

RESEARCH ARTICLE

PHOTOCATALYTIC DEGRADATION OF ETHYLBENZENE ON AN INCLINED 6 STEP FIXED BED PHOTOCATALYTIC IMMOBILIZED REACTOR

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ABSTRACT

The study of photocatalytic degradation of ethylbenzene was exploited using semiconductor oxide catalysts, titanium dioxide (TiO₂), immobilized on an inclined 6 steps fixed bed solar laboratory scale photocatalytic reactor. Percentage degradation of ethylbenzene was investigated at optimum pH 6.0, concentration of 100 mg/L, oxidant (H₂O₂) of 12 ml, over a batch system using direct sun light with six beakers on a shaker. The results show that the percentage degradation of ethylbenzene on an immobilized reactor has 85.22%, which has a better degradation than that of the batch system using beaker with shaker 55.09%. These may be, the immobilized system has more ability of absorption capacity in the visible region of TiO₂ and can thus better utilize photons in the visible range for photocatalytic reactions.

Key words: Photocatalysis, Immobilization, Titanium dioxide, Solar irradiation, and Inclined six steps fixed bed.

INTRODUCTION

Inadequate access to clean drinking water and sanitation has become one of the most common problems affecting people all around the world. In 2010, the United Nations declared the access to clean drinking water a human right (*The Human Right to Water and Sanitation*, (1989). and how a more sustainable water management is critical to achieve the Millennium Development Goals. However, due to industrial development, global population growth, and long term droughts caused by climate change, the number of people without access to clean drinking water is just expected to increase (Chong *et al.*, 2010). According to Malato *et al.*, (2009), it is estimated that around 4 billion people worldwide have little or no access to clean or sanitized water supply. Although the lack of access to clean drinking water and sanitation pose a global challenge, the problem is worse for developing countries where water resources are limited and about half of the population suffers from one of the main waterborne diseases caused by microbial and viral pathogens (such as diarrhea), worm infestation (such as *Ascaris* and *Hookworm*), and bacteria (such as trachoma) (Gadgil *et al.*, 1998). Photocatalysis is an attractive technology because of its various potential applications in disciplines such as selective chemical synthesis (Carp *et al.*, 2014), environmental technology (Chen *et al.*, 2000), and medicine (Blake *et al.*, 1999). Although heterogeneous catalysis in selective processes is not frequently employed, there is increasing interest in those

processes due to its possibility to avoid heavy metal catalysts, strong chemical oxidants or reducing agents, and high operating temperature and pressure (Zhang *et al.*, 2012)]. Selective photocatalytic applications include organic transformations for the synthesis of fine chemicals such as the reduction of carbon dioxide into methanol (Zhang *et al.*, 2012; Li *et al.*, 2016; Motegh *et al.*, 2013; and Van *et al.*, 2007), water splitting for hydrogen production (Carp *et al.*, 2004; Chen *et al.*, 2000; Zhang *et al.*, 2012), and selective oxidation of organic compounds such as alcohols to carbonyls (Carp *et al.*, 2004). The aim of this research is to develop an inclined 6 step fixed bed photocatalytic reactor, which will integrate hydrodynamics, mass transfer, UV radiation, and surface photoreactions, for simulating the performance of surface coated UV photocatalytic reactors, and to compare the percentage degradation of the immobilized reactor and our previous result on batch system.

Mechanism of photocatalytic oxidation

Figure 1 presents the schematic of photocatalytic oxidation using TiO₂ as the photocatalyst. During the photocatalytic oxidation, the most important step of photoreaction is the formation of hole-electron pairs which need energy to overcome the band gap between the valence band (VB) and conduction band (CB) (Hufschmidt *et al.*, 2004). When the photon energy is equal to or greater than the band gap energy (E_g) of the semiconductor (3.2 eV for anatase phase titanium dioxide) which are incidents upon its surface semiconductor, the electron hole pairs are created in the semiconductor, dissociating into free photoelectrons in the conduction band

