IMPACT OF CATALYST ON THE HERBICIDES DEGRADATION

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ABSTRACT

For the purpose of determining the optimal dosage of the catalyst required to degrade herbicide residues, photocatalysis was carried out with a range of different concentrations of the catalyst, which included 10 mg/L all the way up to 200 mg/L. In order to accomplish this, a pesticide formulation with a concentration of 1 mg/L was applied to the water samples, and simultaneously, ZnO nanoparticles with concentrations of 10, 50, 100, 150, and 200 mg/L were added. Additionally, a control sample that has not been supplemented with ZnO nanoparticles is retained for the purpose of comparison. After being exposed to sunshine and having aliquot samples obtained at predetermined intervals, the samples were injected into an HPLC in order to analyze the herbicide residues. This was done after the samples had been exposed to sunlight. In the aftermath of the addition of herbicides to the water samples, one group of samples was stored in the dark, another group of samples had ZnO nanoparticles added to them and was likewise stored in the dark, and a third group of samples was stored in the sunlight. For the purpose of the experiment, an aliquot of samples was taken at predetermined intervals, and the ideal concentration of ZnO nanoparticles for each herbicide was utilized.

KEYWORDS:

Catalyst, Herbicides, Degradation

INTRODUCTION

Specifically, the objective of the study was to investigate the ways in which deterioration impacts both aerated and non-aerated systems. Nitrogen gas was used to debubble one set of spiked water samples in order to eliminate the dissolved oxygen. This was done in order to investigate the effect that aeration has on the effects of the water. An additional group of water samples were kept in the presence of direct sunshine and were continually supplied with oxygen. During the course of the experiment, the suitable amount of catalyst was utilized for each and every herbicide. A number of samples were collected in aliquots, and the residue degradation of those samples was investigated.

Hydrogen peroxide (H_2O_2) and sodium sulfate ($S_2O_8^{2-}$) were two additional electron acceptors that were added to the reaction mixture at a dose rate of 100 mg/L in order to investigate the effect that these electron acceptors had on the photocatalytic degradation process. After the oxidant and nanoparticles were introduced to the reaction mixture, certain samples were taken at predetermined intervals and analyzed to see whether or not any residues were present.

An investigation was conducted to determine the adsorption of herbicides on ZnO nanoparticles at a concentration of 1.0 mg/L. This observation was carried out over a period of five hours, during which time there was no aeration, continual stirring, and darkness. During each hour, duplicate aliquots of water samples were collected, centrifuged, and the residues were examined. This process was repeated every hour.

The herbicides Metribuzin, sethoxydim, Carfentrazone, and Dacthal were spiked at two different concentrations, namely 1 mg a.i./L and 2 mg a.i./L, in order to investigate the photocatalytic activity of each herbicide in water. Milli-Q water and three different aqueous buffer solutions with pH values of 4.0, 7.0, and 9.0 were utilized for the research project. At each and every level of fortification, three replications were prepared in addition to control samples for the purpose of measurement and comparison. Two different sets of spiked concentrations are complete and ready for the research. The catalysts that were added to one set

of samples were sodium persulfate and zinc oxide nanoparticles. On the other hand, the second set of samples was analyzed without the addition of any catalyst or oxidant ($Na_2S_2O_8$). The dissolved oxygen in the test solutions was removed with the help of nitrogen gas, which also served to debubble the solutions being tested. The samples were exposed to the sun through its whole. Aliquots of samples were taken at intervals that had been previously determined. From 25 to 44 degrees Celsius, water samples were measured at that time. Sunlight levels ranged from 22500 to 178400 LUX during the duration of the photoperiod. Throughout the course of the research project, a hygrometer and a LUX meter were utilized to measure the temperature as well as the intensity of the sunshine. Samples were collected at various times throughout the sample process. Following the filtration process with a 0.2 µm PTFE membrane filter, the filtrates were collected into vials of an amber tint. Following the enrichment of the samples with zinc oxide nanoparticles, the samples were centrifuged for four minutes at a temperature of two degrees Celsius using a Beckman cooling centrifuge that was set to 10,000 rotations per minute. In order to stop the chemical from deteriorating any further, the supernatant was transferred into the vials of amber hue and stored at a temperature of 5 degrees Celsius in the dark until the analysis was performed.

