

Proceeding Paper

ZnO and TiO₂ Assisted Photocatalytic Degradation of Butachlor in Aqueous Solution under Visible Light †

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Abstract: Butachlor usage is increasing due to the increasing demand for agricultural products. However, it has toxic effects on surface and underground water. The experiment was conducted under visible light and the effects of parameters such as pH, adsorbent quantity, contact time, and the initial concentration of pesticides were investigated on the degradation of different pesticide solutions. The optimum dosing for ZnO and TiO₂ was 0.5 g/L. Degradation by ZnO reached 96.3% and that by TiO₂ reached 98.5%. The degradation effect of pH change was also analyzed and found to be higher in the basic region. The COD value was reduced effectively with TiO₂. The results showed that TiO₂ is more effective for degradation.

Keywords: butachlor; degradation; ZnO; TiO₂



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1. Introduction

Agriculture is an essential element of the economy. The usage of pesticides is increasing day by day due to the ever-increasing demand for agricultural products. However, they have toxic effects on surface and underground water. Pesticides are deemed the second greatest cause of aquatic pollution; in particular, drinking water is increasingly polluted by pesticides [1]. Butachlor is frequently used as a herbicide-based pesticide in different crops, especially in cotton, corn, and sugar cane. Butachlor has been used for killing weeds as a herbicide, including Cyprus Deformis, Eclipta Alba, Echinochloa Crus-galli etc. (Choudhry et al., 2016). EU regulations have recommended that the butachlor concentration should not reach more than 0.1 ng/mL [2]. The processes are based on visible light radiation to a semiconductor substance as a catalyst for the degradation of pesticides. In current study, we aimed to investigate the effectiveness of the photocatalytic degradation of butachlor pesticide by different catalysts and also study the different parameters during degradation, such as contact time, absorbent dosing, initial concentration pH, and COD.

2. Materials and Methods

2.1. Materials

The materials selected for the experiment had high lab grades and purity. Butachlor was purchased in pure form with 99% purity from the Jaffar group of the Lahore company. ZnO nanoparticles were purchased from Global Chemical Co., Ltd. (Bangpoo Samutprakarn, Thailand), with purity higher than 93.5% and a particle size of 10–30 nm. TiO₂ nanoparticles were purchased from KRONOS (ISO 9001), with purity higher than 98.5% and a particle size of 10–25 nm. For pH value measurement, a pH meter was used (model BASIC20), made in Germany. Acetonitrile CHROMASOLV, for HPLC, gradient grade, 99.9% was purchased from Honeywell Riedel-de Haen. A clear GC vial, with a black screw

cap with holes up to 2 mL, was purchased in Germany from Hadi Traders Anarkali Lahore. A 0.45 μm syringe filter, with a diameter of 13 mm (Nylon), item code SFNY01304 5NA, in a universal experimental ultrasonic cleaner (DSA100-SK1-2.8 L), was used. A HPLC device (Model SHIMADZU), UV detector, and C18 column ($4/6 \times 250$ mL) were used.

2.2. Experimental Procedure

We prepared the butachlor solution of 1 mL/L in a stock solution of drinking water for the experimentation. Samples of the following desired concentrations were prepared: 5, 15, 30, 40, 50 mg/L. The sample mixtures were subjected to magnetic stirring at 350 rpm for proper mixing. Numerous parameters were studied during the experimentation, such as absorbent concentration (0.1, 0.5, 1.5, and 3.0 g/L), contact time for degradation (5, 15, 30, 45, and 60 min), toxin concentration (5, 15, 30, 40, and 50 mg/L), pH (3, 5, 7, 9, and 11), and COD. The experiment was performed in a photocatalytic reactor. The procedures were also carried out in the photocatalytic reactor with different concentrations of polluted solution with selected absorbent concentrations, namely ZnO and TiO₂, at ambient temperature. Samples were collected in HPLC vials after regular intervals of time. In order to ensure the degradation efficiency, a HPLC device with a C18 column (4.2×4.2 mm) with an ultraviolet detector was utilized. Mobile phase for butachlor analysis was acetonitrile and distilled water (90:10 *v/v*) with a flow rate of 1 mL/min in HPLC. In HPLC, samples were detected at a wavelength of 212 nm for butachlor.

3. Results and Discussion

After collecting the results for the different samples following HPLC, we drew a calibration curve. Then, we calculated the degradation efficiency as a percentage (%) by the following formula:

$$\text{Percentage Degradation} = \left(\frac{C_0 - C}{C_0} \right) * 100$$

C_0 = concentration before degradation, C = concentration after degradation.

3.1. TiO₂ Degradation Efficiency at Different pH

Figure 1a shows the effect of pH changes on the degradation efficiency of different butachlor pesticide samples. At pH 9, optimum degradation was achieved with respect to other pH values due to ozonation processes [3,4].