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and photo holes in the valence band, respectively. Simultaneously, the photo oxidation and reduction reactions occur in the presence of air, oxygen and pollutant molecules. During the reactions, the hydroxyl radical (OH[•]), coming from the oxidation of adsorbed water or OH⁻, is highly reactive. In addition, the reducing power of the electrons can induce the reduction of molecular oxygen (O₂) to superoxide O₂^{-•}. The highly reactive species OH[•] and O₂^{-•} show strong ability to degrade microorganisms (Kikuch *et al.*, 1997; Agrios *et al.*, 2005) as well as organic (Agrios *et al.*, 2005; Demeestere *et al.*, 2007) and inorganic pollutants (Demeestere *et al.*, 2007; Toma *et al.*, 2004). TiO₂ photocatalysis is capable of destroying many organic contaminants completely (Cao *et al.*, 1999; Gaya *et al.*, 2008; Hoffmann *et al.*, 1995). A photo excited TiO₂ generates an electron (e⁻) and hole (h⁺) when photon energy equal to or greater than the band gap of the semiconductor (3.2 eV for anatase phase titanium dioxide) are incidents upon its surface as shown in Figure 1.

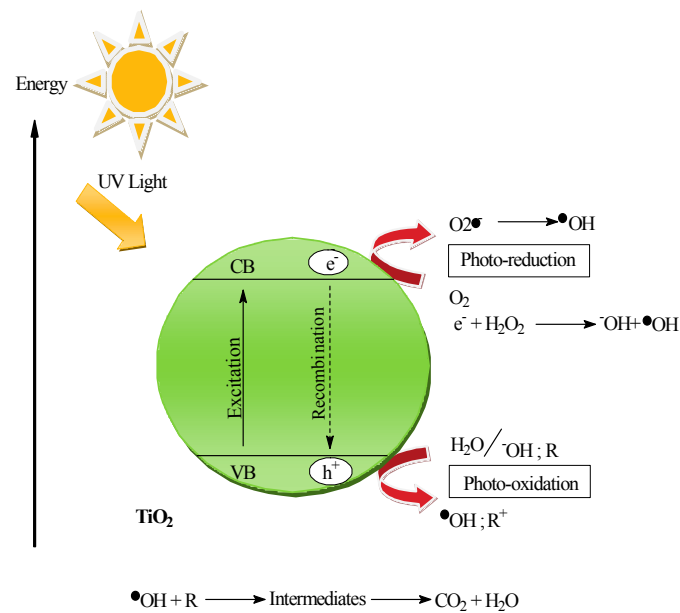
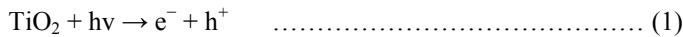
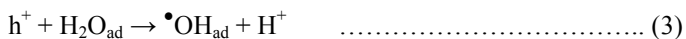
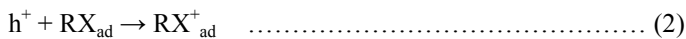


Figure 1. Irradiated TiO₂ Semi-Conductor Particle.



Electron transfer from the adsorbed substrate (RX_{ad}), adsorbed water or the OH_{ad}⁻ ion, to the electron-hole.



The third step is due to high concentration of OH⁻, water dissociates into ions.



Molecular oxygen (O₂) acts as an acceptor species in the electron transfer reaction.



Super oxide anions (O₂^{-•}) can be involved in the following reactions.

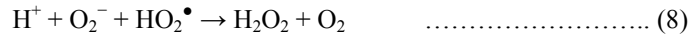
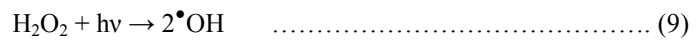
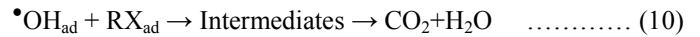


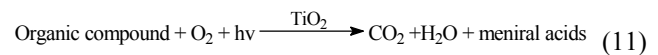
Photo conversion of hydrogen peroxide gives more •OH free radical groups.



