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Study of Photo catalytic Degradation of Bispyribac Sodium

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Abstract - This study explains how the pyrimidinyloxybenzoic herbicide Bispyribac sodium can be broken down by sunlight and other sources, making it safer for use in paddy fields. ZnO/$Na_2S_2O_8$ was studied as a photo sensitizer / oxidant in an aqueous suspension to determine its degradation. Bispyribac sodium photocatalysis was investigated in daylight using three different aqueous buffer solutions (pH 4, 7, and 9). We also looked into how bispyribac sodium and its metabolites impacted green algal development in this study (Pseudokirchneriella subcapitata). When compared to photolysis experiments, the results demonstrated that the inclusion of a photosensitizer significantly improved pesticide removal. This method also rapidly increases the reaction rate. Compared to using just ZnO, the addition of the oxidant ($Na_2S_2O_8$) speeds up the reaction and provides additional benefits. Degradation of sodium bispyribac occurs with first-order kinetics. Statistics were used to calculate green alga growth rates (Er) and yield percentages (Ey). There was a significant decrease in growth rate inhibition with increasing irradiation time.

Keywords - Bispyribac Sodium Photocatalysis, Photosensitizer, Green algal development, Aqueous buffer solutions

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INTRODUCTION

i) Specificity

In order to investigate the method's specificity, acetonitrile, orthophosphoric acid, milli-Q water, buffer solutions, and a bispyribac sodium reference analytical standard were injected into a sample in rapid succession. At the retention time of the investigated herbicide, the results showed no interference was present.

ii) Linearity

The linearity of the devised analytical technique for the dcetermination of bispyribac Sodium in the concentration range of 0.01-10 mg/L was determined to be 0.9999. The limit of detection (LOD) was determined to be 0.01 mg/L based on a signal-to-noise ratio of 3:1, while the LOQ was determined to be 0.05 mg/L based on linearity. Table 1 summarises the findings, and Figure IV.1 shows the calibration curve.

iii) Recovery

Bispyribac Sodium was recovered at a mean of 89% in Milli-Q water, 88% in acidic water, 89% in neutral water, and 87-94% in basic water across a range of fortification levels of 0.05, 0.5, and 2.0 mg/L.

REVIEW OF RELATED LITERATURE

Using PANI/ZnO-CoMoO4, **Adabavazeh et al. (2021)** created a Z-Scheme photocatalyst system for the process of photocatalysis. Imidacloprid, an insecticide, was utilised in the photocatalytic breakdown process. In this experiment, photocatalytic performance was studied in the presence of visible light. The effects of different amounts of catalyst, pH, and pesticide concentration were investigated. In this study, the photocatalyst was easily recovered and re-used using a centrifugation procedure, and 97% of imidacloprid was destroyed within 180 minutes of irridation.

To neutralise the poisonous temephos, **Serrano-Lázaro et al., (2021)** created nanostructured Zinc oxide (ZnO) photocatalyst films. In order to absorb visible light, a basic ZnO film with a nano floral

shape with a band gap energy of 3.2 eV and a high concentration of naturally occurring defects was created. The half-life of temephos, together with its transition products, was shown to be drastically shortened by a factor of seven.

Zinc oxide (ZnO) photocatalysts doped with tungsten (W) were utilised in the photocatalytic breakdown of glyphosate by **Russo et al., (2021).** Bandgap energy fell from 3.22 in pure ZnO to 3.19 in doped ZnO after W doping. After 180 minutes of exposure to solar simulated light, glyphosate degradation and mineralization were found to be 74% and 30%, respectively. Catalysts at a concentration of 1.5 g/L were most effective, and a pH of 7.0 was ideal. It was the O2 radicles that did most of the photocatalysis.

By **Zihan Zhu, et al (2020)** We used a hydrothermal synthesis approach to synthesise a ZnO/rGO nanocomposite for photocatalytic degradation of dimethoate. The ZnO/rGO nanocomposite was found to be 4 and 1.5 times more effective in photodegrading dimethoate than bare ZnO. ZnO/rGO nanocomposite's improved photocatalytic activity was traced to rGO's ability to reduce the electron-hole recombination rate and facilitate efficient carrier transport.

