, %45, %60, %75), initial concentration of the pollutant (100-1000ppm), superficial gas velocity (0-2.4cm/s), and amount of catalyst loading on substrate influence the efficacy of the catalyst (6 Fixed Weight). Herein, we systematically explore the catalysts' efficacies as a function of these variables. Fig. 1 illustrates the scheme of the fluidized bed reactor made of a glass cylinder with an internal diameter of 40 mm and the height of 100mm. A 15-W UV lamp is embedded at the center of the cylinder with four

additional lamps symmetrically placed on the external wall of the reactor. In order to determine the minimum fluidization velocity (U_{mf}) of the catalyst, pressure drops across 1-m deep beds were subjected to a superficial gas velocity. A grid screen was used to properly distribute the air in the reactor. The concentrations of toluene (100–800ppm) and relative humidity (15–75%) were varied by passing air through impingers (Fig. 1) containing toluene and water. The inlet (C_{in}) and the outlet (C_{out}) toluene concentrations were measured using Frost Check and gas chromatography apparatuses.

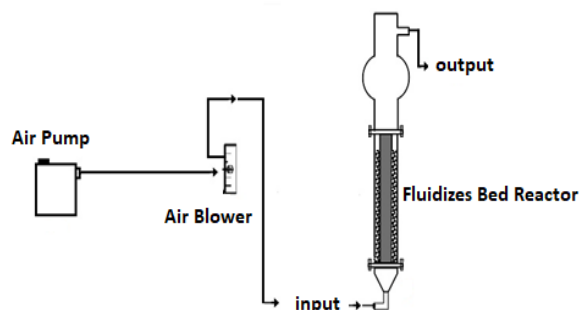


Fig. 1: Scheme of the fluidized bed reactor accompanied by the sample preparation system

The GC-MS analysis was performed using an HP 5MS column (cross-linked 5% methyl phenyl silicone, 30m x 0.25-mm i.d., 0.25-mm film thickness). The column oven temperature was initially held at 70°C for 2 min, then programmed to reach 230°C at a rate increase of $20^\circ\text{C}/\text{min}$ and held for 2 min. The total run time was 12 min. The temperatures of the injector port and the interface were set at 250°C and 280°C respectively. The carrier gas (helium) flow rate was 1mL/min. The ionization energy was set at 70eV .

RESULTS

In order to characterize catalysts, X-ray differentiation of ZnO was carried out to determine the crystalline structure of photocatalysts. Table 1 shows the size of the crystallite as a function of calcination temperature. The results indicate that the size of the crystallite increases with the increase in calcination temperature.

Table 1: Size of ZnO crystallites based on XRD evaluations

| Calcination temperature ($^\circ\text{C}$) | Crystallite size, D (nm) |
|--|--------------------------|
| 300 | 64 |
| 500 | 74 |
| 700 | 131 |
| 900 | 187 |

We also reported the X-ray differentiation pattern of TiO_2 (P25) in Fig. 2, which indicates that the TiO_2 catalyst also has a crystalline structure.

The 2θ angles of 25.3° and 27.4° in the XRD pattern indicate the anatase and rutile transformation phases in the TiO_2 catalyst (Fig. 2).

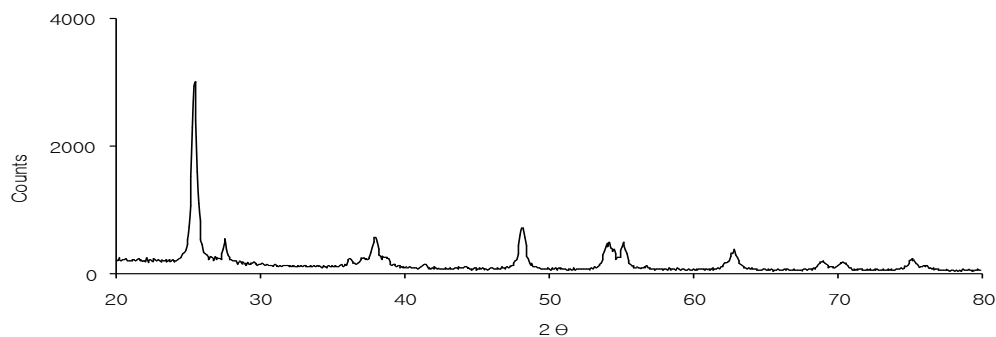


Fig. 2: X-ray diffraction pattern of TiO_2 (P25)

After placing the photocatalysts on the silica gel substrate, micrographs of the surface structures were obtained from scanning electron microscopy (SEM),

which show that the photocatalysts form a layer above the silica gel support (Fig. 3).

