TIO_2/ZNO NANOPARTICLES APPLIED TO THE PHOTOCATALYTIC DEGRADATION OF SIMAZINE IN AQUEOUS SOLUTION

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Abstract

As use of herbicides and pesticides widely increases from anthropogenic processes such as farming, the concentrations of these types of chemicals in the natural are environment increasing. These chemical substances and structures designed to reduce pests have unintended effects on environmental and human health. Recently photocatalytic degradation has been shown to be an efficient mechanism for degrading resistant compounds in aqueous solution. Persistent organic pollutants such as simazine in exist in both surface and groundwater systems and have negative health effects. In the current study, the photocatalytic materials titanium dioxide(TiO_2) on zinc oxide(ZnO) were investigated for the degradation of simazine from aqueous solution. The current study to investigate the effect of light, pH, time, and catalyst loading. The synthesized nanomaterials were characterized using XRD and RAMAN spectroscopy. XRD show the presence of both TiO_2 (in the Anatase and rutile phases) and the ZnO in the hexagonal crystal structure. The optimum binding was determined to occur at pH 3 using UV light. In addition, the optimum loading mass of catalyst was determined to have been 5mg.

Introduction

As the use of pesticides increase in our environment, more research has shown effective results in the degradation of them, such as the 2018, Suhaimy et al. study, whose primary objective was to determine the modification of TiO2 nanotube structure along with increased anodization duration time, conditions, and applications. In this investigation, the main focus was on the effects of pH on both the kinetics and the photocatalytic process.

Objectives & Hypothesis

- *To Investigate the effectiveness of ZnO@TiO2 nanoparticles for the photocatalytic degradation of simazine*
- *To investigate the effects of pH on the removal of simazine from water using photocatalysis.*

Hypothesis: *The ZnO@TiO2 nanoparticles will be effective in removing simazine.*

Methodology

TiO2 & ZnO@TiO2 synthesis:

- A solution containing $TiCl_3$, $NaC_2H_3O_2$, and 200mL of deionized water was stirred and heated at 80° for 3 h
- The solution was centrifuge at 3200rpm three times each with acetone and water.
- 20% of ZnO was calculated from TiO_2 mass, and mixed with TiO_2 in 200mL of deionized water and titrated with 50mL of NaOH

pH studies:

- At each pH ranged from 2 through 6 a 5 mL aliquot of 30 ppm Simazine was extracted in triplicate and 15mg of catalyst was added. A second set of triplicate control samples which consisted of only the simazine.
- The samples were taken to an Innova 44 incubator and reacted (under UV light, visible light, and UV light while constant stirring) for 1 h.
- After reaction all samples were centrifuged and to be analyzed using HPLC.

Kinetics:

- Samples were reacted at pH 3 for times of 15min, 20min, 45min, 60min, & 120min.
- After reaction all samples were centrifuged and to be analyzed using HPLC.

Mass of Catalyst:

- 30 ppm samples of simazine were reacted at pH 3 with either 5mg, 10mg, 20mg, 40mg, or 80mg for 2 hours.
- After reaction, all samples were centrifuged and to be analyzed using HPLC

HPLC Analysis:

- A 0.1 M Ammonia/acetate buffer pH adjusted to 6 and mixed with Acetonitrile at a 65:35 mixture.
- A C18 reverse phase column and a Thermo fisher Ultimate 3000 HPLC, equipped with a manual injector with a 20 µL loop.
- Analysis was performed at a flow rate of 1.0 mL/min and a detector was 225 nm.

Results

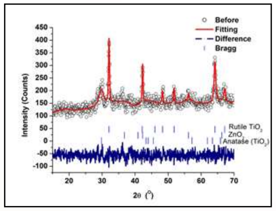

Figure 1: X-ray powder diffraction pattern of ZnO@TiO_2 nanoparticle catalyst before reaction.

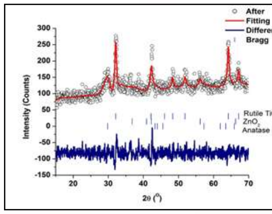

Figure 2: X-ray powder diffraction pattern of ZnO@TiO_2 nanoparticle catalyst after reaction

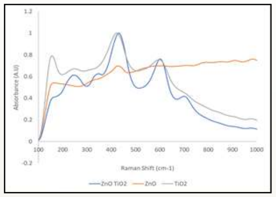

Figure 3: Raman Spectra for the ZnO@TiO_2, TiO_2 and ZnO nanomaterials.

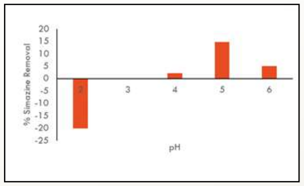

Figure 4: Effect of UV light on the degradation of simazine in aqueous solution.

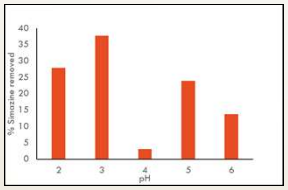

Figure 5: Effect of UV light one the degradation of simazine in aqueous solution under constant stirring.

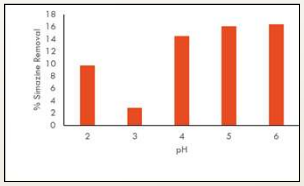

Figure 6: Effect of Visible light on the removal of Simazine

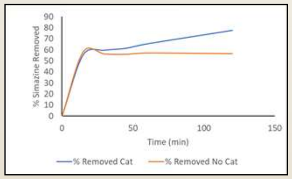

Figure 7: Kinetics plot for the removal of Simazine from solution using Catalyst and no catalyst under UV light.

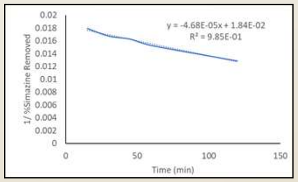

Figure 8: Effect of Mass of catalyst on removal of simazine

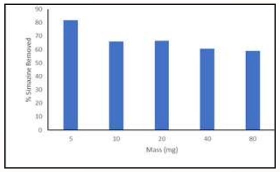

Figure 9: Linearized kinetics plot of simazine removal (second order kinetics)

Discussion

XRD analysis & Raman spectra:

- XRD results show that the composition of the catalyst did not change before and after, it consisted of: anatase (10%), rutile (70%) and ZnO (20%).
- Raman confirmed the presenc of ZnO and TiO_2 in the sample

pH results:

- Figure 2 shows the effect of UV light, pH 2 has a negative inhibition possibly due to low pH level.
- Figure 5 shows pH with the most effective result showing 40% of SIM removal
- Figure 6 shows the samples under visible light in which removal effectiveness was only 15 percent of the total simazine in solution.

Kinetics results:

- Figure 7 shows the kinetics plot for the removal of simazine, it can be inferred that the most effective time is 120min in 80% removed SIM, whereas the no catalysts samples was kept constant throughout 60 & 120minutes.
- Figure 8 shows a higher rate of removed SIM in a prolonged period of reaction time

Effect of mass catalyst:

- As can be seen below, figure 8 shows 5mg of catalyst mass to be most effective in removing 80%, followed by 65% of 10 & 20mg, and 60% with 40 and 80mg

Conclusions

- *pH affected the removal of simazine pH 3 stirred solution was highest*
- *120 min of reaction time was necessary for the reaction to work*
- *5mg of catalyst mass was the optimum.*

Future Research

- *Extend the study pHs*
- *Perform kinetics at different temperatures*
- *Performed Bandgap measurements*
- *Use other pesticides such as atrazine*

References

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