MATERIALS AND METHODS

Hplc Seperation Parameters

BISPYRIBAC SODIUM

Instrument	:	Agilent 1200 series HPLC - Binary pump, degasser, Auto sampler and thermostat, interfaced with Chem station software.
Detector	:	Diode Array Detector
Column	:	Agilent Eclipse XDB C18 (150 mm x 4.6 mm x 5 micron)
Mobile Phase A	:	0.1% Orthophosphoric acid in Milli-Q water (50%)
Mobile phase B	:	Acetonitrile (50%)
Flow	:	0.7 mL per minute
Column oven		
Temperature	:	40°C
Wave length	:	246 nm, 4 BW
Injection volume	:	10 µL
Total Runtime	:	10 min
Retention Time	:	6.1 min (Approximately)

Table 1: Calibration Details-Bispyribac Sodium

Concentration (mg/L)	Peak Area (mAU*Sec)
10	516.3
2	105.6
1	50.1
0.5	23.6
0.1	5.73
0.05	2.48
0.01	0.24

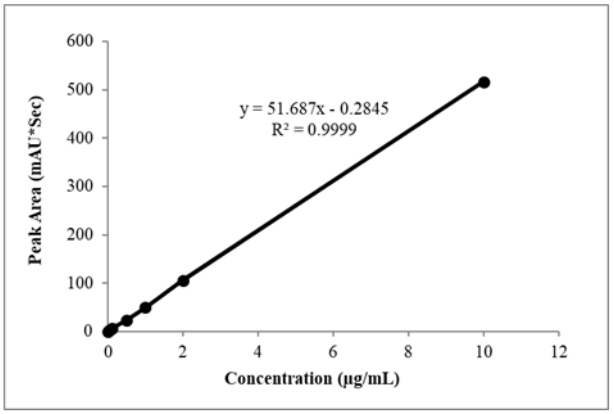

Figure 1: Calibration Curve -Bispyribac Sodium

The Impact of Catalyst Content on Bispyribac Sodium Degree of Degree

This research was carried out to determine the optimum catalyst dose for degrading the residues. The results showed that a concentration of 150 mg/L was optimal for the breakdown of the residues. In a range of catalyst concentrations from 10–50–100–150–200 mg/L, the catalyst's performance steadily improved. The catalyst's degrading efficiency was maximised up to 150 mg/L, and then it dropped down. There may be two conflicting outcomes if the catalyst's load is increased. When a catalyst is

applied to a material, two things can happen: the particles' surfaces become covered with active sites that can be used for adsorption, and the particles themselves may spread a brighter light. As a result, electron-hole pairs cannot be created by these particles. According to Mendez-Arriaga, et al. (2008). However, Neppolian et al. found that collision killed the active ZnO nano particles (2002). Based on these findings, we found that a consistent quantity of 150 mg/L catalyst was optimal for all of our bispyribac sodium photocatalysis tests. Figure 2. is a visual depiction of the findings.

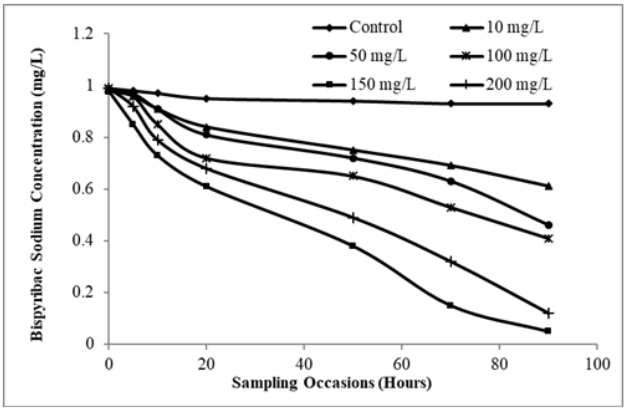

Figure 2: Effect of Amount of Catalyst – Bispyribac Sodium

iii) Effect of Light Source on the Degradation

aving both sunlight and ZnO nano particles available accelerates the photocatalysis of sodium bispyribac. The reaction rate is poor in the dark, both with and without a catalyst. See Figure 3 for the visual representation of the findings.