In order to determine whether or not the catalyst could be reused, it was separated by centrifugation and then dried at a temperature of 100 degrees Celsius for a period of four hours after the photocatalysis experiment was completed. Following a series of five cycles in a row, the recovered catalyst was put through an efficiency test with the herbicide solution that had just been made. The reusability test was carried out under the same conditions as were used for the photocatalysis demonstration. For the purpose of determining the photocatalytic stability of ZnO nanoparticles and the efficiency with which the catalyst contributes to degradation, the following formula was utilized.

$$\ln (m/m_0) = -Kt$$

In this equation, K represents the predicted decay constant, m0 represents the degradation efficiency during the initial use, and m represents the catalyst efficiency after the fifth pass through the process.

Experimental Section

Specifically, the process by which Metribuzin adsorbed on ZnO nanoparticles was examined. In the absence of light, experiments for the recovery of Metribuzin were conducted with ZnO nanoparticles at a concentration of 150 mg/L contained in Milli-Q water and a variety of buffer solutions. Whereas the range of mean percent recoveries for Metribuzin in Milli-Q water was 89 to 95%, the range in acidic water was 90 to 94%, the range in neutral water was 88 to 93%, and the range in basic water was 91 to 95%.

In order to determine whether or not the catalyst could be reused, it was separated by centrifugation and then dried at a temperature of 100 degrees Celsius for a period of four hours after the photocatalysis experiment was completed. Following a series of five cycles in a row, the recovered catalyst was put through an efficiency test with the herbicide solution that had just been made. In the course of five successive tests, the ZnO nanoparticles' degradation effectiveness dropped from 96.8% to 93.6%, which is a significant decrease from its original capacity to deteriorate. It was observed that there was almost no fluctuation in its efficiency as a consequence of this. X-ray diffraction (XRD) data was collected for the ZnO nanoparticles that had been repurposed after five successive runs. The results were consistent with the ZnO nanoparticles that were initially used, and there is no evidence of any other phases.
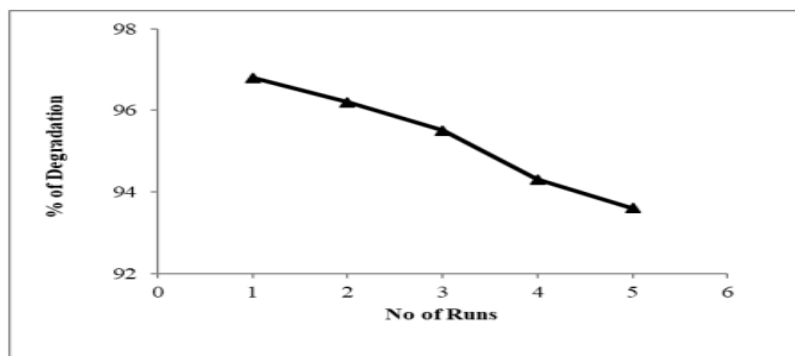
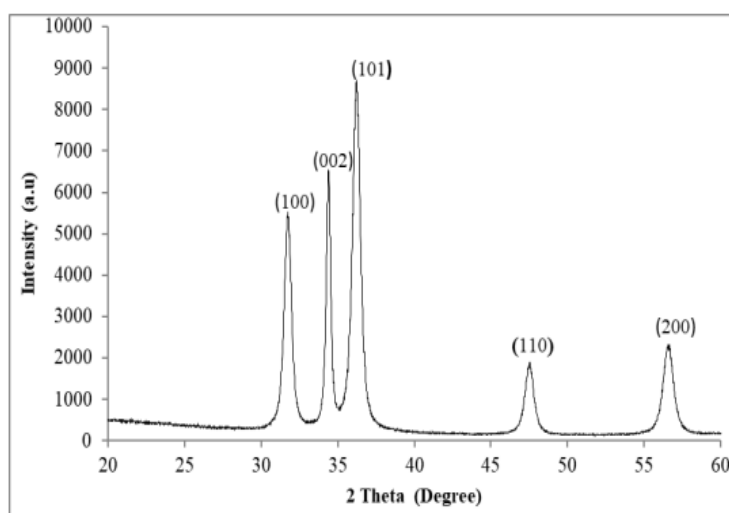**Figure 1 Reusability of ZnO Nano Particles**

Figure 2: XRD Pattern of the ZnO Nanoparticles after 5 Successive Runs

Over the course of one day, the initial concentration of Metribuzin in basic water was 1.98 mg/L for the T2 dosage (2.0 mg/L) and 0.99 mg/L for the T1 dosage (1.0 mg/L), respectively. In basic water, the quantity of Metribuzin residue remained after 200 hours, reaching below detectable levels in the 250th hour, and 0.06 and 0.13 mg/L in the T1 and T2 dosages, respectively. This was the case for both dosages.