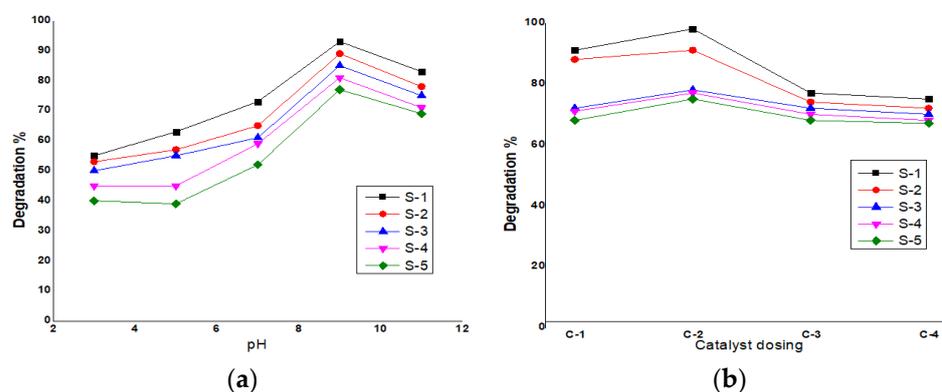


Figure 1. (a) The degradation efficiency of TiO₂ with different pH of butachlor sample; (b) the degradation efficiency of TiO₂ with different samples.

3.2. TiO₂ Catalyst Degradation Efficiency at Different Doses

Figure 1b shows that maximum degradation was achieved at C-2 of S-1. Toxin elimination was fixed or decreased with the increasing volume of the catalyst (greater than 0.5 g/L). The increase in the quantity of ZnO nanoparticles might have been due to reduced light

penetration, light dispersion, or the accumulation and sedimentation of the high catalyst concentration [5].

3.3. ZnO Degradation Efficiency at Different pH in Samples of Butachlor

For butachlor, Figure 2a below shows that pH changes affected the degradation efficiency for different samples; this graph shows that maximum degradation was achieved for S-1. It also shows an increasing trend in acidic medium and it gives the maximum value of degradation in the neutral region. At a basic pH (above 7), the catalyst surface becomes negatively charged. Therefore, there is a possibility of repulsion, leading to low adsorption of pesticide molecules and decreasing the degradation efficiency [6].

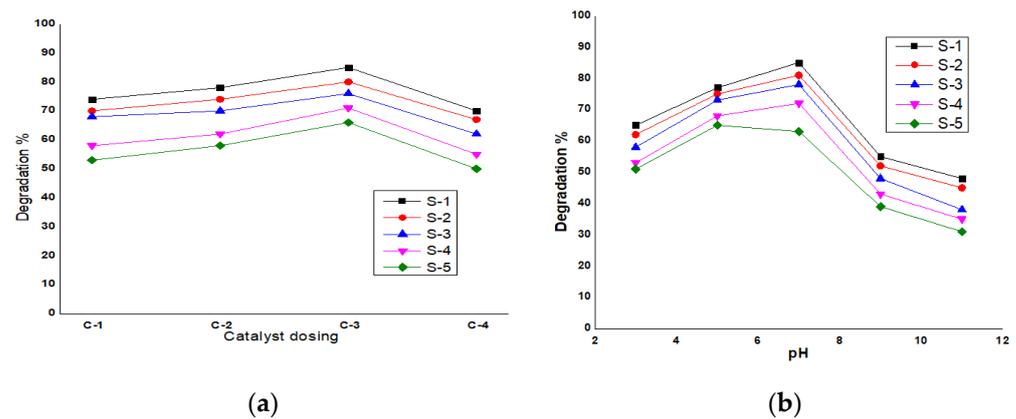


Figure 2. (a) The degradation efficiency of ZnO with different samples; (b) the degradation efficiency at different pH of butachlor samples with ZnO.

3.4. ZnO Catalyst Degradation Efficiency at Different Doses

Figure 2b below shows that maximum degradation was achieved at a catalyst dosing of C-3 for S-1 of approximately 85% [7]. It will be at C-3 ZnO. When the initial amount of pesticide increases, a greater amount of pesticide molecules is adsorbed on the catalyst surface, leading to reduced hydroxyl radical generation and only a few active sites in which the adsorption of hydroxyl ions takes place [8].

3.5. Comparison of Degradation Efficiency of ZnO and TiO₂

Figure 3a shows, at different pH values, the degradation efficiency for butachlor pesticides with two catalysts. In the figure, butachlor with TiO₂ in the acidic region had a lower degradation rate with respect to the basic region, i.e., at pH 9, it showed maximum degradation efficiency with TiO₂. On the other hand, butachlor and ZnO displayed the optimum degradation rate at neutral pH.