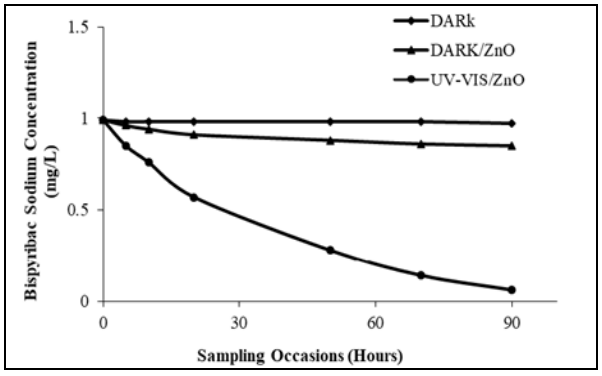

Figure 3: Effect of Light Source on degradation of Bispyribac Sodium

iv) Effect of Aeration on the Degradation

Herbicide residue samples were constantly aerated and aliquots were collected and injected in order to analyse the impact of aeration on the breakdown of the herbicide. Based on the findings, it was determined that the deterioration rate was greater when the solution was exposed to air. Rising levels of dissolved oxygen in water samples promote the production of oxonium ions, which in turn speeds up the breakdown process. Inorganic contaminants with aromatic rings are being cleaved due to the presence of dissolved oxygen. Figure 4 displays the observed data.

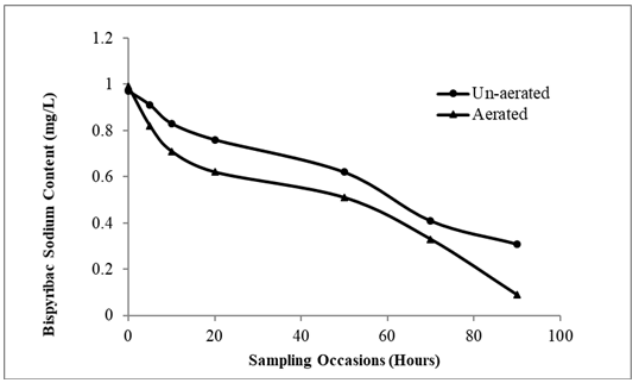

Figure 4: Effect of Aeration on Bispyribac Sodium

The Impact of Oxidant Addition on Herbicide Residue Photo decomposition

ZnO nano suspensions have been studied extensively, and it has been found that combining them with other strong oxidising agents like hydrogen peroxide (H_2O_2) or sodium persulphate ($Na_2S_2O_8$) can increase the rate of photocatalytic degradation by better trapping the photogenerated electrons than molecular oxygen alone can. When testing the effectiveness of hydrogen peroxide on the photo oxidation of various pesticides, unfavourable findings were reported (Navarro et al., 2009). A large enough concentration of peroxide causes it to become an OH• scavenger. When $Na_2S_2O_8$ (100 mg/L) was added, however, the rate at which intermediate compounds were oxidised was greatly increased for three reasons: (1) the oxidant greatly accelerated the reaction rate and increased the number of trapped electrons; (2) it caused a greater production of radicals and other oxidising species; and (3) it accelerated the rate at which the original reaction occurred. Increasing the oxidant concentration did not noticeably alter the reaction rates. Both electron scavenging and the generation of new oxidising species contribute to the peroxydisulfate enhancement effect. It prevents photo-generated electrons from recombining with positively charged holes by acting as a barrier. When this inorganic oxidant is added, additional hydroxyl radicals are created along with SO4• radicals, which

are likewise powerful oxidising species (Eo= 2.6 eV). For these reasons, including an oxidant into the reaction mixture is preferable to ZnO alone since it speeds up the reaction and shortens the treatment time.