According to the following, the levels of Metribuzin that were lost in basic water were as follows: In the fifth hour, the concentrations were 0.96 mg/L (T1) and 1.92 mg/L (T2); in the tenth hour, the concentrations were 0.91 mg/L (T1) and 1.85 mg/L (T2); in the twenty hour, the

concentrations were 0.86 mg/L (T1) and 1.71 mg/L (T2); and in the fifty-first hour, the concentrations were 0.75 mg/L (T1) and 1.56 mg/L (T2).

According to the samples taken at the 70th hour, the levels of residue were 0.64 mg/L (T1) and 1.31 mg/L (T2); at the 90th hour, they were 0.58 mg/L (T1) and 1.24 mg/L (T2); and at the 120th hour, they were 0.42 mg/L (T1) and 0.86 mg/L (T2), respectively. Samples taken at the 150th hour showed residues at concentrations of 0.36 mg/L (T1) and 0.76 mg/L (T2); samples taken at the 180th hour showed residues at concentrations of 0.21 mg/L (T1) and 0.41 mg/L (T2). DT50 values for Metribuzin in basic water were 64.75 and 65.93 hours, whereas DT90 values for T1 and T2 dosages were 215.10 and 219.00 hours, respectively. These values were determined by comparing the DT50 values to the DT90 values.

As a general rule, the rate constant and the rate of deterioration both rise in tandem with the increasing amount of catalyst loading. The greater surface area of the catalyst, which makes it more available for the adsorption and breakdown of the pesticide in solution, is assumed to be the origin of this phenomenon. On the other hand, the rate of photocatalytic degradation of propazine, simazine, and isoproturon slowed down when the concentration of TiO_2 became closer to 5 g liter^{-1}.

This screening effect is produced by the TiO_2 particles when they are present in extremely high concentrations. The degradation rates of the three pesticides are reduced as a consequence of the great opacity of the solutions, which prevents the catalyst from being exposed to light. Consequently, there is a decrease in the intensity of ultraviolet (UV) absorption onto the surface of the catalyst as a consequence of a greater quantity of UV being reflected from the mixture.