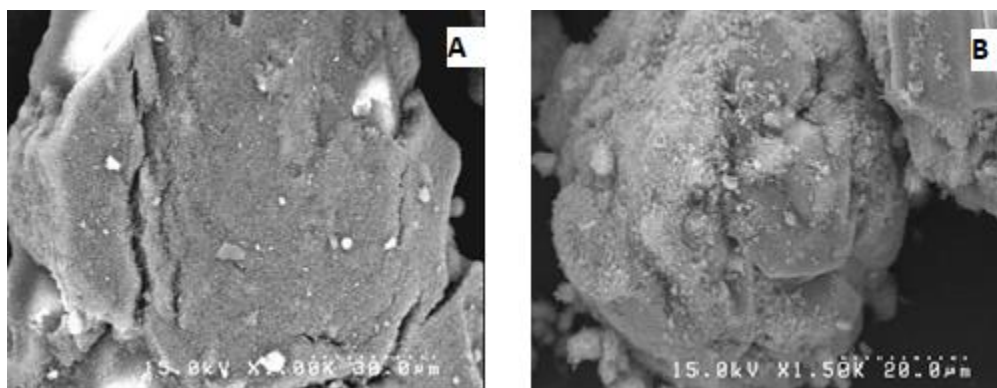


Fig. 3: SEM image of ZnO/SiO_2 (A) & $\text{TiO}_2/\text{SiO}_2$ (B)

Superficial gas velocity is one of the important variables of fluidized bed reactors, and it is often expressed as the coefficient of the minimum fluidization rate. To determine the minimum fluidization rate in vitro, the bed pressure drop changes were monitored with different gas superficial velocities. The plot, illustrated as (Fig. 4) with pressure drop vs superficial gas velocity, provides the minimum fluidization rate of catalysts, which can be identified as a point at which changes in the superficial gas velocity causes no significant changes in pressure. In our measurements, the minimum fluidization rates were 0.7 and 1.35 cm/s for $\text{TiO}_2/\text{SiO}_2$ and ZnO/SiO_2 , respectively.

In the fluidized beds, the static height of the bed is expressed as the ratio (H/D) of bed height (H) and bed diameter (D). The static height of the bed has a direct influence on the pressure drop; in other words, the higher the stable static height of the bed is, the higher is the bed pressure drop. Figs. 5-1 and 5-2 show that the higher the static height of the bed had a similar trend of bed pressure drop for both $\text{TiO}_2/\text{SiO}_2$ and ZnO/SiO_2 catalysts, respectively.

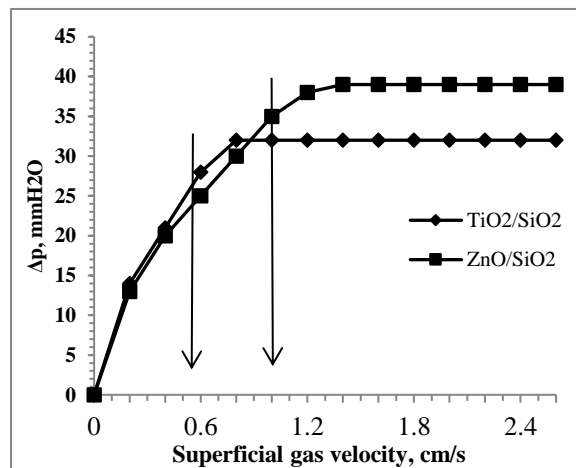


Fig 4: Determination of the minimum fluidization rate for ZnO/SiO_2 and $\text{TiO}_2/\text{SiO}_2$ catalysts in a stabilized static bed height ($H/D = 3$)