Finally, •OH radicals oxidize organic adsorbed molecules (RX_{ad}) onto the surface of the titanium dioxide particles.



The •OH radicals are very active oxidizing agent and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water. Much of the interest in TiO₂ photo catalysis is due to the many advantages it has over traditional water and air treatment technologies; one such advantage being the fact that organic pollutants can be potentially degraded to carbon dioxide, water and mineral acids. Reaction equation (11) summarizes the mineralization process produced by the TiO₂ photocatalytic oxidation of organic compounds.



MATERIALS AND METHODS

Materials: The chemicals used in this study were titanium dioxide (TiO₂), Ethylbenzene (C₈H₁₀), NaOH, and HCl. They were of analytical grade, and used as such without further purification. Distilled water was used throughout for all experiments.

Photocatalytic Reactor: Ethylbenzene degradation experiments were carried out in an inclined 6 steps fixed bed solar photocatalytic reactor. The experimental equipment schematically depicted in Figure 2. The basic part of the apparatus is the photoreactor with immobilized TiO₂. The body of the reactor was made of stainless plate. The reactor casing is made of a rectangular stainless vessel having 6 steps, with an inclination angle of 45°. An illuminated area of External dimensions 2622 inch (Length of reactor 34.5 inch x Width of reactor 15.2 inch x Height of reactor 5.0 inch). And the Internal dimensions, Length of reactor bed surface is 15.0 inch, Width of average reactor bed surface is 4.5 inch, Height of average reactor bed surface is 1.8 inch, and the thickness of the stainless plate is 1.5 mm. The setup of the reactor consist of a plastic contaminant reservoir tank with a total volume of 4 liters, and a ELOTEC NOCIHI model, CE 1365 Electric pump, from which the wastewater is pumped to a distributor located at the top of the reactor, The photoreactor set up was opened to air, and it was operated in a batch recycling mode.

Immobilization of TiO₂ catalyst: The inclined 6 step fixed bed photocatalytic reactor was locally fabricated. After the fabrication, it washed with normal tap water, and with distilled water to remove dirt, and then allowed to dry overnight in a room temperature. The reactor was then coated with TiO₂ Degussa P25 photocatalyst. 250 g of TiO₂ catalyst was mixed with 1 liter of water and stirred vigorously with a special locally prepared wooden paddle to form viscous slurry, and then applied manually with the aid of a hand painting brush on the bed surface of the reactor as a thin film coating 1

mm thickness. The coated bed of photoreactor was allowed to dry in the sun and the surrounding air for one day (24 hours).

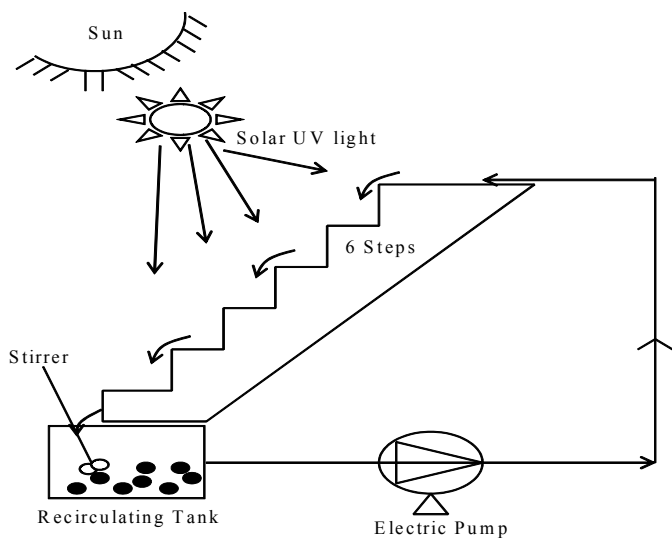


Figure 2. schematic diagram of an inclined 6 step fixed bed photocatalytic reactor