As the concentration of the catalyst climbed above the level that would be considered ideal, the amount of light scattering increased. As a consequence of this, the photocatalytic efficacy was reduced, and the light intensity was distributed unevenly. The optimal concentration of each and every catalyst varies according to the type of catalyst.
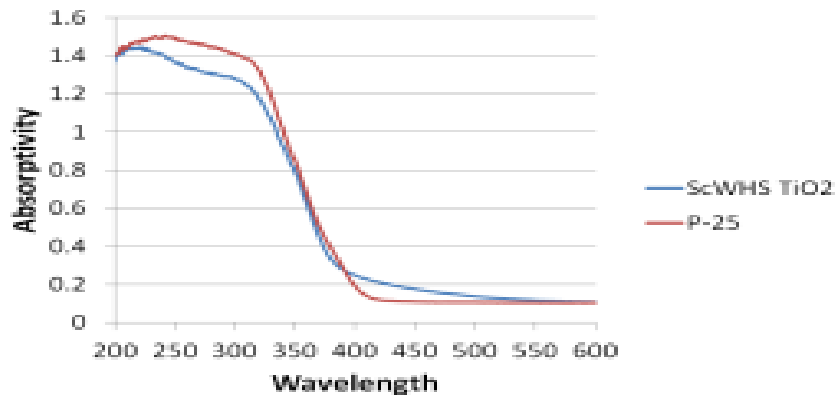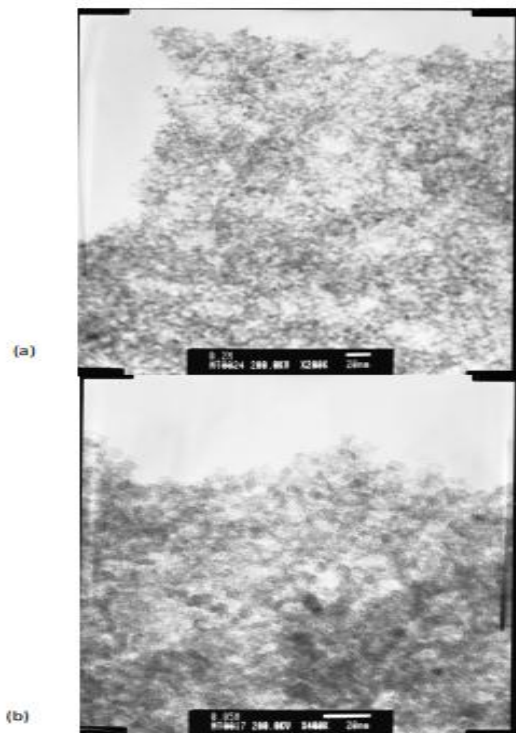
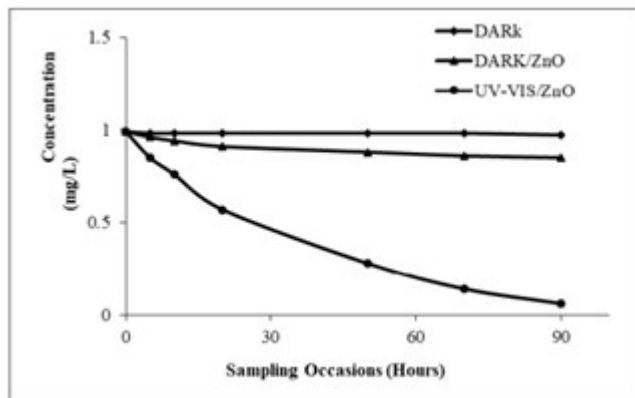**UV-Vis spectroscopy of the P-25 TiO2 comparing with the synthesized TiO$_2$**