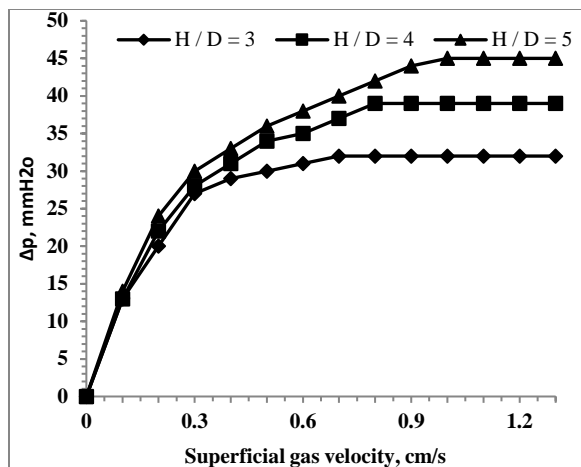


Fig. 5-1: Pressure drops as a function of superficial gas velocity on $\text{TiO}_2/\text{SiO}_2$ reactor beds of various static heights

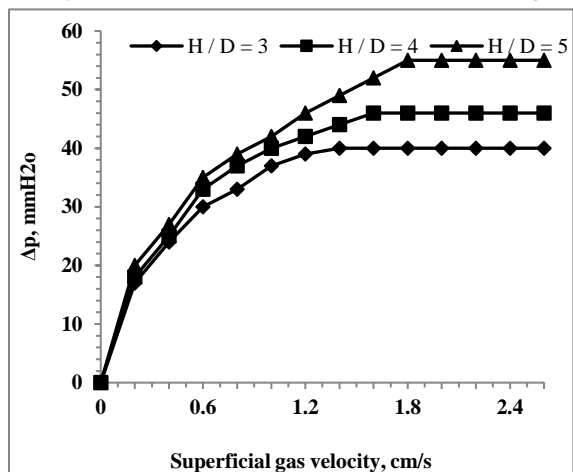


Fig. 5-2: Pressure drops as a function of superficial gas velocity on ZnO/SiO_2 reactor beds of various static heights. The catalytic efficiency in the photo-oxidation of 300ppm toluene in the air with relative humidity ranging from 15% to 75% was calculated. The results indicate that the maximum efficacy is achieved with relative humidity around 45%. With 15% relative humidity, the photocatalytic transformation rate of the pollutant is relatively low. Photo-oxidation in a relatively humid condition (60–75%) is also undesirable. The reduced photocatalytic oxidation rate in low humidity could be attributed to the reduction in hydroxyl radical formation, whereas high humidity could cause moisture absorption by the active sites leading to catalyst deactivation.

The rate of photo-oxidation also depends on the amount of catalyst loading. In (Fig. 6), the reaction rates are shown for three different concentrations of toluene and various catalyst loading amounts (5–20 wt). The oxidation reactions were carried out in 2 Umf in 45% humidity. The results show that the oxidation rate shows very little dependence on the catalyst loading when the toluene concentration is low

(100ppm), whereas the catalyst loading exerts a significant effect on the reaction rate at 700ppm toluene concentration. Furthermore, the oxidation rate due to ZnO/SiO_2 catalyst is higher for all measures, suggesting that ZnO/SiO_2 is a more reactive catalyst than $\text{TiO}_2/\text{SiO}_2$.

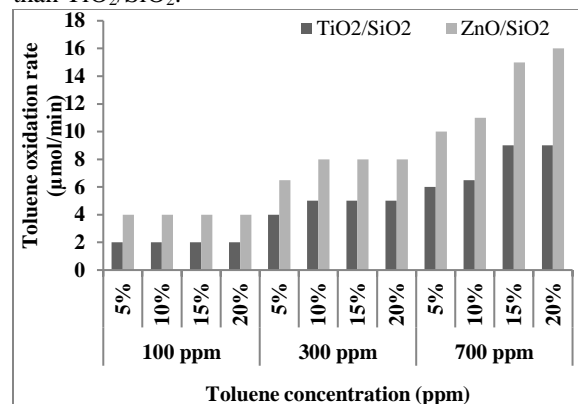


Fig. 6: Toluene photocatalytic oxidation rate by $\text{TiO}_2/\text{SiO}_2$ and ZnO/SiO_2 catalysts. Catalyst loading = 5–20 Wt%; toluene concentration 100–700ppm; gas superficial velocity=2 Umf; humidity = 45%, H/D =3

The dependence of toluene initial concentration (100–1000ppm) on the photocatalytic oxidation is collectively shown in Figs. 7-1, 7-2, 7-3 and 7-4. From these figures, it can be concluded that the increase in the initial concentration of toluene, from 100 to 1000ppm under stable conditions of relative humidity, reduces the photocatalytic transformation rate over time. This trend of decrease in performance over a long period suggests catalyst deactivation due to toluene concentration. The catalyst deactivation was less prominent in ZnO/SiO_2 than in $\text{TiO}_2/\text{SiO}_2$, suggesting that ZnO/SiO_2 could have relatively more active sites. Without catalyst deactivation, the rate of toluene conversion increases with increase in toluene concentration.