ZnO's photocatalytic oxidation rate is limited by the production of photogenerated holes. It is common knowledge that inhibiting the recombination process raises the oxidation rate. There is evidence that peroxydisulfate is a superior and less expensive electron acceptor (Masoud et al., 2010). Figure IV.6 presents the aforementioned study's findings in graphical form.

$$e^- + S_2O8_2^- \rightarrow SO_4^- + SO_4^{2-}$$

$$OH^{\cdot} + SO_4^{2-} \rightarrow OH^- + SO_4^-$$

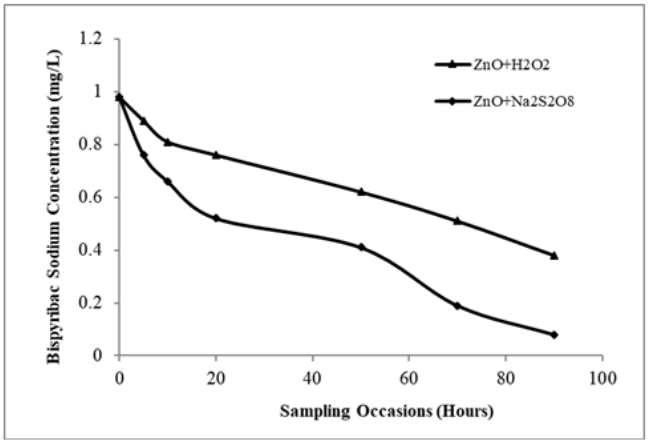

Figure 5: Effect of Addition of Oxidant on Bispyribac Sodium

HERBICIDE ADSORPTION ON THE CATALYST

This research looked into how well bispyribac sodium adsorbs onto ZnO nanoparticles. Bispyribac sodium recovery tests using Milli-Q water and various buffer solutions containing ZnO nanoparticles at 150 mg/L were performed under incandescent conditions. Recoveries of bispyribac Sodium in Milli-Q water varied from 89% to 95% on average, 91% to 95% in acidic water, 88% to 93% in neutral water, and 91% to 95% in basic water.

REUSABILITY OF THE CATALYST

After the photocatalysis experiment was completed, the catalyst was centrifuged off and dried at 100 °C for 4 hours to determine if it could be reused. After 5 iterations, the recovered catalyst was used to test the effectiveness of the catalyst with the freshly generated herbicide solution. After five iterations, the degrading efficiency of the ZnO nano particles dropped from 96.8% to 93.6%. As a result, it showed essentially little efficiency loss. In a series of five repeats, XRD data was collected on the recycled ZnO nanoparticles. No other phases were detected, and all the numbers lined up with those for pure ZnO nanoparticles. Figure 6 shows a graphical representation of the catalyst's reusability, and Figure 7. displays the XRD pattern of the recycled ZnO nanoparticles.