Results
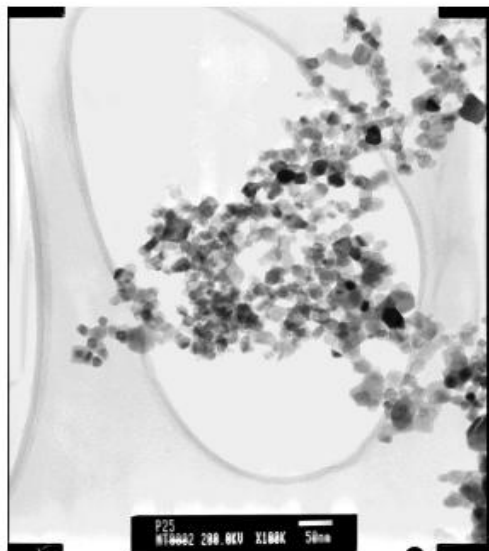
TEM photograph of P-25 TiO2 in aqueous suspension   **TEM photograph of synthesized TiO2 in aqueous suspension (a fine particles with the size of 10-15 nm (b) start to agglomerate due to high surface area**
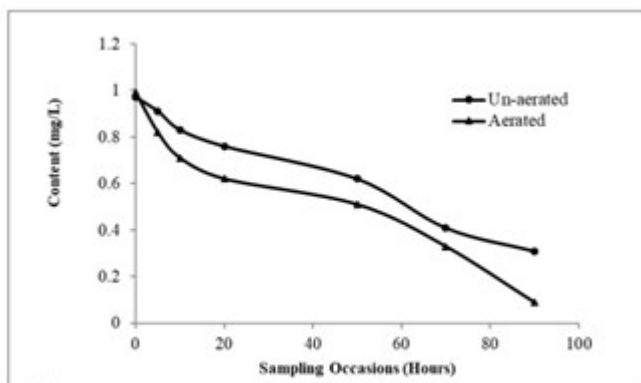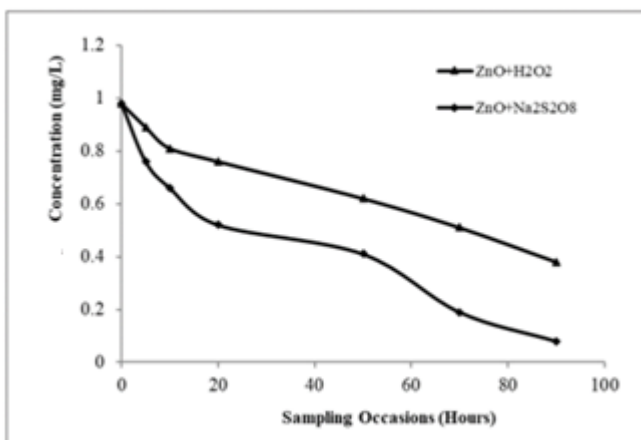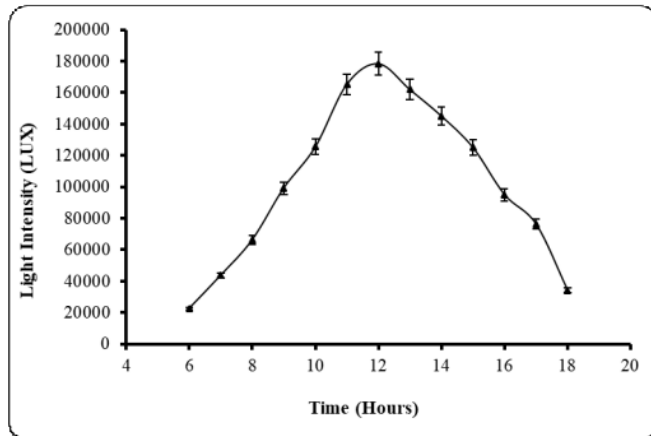
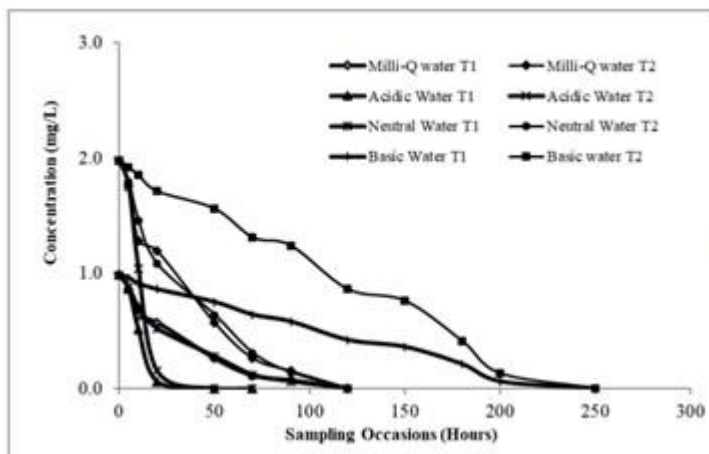**Effect of Light Source on degradation of Metribuzin**
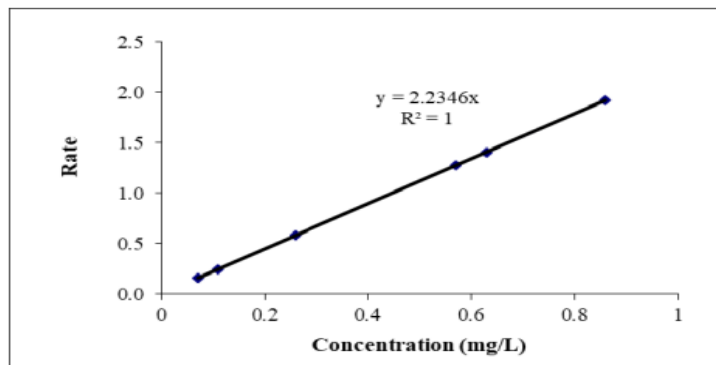