Experimental procedure: In our previous work, the photocatalytic degradation of ethylbenzene on aqueous solutions using titanium dioxide as catalyst; the optimum conditions for the degradation of ethylbenzene initial concentration was 100mg/L, pH 6.0, and Oxidant (H₂O₂) of 12 ml. Thus, in this work, the same optimum conditions were used to prepare the stock solution (simulated waste water) containing ethylbenzene (Ozogu *et al.*, 2016). The experiment was conducted under solar radiation from 11 AM to 4 PM in the month November. 1000 ml of optimum concentration (100 mg/L) with optimum of Oxidant (H₂O₂) of 12 ml and Optimum pH 6.0 was prepared. And it was introduced into the system from the reservoir tank kept at uniform concentration with the help of a manual stirrer. The analysis was run continuously under the sun for 2 hours. About 10 ml of the sample were withdrawn at 20 mins interval. The samples were filtered through 110 mm x 100 circles, Whatmann filter paper, and then analysed with UV-Vis spectrophotometer to know the percentage degradation. The face of the reactor were left open to the atmosphere, further increasing efficiency by eliminating light adsorption by the reactor. Figure 3 shows the side view of an inclined 6 steps fixed bed photocatalytic reactor setup. The “Waterfall” effect created by the reactant fluid cascading from one step to the next was designed to reduce mass transfer constants by creating a more disturbed flow regime as well as increasing the rate of oxygen transfer from the atmosphere to the reactant fluid.



Figure 3. Side view of an inclined 6 steps fixed bed photocatalytic reactor (Source: Author)

RESULTS AND DISCUSSION

UV-Vis Spectrometric Measurement for Ethylbenzene:

The photocatalytic experiments were conducted under the solar light. The degradation was recorded in term of change in intensity of characteristics peak of wavelength Ethylbenzene solution shows the absorption peak at 275.0nm and absorbance 2.371 um/L. Figure 4 shows the UV – Vis spectrometric reading of Ethylbenzene which dissolved in 100% of ethanol. From the spectrum λ_{max} shows the wavelength of ethylbenzene to be 275.0nm.

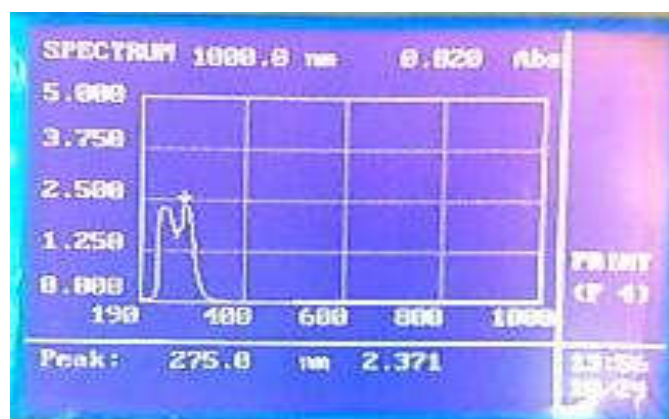


Figure 4. UV-Vis Spectrometric Reading of Ethylbenzene Dissolved in 100% Ethanol

Percentage Degradation in a Batch System: Figure 5 shows the percentage degradation of TiO₂. The result shows that as time increased in TiO₂ from 0 to 120 mins, the percentage degradation increased from 0 to 55.09%. This may be due to the fact that as time progresses, Ethylbenzene molecules are being absorbed on the surface of TiO₂ and degradation which implies that the concentration of Ethylbenzene in the aqueous solutions reduces with time.

Table 1. Percentage Degradation of Ethylbenzene in a Batch System

Time (mins)	Initial Conc. (mg/l)	Final Conc.	Abs	% Degradation
0	0	192.38	2.783	0
20	50	149.4	2.568	10.379
40	100	120.4	2.432	15.768
60	150	115.4	2.398	22.355
80	200	113.4	2.388	32.735
100	250	109.4	2.368	39.92
120	300	105.2	2.347	55.09