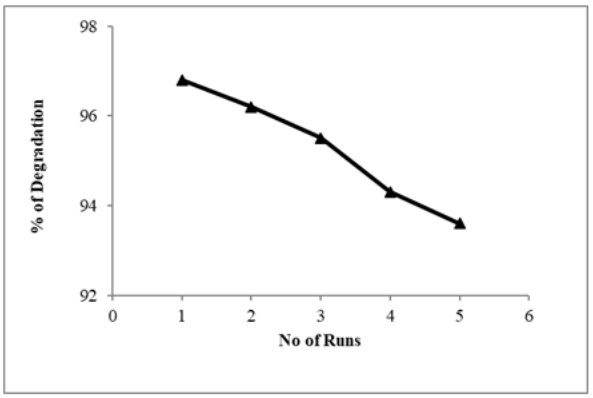

Figure 6: Reusability of ZnO Nano Particles

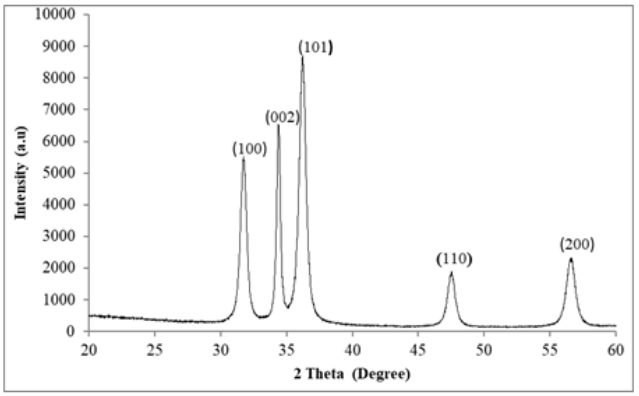

Figure 7: XRD Pattern of the ZnO Nanoparticles after 5 Successive Runs

DISCUSSIONS AND CONCLUSIONS

Milli-Q water, pH 4, pH 7, and pH 9 buffer solutions were all employed satisfactorily in the current investigation to degrade several classes of persistent herbicide residues. Herbicides containing pyrimidinyloxybanzoic acid, such as bispyribac sodium, sulfonyl urea, such as Orthosulfamuron, dinitroaniline, such as pendimethalin, and diphenyl ether, such as fomesafen, degrade photocatalytically in the presence of optimal concentrations of ZnO

and TiO2 nano particles according to first-order kinetics. The optimal catalyst concentration for herbicide degradation was 150 mg/L for bispyribac sodium and 100 mg/L for the other three herbicides, all of which were present in very low concentrations. At acidic pH, herbicides including bispyribac sodium, orthosulfamuron, and pendimethalin reacted quickly, while at basic pH, fomesafen quickly decomposed. Degradation of herbicide residues was much more rapid in the photocatalytic reaction than in the photolytic reaction. For the degradation of bispyribac sodium, orthosulfamuron, and pendimethalin, an acidic pH 4 was superior to mill-Q water, a neutral pH 7 was superior to pH 9, and a basic pH 9 was superior to pH 4. For fomesafen, the order was pH 9 (basic) > mill-Q water, a neutral pH 7 was superior to pH 4, and a basic pH 9 was superior to pH 4. (acidic).

Under sunlight and with the catalyst present, the photocatalytic process proceeded quickly, while in the absence of light, no degradation of the herbicide residues was seen. Based on the results of the degradation tests, it was shown that the degradation rate was significantly higher in aerated water compared to non-aerated water. This occurs because oxonium ions are produced when the dissolved oxygen level of water samples is increased.

Incorporating oxidants (H_2O_2 and $Na_2S_2O_8$) into the reaction mixes sped up the degradation process. Sodium persulfate was found to speed up the reaction more so than hydrogen peroxide did. By adding this inorganic oxidant, more hydroxyl radicals are created, which are likewise strong oxidising species (SO4• radicals). So, compared to using just ZnO, adding an oxidant to the reaction mixture speeds up the reaction and decreases the treatment time.

Additionally, the photocatalysis catalyst was reused for five separate runs with no loss of activity reaction. The efficacy of ZnO and TiO_2 nanoparticles in degrading was compared in an experiment. In comparison to TiO2 nano particles, ZnO nano particles exhibited greater photocatalytic activity. ZnO nanoparticles, when exposed to sunlight, showed significantly higher photo catalytic activity than TiO_2 nanoparticles.

Herbicides were studied to learn what byproducts of the photocatalytic breakdown process were most common.

Sodium bis(2,6-dimethoxypyrimidin-2-yloxy) benzoate -

Sodium 2-(4, 6-dimethoxypyrimidin-2-yloxy)-6-(4-hydroxy-6-methoxypyrimidin-2-yloxy) benzoate

Sodium 2-(4-hydroxy-6-methoxypyrimidin-2-yloxy)-6-hydroxybenzoate

Sodium 2-(4, 6-dimethoxypyrimidin-2-yloxy)-6-hydroxybenzoate

4,6-dimethoxypyrimidin-2-ol

Orthosulfamon- 1-(4-hydroxy-6-methoxypyrimidin-2-yl)-3-[2-=(dimethylcarbamoyl)phenylsulfamoyl]

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