Effect of Aeration on Metribuzin

Effect of Addition of Oxidant on Metribuzin

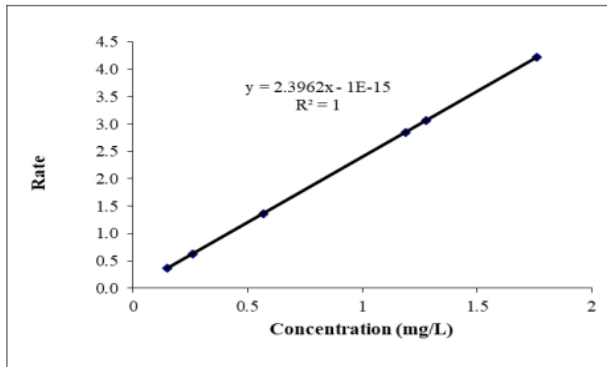**Sunlight Intensity during the Study Period**

Dissipation Curve of Metribuzin-Photocatalysis

$$y = 2.2346x$$
$$R^2 = 1$$

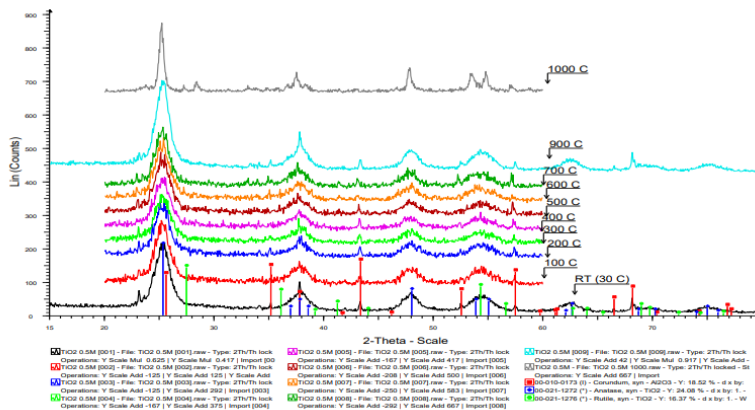**Rate of the reaction-Milli-Q water (T1 & T2 Dosages)**
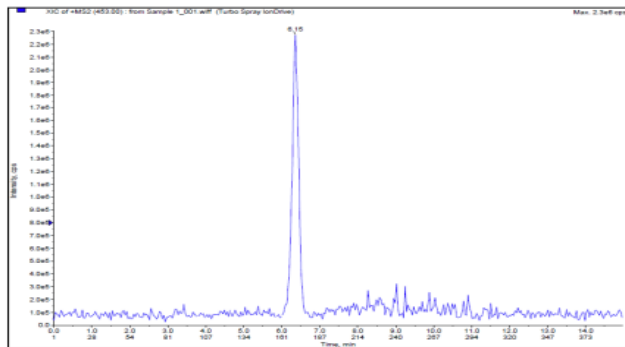
Representative LC-MS/MS Spectra of Metribuzin

Results of XRD analysis of synthesized TiO2 sintered at different temperatures (30-1000 ºC)

Photograph of synthesized TiO2 after sintering at 900 °C for an hour

CONCLUSION

According to the findings of the studies that were conducted, the ideal concentrations of the catalysts have been shown to range anywhere from 0.15 to 8 grams per liter. This difference can be related to a number of different factors, such as the design of the reactor, the chemical compounds included, the operational parameters, and fluctuations in the system. It was that the optimal concentration for the photocatalytic degradation of isoproturon using P-25 TiO_2 in an immersion well reactor was approximately 3 g liter-1. These findings are comparable to the findings of our experiment. In a small stirred reactor, study discovered that an efficient catalyst concentration for isoproturon degradation was 1 g liter^{-1} at neutral pH. This was accomplished by utilizing TiO_2 that was doped with carbon, nitrogen, and sulfur. The optimal concentration of P25 TiO_2 for the photocatalytic degradation of 5 mg liter^{-1} of isoproturon in a Pyrex batch reactor was 1.95 grams per liter at a pH of 3.8. For this particular reaction system, the optimal concentration of P-25 TiO_2 was 5 grams per liter in a stirred reactor with a pH of neutral.

We have prepared ZnO amd TiO_2 nanoparticles and then studied their effect on Herbicide Metribuzin at different concentrations and their results are interpreted to study the effect of catalyst on herbicide. Herbicides are used in agriculture and have impact on environment so its study is important so that on the basis of selectivity, nature, catalyst impact, photocatalytic degradation we can choose ideal option for agriculture.

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