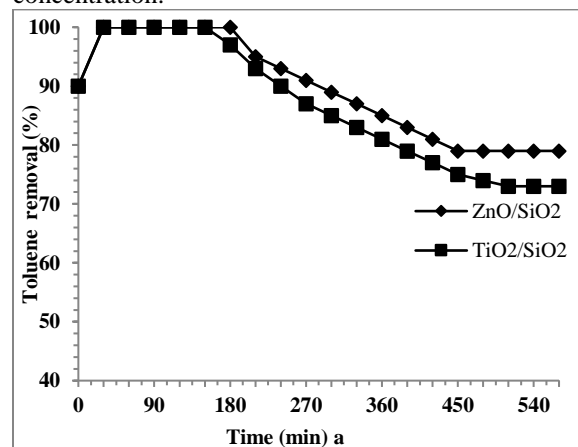


Fig. 7-1: Photocatalytic transformation of 100ppm toluene in the fluidized bed reactor by ZnO/SiO_2 and $\text{TiO}_2/\text{SiO}_2$, Relative humidity=45%; catalyst loading=20%; gas superficial velocity=2 Umf

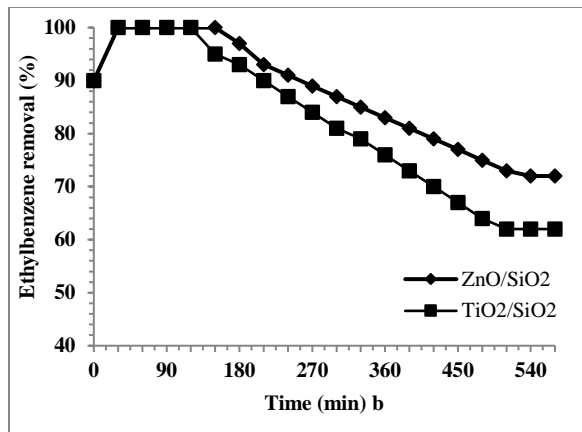


Fig. 7-2: Photocatalytic transformation of 300ppm toluene in the fluidized bed reactor by ZnO/SiO₂ and TiO₂/SiO₂. Relative humidity=45%; catalyst loading=20%; gas superficial velocity = 2 U_{mf}

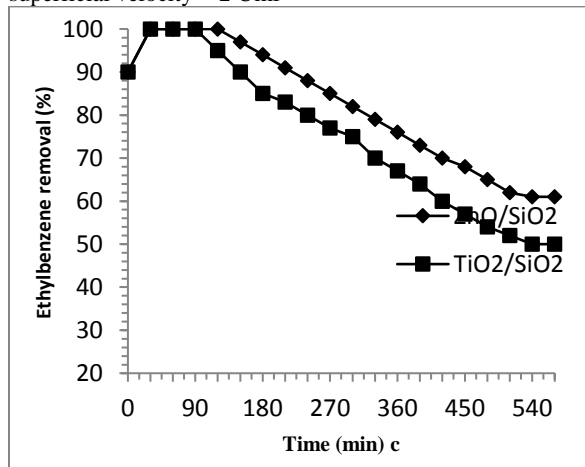


Fig. 7-3: Photocatalytic transformation of 700ppm toluene in the fluidized bed reactor by ZnO/SiO₂ and TiO₂/SiO₂. Relative humidity= 45%; catalyst loading rate on substrates=20%; gas superficial velocity = 2 U_{mf}