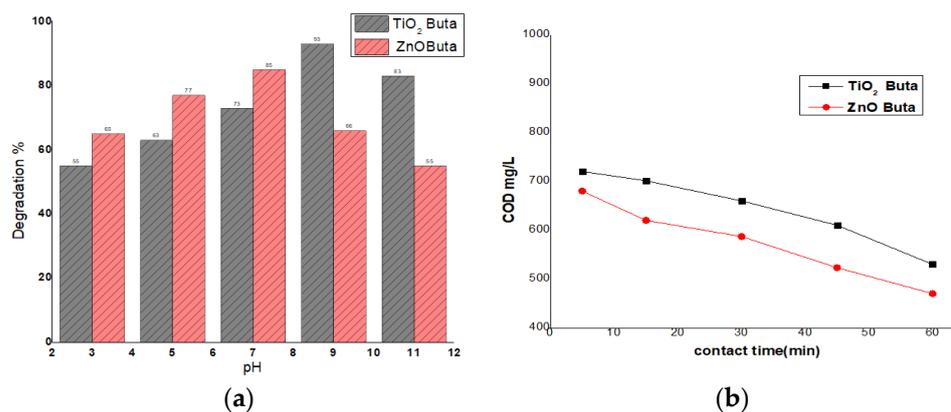


Figure 3. (a) The comparison of degradation efficiency of ZnO and TiO₂ at different pH; (b) COD value of S-1 for butachlor.

3.6. Comparison of COD Values of ZnO and TiO₂ over Time

Figure 3b shows that the value of COD gradually decreased with respect to time. The maximum degradation value of COD for butachlor was achieved with TiO₂ [9].

4. Conclusions

The photocatalysts TiO₂ and ZnO can degrade toxins under optimal conditions. Up to 98.40 and 81.2% of butachlor was degraded by TiO₂ and ZnO, respectively, at different amounts of absorbent. In terms of contact time up to 1 h, the degradation efficiency was decreased for butachlor by TiO₂ until 5 min and by ZnO until 15 min, having the greatest impact on the removal of the pollutant. In the case of TiO₂ for butachlor, the rate of degradation at pH 9 was optimal. On the other hand, ZnO with Butachlor showed the maximum degradation rate at a neutral pH. This process can be utilized to degrade pollutant contaminants in various chemical industries. The photocatalytic method utilizing TiO₂ nanoparticles under visible light irradiation had also higher efficiency in butachlor degradation with respect to ZnO.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Giannakopoulou, T.; Papailias, I.; Todorova, N.; Boukos, N.; Liu, Y.; Yu, J.; Trapalis, C. Tailoring the energy band gap and edges' potentials of g-C₃N₄/TiO₂ composite photocatalysts for NO_x removal. *Chem. Eng. J.* **2017**, *310*, 571–580. [[CrossRef](#)]
- Abdollahi, Y.; Abdullah, A.H.; Zainal, Z.; Yusof, N.A. Photocatalytic degradation of p-Cresol by zinc oxide under UV irradiation. *Int. J. Mol. Sci.* **2012**, *13*, 302–315. [[CrossRef](#)] [[PubMed](#)]
- Abigail, M.; Samuel, S.M.; Ramalingam, C. Addressing the environmental impacts of butachlor and the available remediation strategies: A systematic review. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 4025–4036. [[CrossRef](#)]
- Hashemi, M.; Ashoornia, M.; Panahandeh, M. Removal of Butachlor Toxin Polluted Water Using Ozonation, A Case Study of Groundwater Resources in Guilan Province. *J. Water Wastewater* **2015**, *26*, 114–123.
- Nozhat, S.; Fazilati, M.; Hassani, A.H. Butachlor and Diazinon Elimination from Aqueous Solution using TiO₂/ZnO nano-photocatalysts. In Proceedings of the International Congress on Engineering Science and Sustainable Urban Development, Copenhagen, Denmark, 4 September 2018.
- Premalatha, N.; Miranda, L.R. Surfactant modified ZnO–Bi₂O₃ nanocomposite for degradation of lambda-cyhalothrin pesticide in visible light: A study of reaction kinetics and intermediates. *J. Environ. Manag.* **2019**, *246*, 259–266. [[CrossRef](#)]
- Darbandi, Z.; Zazouli, M.A.; Shokrzadeh, M.; Mousavinasab, N.; Ehsan, R. Photocatalytic degradation of diazinon using ZnO/TiO₂ nano-photocatalysts. *KOOMESH* **2016**, *18*, 343–349.
- Jonidi-Jafari, A.; Shirzad-Siboni, M.; Yang, J.; Naimi-Joubani, M.; Farrokhi, M. Photocatalytic degradation of diazinon with illuminated ZnO–TiO₂ composite. *J. Taiwan Inst. Chem. Eng.* **2015**, *50*, 100–107. [[CrossRef](#)]
- Sraw, A.; Kaur, T.; Pandey, Y.; Sobti, A.; Wanchoo, R.K.; Toor, A.P. Fixed bed recirculation type photocatalytic reactor with TiO₂ immobilized clay beads for the degradation of pesticide polluted water. *J. Environ. Chem. Eng.* **2018**, *6*, 7035–7043. [[CrossRef](#)]