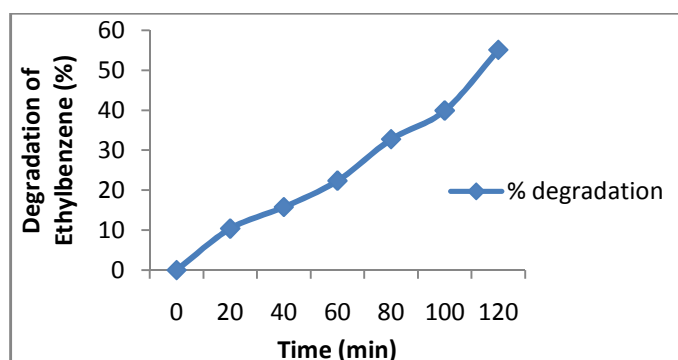


Figure 5: Percentage Degradation of Ethylbenzene in a Batch System

Percentage Degradation of Inclined 6 Steps Fixed Bed Photocatalytic Reactor: Figure 6 shows the percentage degradation of ethylbenzene at optimum pH 6.0, concentration of 100mg/L, oxidant (H₂O₂) of 12ml. These results show that as time increased from 0 – 2 hours, the percentage degradation increased from 17.6% - 85.22%. This may be due to the fact that as time progresses, ethylbenzene molecules are being adsorbed on the surface of the immobilized TiO₂ and degraded which implies that the concentration of ethylbenzene in the aqueous solution reduces with time. Table 2 shows a comprehensive result of the analysis.

Table 2. Percentage Degradation of Ethylbenzene in an Inclined 6 Steps Fixed Bed Photocatalytic Reactor

Time (mins)	Initial Opt. Conc. (mg/l)	Final Conc.	Abs	% Degradation
0	100	82.40	2.233	17.6
20	100	73.01	2.186	26.99
40	100	57.29	2.108	42.71
60	100	44.53	2.004	55.47
80	100	36.61	2.004	63.39
100	100	23.91	1.941	76.09
120	100	14.78	1.895	85.22

Table 3. Percentage Degradation of Ethylbenzene on TiO₂ Immobilized System and Batch System

Time (mins.)	% Degradation of TiO ₂ Immobilized Reactor	% Degradation of Batch System
0	17.6	0
20	26.99	10.379
40	42.71	15.768
60	55.47	22.355
80	63.39	32.735
100	76.09	39.92
120	85.22	55.09

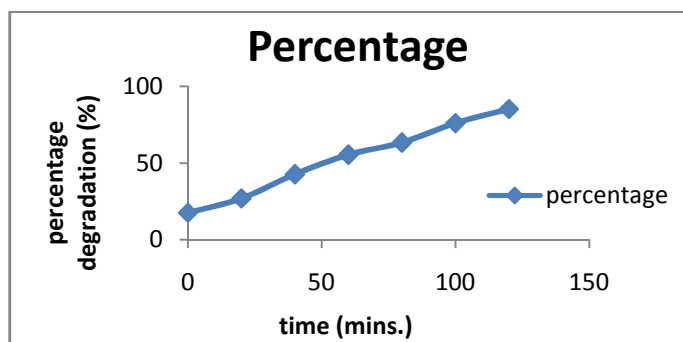


Figure 6. Percentage Degradation of Ethylbenzene at Optimum pH of 6.0, Optimum Concentration of 100 mg/L oxidant (H₂O₂) of 12 ml in an Inclined 6 Steps Fixed Bed Photocatalytic Reactor

$$\% \text{ degradation} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100$$

Where; C₀ = Initial concentration, and C_t = Final concentration.

Comparison of results on percentage degradation of TiO₂ on immobilized reactor, and a batch system using direct sun light: The results show that the percentage degradation of ethylbenzene at optimum pH of 6.0, concentration of 100 mg/L oxidant (H₂O₂) of 12 ml on TiO₂ immobilized reactor has 85.22%, and that of the batch system using direct sun light is 55.09%. The TiO₂ immobilized reactor has a better degradation than the batch system. These may be, the immobilized system has more ability of absorption capacity in the visible region of

TiO₂ and can thus better utilize photons in the visible range for photocatalytic reactions.