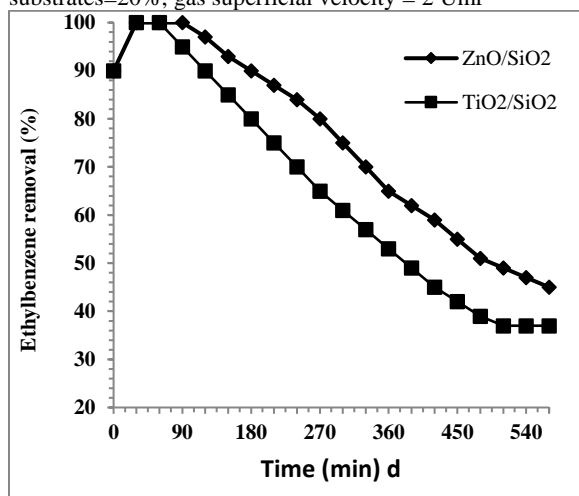


Fig. 7-4: Photocatalytic transformation of 1000ppm toluene in the fluidized bed reactor by ZnO/SiO₂ and TiO₂/SiO₂. Relative humidity = 45%; catalyst loading rate on substrates = 20%; gas superficial velocity = 2 U_{mf}

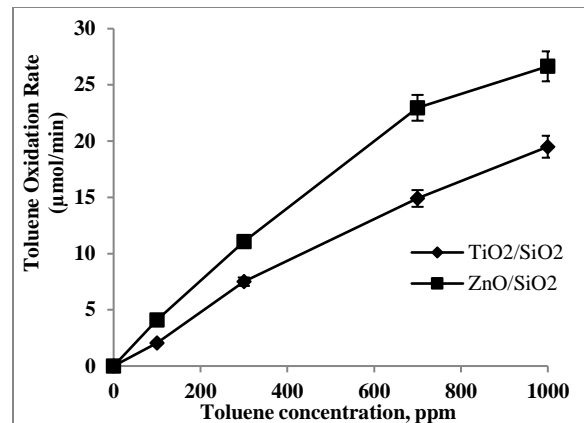


Fig. 7-5: Comparison of the photocatalytic oxidation rate of toluene for TiO₂/SiO₂ and ZnO/SiO₂

Fig. 8 shows the photocatalytic oxidation of 500ppm toluene with gas superficial velocities that are 1–4 times the minimum fluidization rate. The data indicate that the photocatalytic transformation rate does not decrease when the gas superficial velocity is two times the minimum fluidity value. However, a three or four-fold increase in the gas superficial velocity decreases the rate of transformation. Such trends were observed for both ZnO/SiO₂ and TiO₂/SiO₂ catalysts; however, the catalytic performance decreased much more prominently with TiO₂/SiO₂.

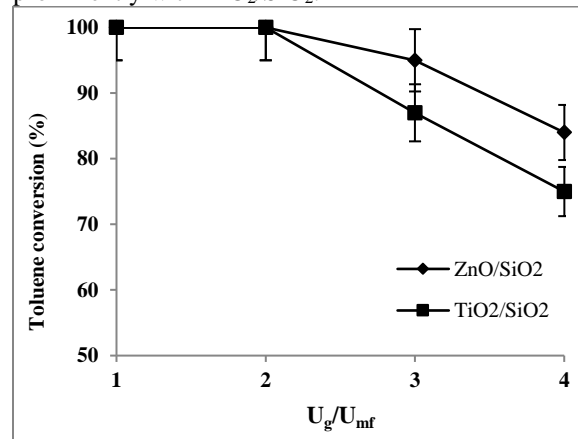


Fig. 8: Efficacy of 500ppm toluene removal for ZnO/SiO₂ and TiO₂/SiO₂. Relative humidity=45%; catalyst loading rate= 20%

DISCUSSION

The effect of various reaction variables on the photocatalytic oxidation of toluene has been compared for ZnO/SiO₂ and TiO₂/SiO₂ catalysts operating in a circular fluidized bed reactor. The evaluation of the humidity dependence revealed that the absorption of H₂O molecules on the catalyst surface produces hydroxyl radicals, which act as the reaction activating agent. The study also showed that an increase in the relative humidity in the 15–45% range would increase the efficacy of toluene oxidation, but more than 45%

relative humidity would decrease the efficacy. This is presumably because more competitive adsorption occurs between H₂O and toluene molecules at high relative humidity. This competitive binding to the active site could result in catalytic deactivation. Interestingly in the 10–50% humidity range, the differences in the photocatalytic oxidation rates relative to the optimum level (45%) are small, suggesting that toluene degradation is still practical in these conditions. A previous study on the photocatalytic degradation of toluene has shown that the optimum level of relative humidity is in the range of 30–45% [14, 15], which is consistent with the results presented here.

