

# PHOTOCATALYTIC DECONTAMINATION CERTAIN HERBICIDES IN AQUEOUS SOLUTION

ANOOP KUMAR  
M.SC. CHEMISTRY

## Abstract

Investigation were conducted to establish the photocatalytic effect on the degradation of six different herbicides anilofos, alachlor, butachlor, azimsulfuron, metsulfuron methyl and sulfosulfuron using  $\text{TiO}_2$  as catalyst. For this purpose three different classes of herbicides (organophosphorus, organochlorine and sulfonyl urea) were studied. The study was mainly conducted in aqueous solutions. The influence of amount of  $\text{TiO}_2$ , temperature, anionic and cationic agents, pH, surfactants and radiant flux were studied. The data generated clearly showed that the addition of  $\text{TiO}_2$  in terms of different quantities, highly influenced the degradation rate. The increase in temperature significantly increased the dissipation rate in the presence of  $\text{TiO}_2$  catalyst up to  $70^\circ\text{C}$ . At different concentrations of the herbicides investigated,  $\text{TiO}_2$  quantity showed significant influence on the degradation rate. This was evident from the fact that 0.5 g/l of  $\text{TiO}_2$  showed optimum dissipation up to the level 20ug/ml. At higher concentration levels even though the dissipation was faster, the results showed the requirement of additional quantities of  $\text{TiO}_2$  as evidenced from the presence of residues.

**Keywords:** Quantity , Influenced , Substance , Degradation, Dissipation, Herbicides

Investigation were conducted to establish the photocatalytic effect on the degradation of six different herbicides anilofos, alachlor, butachlor, azimsulfuron, metsulfuron methyl and sulfosulfuron using  $\text{TiO}_2$  as catalyst. For this purpose three different classes of herbicides (organophosphorus, organochlorine and sulfonyl urea) were studied. The study was mainly conducted in aqueous solutions. The influence of amount of  $\text{TiO}_2$ , temperature, anionic and cationic agents, pH, surfactants and radiant flux were studied. The data generated clearly showed that the addition of  $\text{TiO}_2$  in terms of different quantities, highly influenced the degradation rate. The increase in temperature significantly increased the dissipation rate in the presence of  $\text{TiO}_2$  catalyst up to  $70^\circ\text{C}$ . At different concentrations of the herbicides investigated,  $\text{TiO}_2$  quantity showed significant influence on the degradation rate. This was evident from the fact that 0.5 g/l of  $\text{TiO}_2$  showed optimum dissipation up to the level 20ug/ml. At higher concentration levels even though the dissipation was faster, the results showed the requirement of additional quantities of  $\text{TiO}_2$  as evidenced from the presence of residues.

Anionic and cationic substance also influenced and dissipation of herbicides. The presence of anions such as chloride, per chlorate, sulphate, carbonate and bicarbonate affect the adsorption of the degrading species and thereby affecting the degradation rate. The presence of cations showed both positive and negative effect on the degradation rate. The presence of transition metal ions such as  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  showed marked enhancing effect on the degradation rate. It was also observed that the degradation rate was increased with the increase in the concentration of ferric iron. The presence of the cations cobalt and manganese showed detrimental effect which may be due to the associated anion and the effect of the salts on substrate adsorption.

From the investigation it was observed that at pH 4.0, dissipation rate was found to be enhanced and showed detrimental effect in the rate towards neutral pH. This may be due to influence of pH on the surface charge of the photocatalyst and also the state of ionisation of the substrate and hence its adsorption. At pH 4.0 and 9.0, the photocatalytic degradation was found to be higher. The same phenomena was observed in all herbicides studied. The faster degradation at higher pH's can be attributed due to the rapid hydrolysis of molecules by the free OH radicals.

Surfactant effects were studied by using cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and polyoxy ethylene (23) dodecanol (Brij-35). The degradation of the herbicide was enhanced while using SDS surfactant. The enhancement may be due to the hydrophobic interactions of the herbicide with the anionic micelles. The inhibition of oxidation was observed while using CTAB and Brij-35 surfactants, the inhibitory effect may be due to the lack of hydrophobic or hydrophilic interactions between the herbicide and the surfactants.

The degradation rate of herbicide was found to be proportional to the radiant flux used. At higher fluxes the rate was greater, this means that the process works in a good photocatalytic regime, the incident photons were efficiently converted into active species that act in the degradation mechanism.

From the investigation it was established that the herbicide anilofos was found to degrade within 30 hours completely in ground water when tested at the concentration 20  $\mu\text{g/ml}$ , with the optimum  $\text{TiO}_2$  amount 0.5g/l and at the temperature 40°C. GC-MS analysis also confirms the complete dissipation of this herbicide molecule. No metabolites were identified, under the conditions studied.