Recommendation: A good binder should be used to support the immobilized TiO₂ on the surface of the reactor bed, so that the immobilized TiO₂ will not be stripped off from the bed of the reactor, and it will give better percentage degradation.

Conclusion

The study showed the performances of solar photocatalytic degradation equipped with thin film inclined fixed bed reactor for removal of ethylbenzene solution chosen as model compound. The percentage degradation of ethylbenzene at optimum pH 6.0, optimum concentration of 100mg/L, and Oxidant (H₂O₂) of 12ml were used for the study. The achieved percentage degradation of ethylbenzene was 85.22% in the solar light at wavelength of 275.0nm. This means, a good amount of ethylbenzene molecules are being adsorbed on the surface of immobilized TiO₂. The results show that photocatalysis is an effective process for degradation of ethylbenzene. Inclined step fixed bed photocatalytic reactors are an attractive design because their efficiency is at least equal to other reactor configurations, and their construction offers economic advantages.

REFERENCES

- Adesina, A. 2004. Industrial exploitation of photocatalysis: progress, perspectives and aqueous solutions at titanium dioxide powder. *Journal of the American Chemical Society*, 126, 1233–1240. doi:10.1021/ja03562a011.
- Blake D. M., P.C. Maness, Z. Huang, E.J. Wolfrum, J. Huang, W.A. Jacoby, 1999. Application of the Photocatalytic Chemistry of Titanium Dioxide to Disinfection and the Killing of Cancer Cells, *Sep. Purif. Rev.*, 28, 1–50. doi:10.1080/03602549909351643.
- Carp O, C.L. Huisman, A. Reller, 2004. Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32 33–177. doi:10.1016/j.progsolidstchem.2004.08.001.
- Chen D., M. Sivakumar, A.K. Ray, Heterogeneous Photocatalysis in Environmental Remediation, *Dev. Chem. Eng. Miner. Process.* 8 2000 505–550. doi:10.1002/apj.550080507.
- Chong M.N., B. Jin, C.W.K. Chow, C. Saint, 2010. Recent developments in photocatalytic water treatment technology: A review, *Water Res.* 44, 2997–3027. doi:10.1016/j.watres.2010.02.039.
- Dijkstra, M.F., Panneman, H.J., Winkelman, J.G., Kelly, J.J., and Beenackers, A.A. 2002. Electrode. *Nature*, 238 (5358), 37–38.
- Frank, S.N. and Bard, A.J. 1977. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions at titanium dioxide powder. *J. Am. Chem. Soc.*, 1977, 99 (1), DOI: 10.1021/ja00443a081. pp 303–304.
- Fujishima, A. and Honda, K. 1972. Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 1972 (238) 37–38.
- Fujishima, A. and Zhang, X. 2006. Titanium dioxide photocatalysis: present situation and future approaches. *C.R. Chimie*, 9, 750–760.
- Gadgil A. 1998. Drinking water in developing countries, *Annu. Rev. Energy Env.* 23, 253–86.

- Li Z. 2016. LED-Based Photocatalytic Reactor Design, Delft University of Technology.
- Malato S., P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, (n.d.). doi:10.1016/j.cattod.2009.06.018.
- Ozogu A. N, F. A. Aisien, Udiba U. U, Chukwurah N. C. 2016. Photocatalytic degradation of ethylbenzene on aqueous solutions using titanium dioxide as catalyst. *American Journal of Environmental Engineering and Science*, 3(1): 26-32.
- Motegh M. 2013. Design of Photocatalytic Reactors, Delft University of Technology.
- The human Right to Water and Sanitation (1989).
- Van Gerven T., G. Mul, J. Moulijn, 2007. A review of intensification of photocatalytic process, *Chem. Eng. Process Intenif.* 46,781-789 doi:10.1016/j.cep.2007.05.012.
- Zhang N., Y. Zhang, Y. J. Xu, 2012. Recent process on grapheme based photocatalysts: current status and future perspectives, *Nanoscale.* 4, 5792.doi:10.1039/c2nr31480k.