In this study, variations in the initial toluene concentration revealed that the catalytic efficacy reduces at high toluene concentrations. A notable feature in the catalytic efficacy reduction is that the ZnO/SiO₂ catalyst suffered less catalyst deactivation than the TiO₂/SiO₂ catalyst. In a similar study, Prieto *et al.* showed that an increase in the toluene concentration also inhibited the photocatalytic degradation and ZnO/SiO₂ offers higher efficacy than TiO₂/SiO₂ [10]. Dhada and coworkers also evaluated different photocatalyst coatings on adsorbent beds and indicated that ZnO catalyst shows good performance [16]. The results can be because of catalyst deactivation over time. This reduction in the catalytic efficacy can be attributed to the decrease in the active sites due to the high surface coverage of toluene. In other words, the active sites of the catalysts are saturated more rapidly in high toluene concentrations, which essentially inhibits further toluene transformations.

The overall effect of photocatalyst loading amount on the efficiency indicates that an extensive increase in catalyst mass solely cannot result in the reaction rate enhancement. Herman *et al.* have also indicated that excessive usage of photocatalyst mass is impractical, and a better strategy to improve the efficiency makes photon absorption by the catalysts easier [17, 18]. Here, the effect of photon absorption was not explored; nonetheless, the variation in the photocatalyst loading did not show significant changes in the catalytic efficiencies.

Evaluation of the effect of superficial gas velocity showed that in fluidized beds, the lower velocity means higher fluidity of beds. Huang has shown that a constant gas flow velocity prevents inertia in beds, and the fluidity of the bed remains unperturbed [19]. According to studies, The probability reason can be an improvement of contacts between the reactant gas and the dense phases in a fluidized bed, which could ultimately increase the catalytic efficacy [20].

Evaluation of the effect of bed height in this study revealed that the static height of the bed is directly

related to the pressure drop; in particular, the higher the stable static height of the bed (bed height to bed diameter ratio), the higher is the bed pressure drop. Increase in the bed pressure drop can perturb the fluidity and the flow, which in turn can decrease the photocatalytic oxidation efficacy. It is to be noted that some bubbles could form due to the passage of gas-phase through a dense phase of the reactor bed. The size of the bubbles depends on the pressure drop of the bed [21]. Hence, an increase in the gas superficial gas velocity could result in the deviation from the fluidity regimen and the flow inertia, which in turn could decrease the catalytic efficacy [22].

Results from this study suggest that a decrease in the pressure drop would reduce the size of the bubbles, but the number of bubbles formed could increase. In such circumstances, the efficacy of the catalytic system also increases, which is in agreement with the results of a previous study [23]. The probability reason for an increase in pressure drop can be a long path of passing gas from the bed's height and a greater absorbent resistance to gas passage.

Also, the other reason is blockage of adsorbent pores by pollutant. Also, Yoa [24] used the SiO₂/TiO₂ composite particles as fluidizing media in a fluidized Reactor and showed that the contaminated stream of 1000ppm toluene can make a continuous degradation system that is similar to the result of this study. Therefore, the present study showed that the fluidized bed in photocatalytic systems can be considered to remove the Toluene as an important air pollutant.

CONCLUSION

The results showed that ZnO/SiO₂ catalysts generally have a larger efficacy than TiO₂/SiO₂, presumably because ZnO/SiO₂ has more active sites. Additionally, the ZnO/SiO₂ catalysts offer better fluidity than TiO₂/SiO₂. The photocatalytic transformation rate of the pollutant is relatively low, as the optimum humidity level for appears to be 45%. Further studies are necessary to study the effect of larger particles. Overall, the photocatalytic oxidation reaction of pollutants using TiO₂ and ZnO catalysts are attractive, with the transferability of photons to the catalyst being the only limiting factor, which is also a subject of further research.

ETHICAL ISSUES

Ethical issues including plagiarism double publication and/or submission, redundancy, etc. have been completely observed by the authors.

COMPETING OF INTEREST

The authors have declared that no competing interest exists.

AUTHORS' CONTRIBUTIONS

All authors equally participated in drafting, revising and approving of the manuscript.

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