The identical experiment conducted in ground water clearly shows the complete dissipation of herbicides, alachlor – 40 hours, butachlor- 30 hrs azimsulfuron – 40 hours, metsulfuron methly – 45 hours and sulfosulfuron - 55 hours. At this time points no residues were detected by the respective chromatographic techniques used. This was also evidenced by the confirmatory techniques GC-MS and

LC/MS/MS applied in the study. When conducted the studies using LC/MS/MS for the identification of metabolites, several metabolites were observed in aqueous solutions due to the photocatalytic degradation of alachlor, butachlor, metsulfuron methyl and sulfosulfuron. (Catrol Macomber et. al, 1992 Emmanell Vulliet et al., 2003).

Calculated the dissipation kinetics in terms of  $DT_{50}$ ,  $DT_{90}$  and rate constant. The details are summarised as follows.

Table 73 Kinetics of degradation of herbicides in ground water.

| Chemical              | $DT_{50}$<br>(Hours) | $DT_{90}$<br>(Hours) | Rate constant<br>(hour <sup>-1</sup> ) |
|-----------------------|----------------------|----------------------|--|
| Anilofos              | 8.81±0.90            | 18.61±2.34           | 0.2032                                 |
| Alachlor              | 7.68±1.41            | 29.42±5.69           | 0.1147                                 |
| Butachlor             | 3.04±1.42            | 15.91±3.50           | 0.1245                                 |
| Azimsulfuron          | 11.15±1.21           | 29.42±4.13           | 0.0253                                 |
| Metsulfuron<br>Methyl | 7.80±1.57            | 35.20±7.26           | 0.1089                                 |
| Sulfosulfuron         | 19.43±1.63           | 52.79±.90            | 0.0824                                 |

Results clearly shows that the dissipation following first order kinetics in all the investigation conducted with different herbicides.

The applicability of the method was studied using effluent samples collected from the herbicide manufacturing facility. Due to the inclusion of  $TiO_2$  all the herbicides were found to degrade rapidly. To understand the influence of inherent parameters associated with the effluents, effluent samples spiked with the herbicides were also tested without the addition of  $TiO_2$ . Under the identical study period 18 to 25% dissipation was observed in the samples fortified with 20 ug/ml of herbicide. This unequivocally highlights the inclusion of  $TiO_2$  in photocatalytic degradation of herbicide in ground water and in effluent treatment.

Investigation were further extended to see the plausible bioaccumulation of hericides in fish due to their presence in water. Studies were conducted by following the international guideline (OPPTS 860.1400) and protocol of OECD (OECD guideline 305). Fish samples were collected at the end of the experiment and analysed for the resifues of herbicide. Testing was conducted with all the six herbicides in fish. Results clearly shows no evidence of bioaccumulation of residues at the tested dosages.

The present investigation clearly thus showed the applications of photocatalytic degradation process in decontamination of three different classes of herbicides, organophosphorus, organochlorine and sulfonyl urea in ground water and in effluent. The methods developed in the studies are simple and easy to apply. Cost effectively, the results can be applied at industrial level for the treatment of water and effluent. At higher concentration levels the presence of metabolites, which were confirmed in the studies likely to be a problem. Further investigation are essential under these directions.

### BIOLOGRAPHY

1. Adriana Zaleska, Jan Hupka, Marek Wiergowski, Marek Biziuk, Photocatalytic degradation of Lindane, p.p.'-DDT and methoxychlor in an aqueous environment, **Journal of Photochemistry and Photobiology A : Chemistry** 135, 213, 220 (2003).
2. Aires P. Gel F. Chamarow E., Esplugas S. **J. Photochem. Photobiol. A. Chem.** 68, 121, 129 (1992)
3. Albanis T.A. Hela D.G. Sakellarides T.M. and Konstantinou I.K. Monitoring of pesticide residues and their metabolite in surface and underground water of Imathia "(N.Greece) by name of solid-phase extraction disks and gas chromatography, **Journal of Chromatography A** 3\823, 1-2, 59-71(1998)
4. Andrea Dannenberg and Simo O. Pehkonen Investigation of the heterogeneously catalysed hydrolysis of organophosphorus pesticides, **J. Agric. Food Chem.** 46,325-334 (198)
5. Anpo M., Kubokawa Y., Itoh K. and Honda K., In "Hikarishokubai (Y. Kubokawa, K. Honda and Y.Saito, Eds.) Chap.1 , p-10 **Asakurashoten**, Tokyo, (1989).
6. Antonio Di Corcia and Morcello Marchetti, Multi residue methods for pesticides in drinking water using a graphitized carbon black cartridge extraction and Liquid chromatographic analysis, **Anal Chem.** 63, 580-585 (1991).
7. Atmakuru Ramesh and Sinthalapadi Thulasiramaraja Maheswari, Dissipation of Sulfosuluron in Soil and Wheat Plant under Predominant cropping conditions and in a simulated model ecosystem. **J. Agric Food Chem.** 51, 3396-3400 (2003).
8. Banhemann D.W. Cunningham J. Fox M.A. Pelizzetti E., Pichat P., Serpone N. Helz G.R. Zepp R.G. and Crosby D.G. **Aquatic and surface chemistry**, p.261 (1994)