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EFFECT OF pH, HUMIC ACID AND MOISTURE CONTENT ON PHOTO CATALYTIC DEGRADATION OF HERBICIDES IN LOAMY SAND SOIL

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Abstract

The dissipation kinetics activity of $FeTiO_2$ nanoparticles on four herbicides (dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl) in loamy sand soil was investigated with effect of soil pH, moisture and humic acid content on the decontamination of herbicide in photocatalysis were investigated.

The effective concentration of humic acid required for the rapid decontamination of herbicide residues on soil was established by varying the amount of humic acid in the range of 10 to 40 mg/Kg and the effective concentration of humic acid was 10 mg/Kg for dicamba, 30 mg/Kg for metsulfuron-methyl and clodinafop-propargyl and there was no effect on imazethapyr. The effect of pH of soil on the decontamination of herbicide residues in soil was investigated by varying the pH of soil from 4.0 to 9.7 and the rapid degradation was observed in soil of pH 9.7 for dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl in soil of pH 4 when compare to other pH of soil. The degradation order was pH 4 < pH 6.5 < pH 8.0 < pH 9.7 for dicamba and imazethapyr and for metsulfuron methyl and clodinafop-propargyl was pH 6.5 < pH 8 < pH 9.7 < pH 4. The effect of moisture content on decontamination of herbicide residues in soil was investigated by varying moisture content in soil from 20 to 50 mL/Kg. The effective moisture content for rapid degradation of dicamba was 50 mL/kg, while imazethapyr, metsulfuron-methyl and clodinafop-propargyl was 40 mL/kg.

Key Words: *$FeTiO_2$ Nanoparticles, Herbicide Residues, humic acid, pH, HPLC, moisture content*

Introduction

Most of the countries depending on the agriculture. Swiftly developing global human populace and changing intake patterns of meals have inspired the evolution of agriculture from traditional to modern, intensive systems (Augugliaro et al., 1994). Several pesticides (herbicide, insecticide, fungicide, soil sterilants, and wood preservatives) is used in crop protection to control pest, insects, nematodes, rodents and weed (Cui et al., 2009). Pesticides are also used in public places and in indoor to control diseases which is caused and spreading by mosquitoes and flies for human healthz (Dianbo et al., 2010). The volume of herbicide use potentially

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increased in several folds during the past decade to control weed population (Dong et al., 2010). The herbicides which are classifieds in to different categories based on their chemical nature and includes imidazolinone, chloroacetanilide, triazine, triazole, organophosphorus, urea, carbamate, etc.(Hung et al., 2008) . The sulfonylurea herbicide is being used widely due to their biochemical activity, low effective concentration (approx 100-1000 times) than that of conventional herbicides, low mammalian toxicity and excellent selectivity for weed control (Kamiya and Kameyama, 1998).

The fate of pesticides applied in the agriculture field depends on the influence of the physical and chemical characteristics of the soil system, (such as moisture content, organic matter, clay content and p^H), volatility, sorption/desorption and degradation properties of pesticides and their access to groundwater and surface water (Luu et al., 2010). The presence of residues of pesticides due to long persistence nature of the compound or formation of bound residue in soil produces impact on microbial population in soil, phytotoxicity to succeeding crops and enters into the water reservoirs and other water resources. This associated pesticide exposure creates delayed health effects include leukemia, lymphomas, soft-tissue sarcomas, and brain, bone, stomach cancers in farmers, sprayers, and production workers occurrence of parkinson's disease and developmental defects (Quan et al., 2005). The accumulation of pesticides residues has direct effect not only on human population but also on phytoplankton and zooplankton in ecosystem (Sharma et al., 2008). To protect the soil, water reservoirs and phytoplankton and zooplankton in ecosystem from the toxic contaminants of pesticides residues, several decontamination techniques such as photo chemical oxidation, electro chemical oxidation, sono-photo oxidative, homogeneous and heterogeneous sonolysis, nano-bio redox, membrane filteration, biosorbtion, aerosol, biological treatment and photocatalytic are being used (Vulliet et al., 2003). Heterogeneous photocatalysis is one of the advanced oxidation technology which is being widely used in decontamination of pesticide in soil and water**.** The application of nanoparticles are widely reported in a wide variety of area including advance materials, electronic, magnetic and photoelectronics, biomedicine, pharmaceuticals, cosmetics, energy and catalytic and environmental detection and monitoring (Weber et al., 2007). The heterogeneous photocatalyst nano titanium dioxide (TiO_2) and its analogues for degradation and mineralization of the pesticide in water and soil using solar, UV and visible-light has gained wide attention in the recent years due to its low cost preparation, nontoxic, and effectiveness (Wu et al., 2010). When these nanoparticles are subjected to UV or solar light, it absorbs energy by photons of light and the electrons (e^-) from the Valence Band (VB) get promoted to the Conduction Band (CB) leaving a positive hole (h^+). These electrons (e^-) and positive holes (h^+) are involved in the degradation of pesticides by oxidation / reduction process (Lu et al., 2011). However, low efficiency due to fast recombination of photo-generated electrons (e^-) and positive holes (h^+) within a fraction of second was observed. The availability of UV radiation from solar to earth (3–5%) was another limiting factor (Zhang et al., 2008).

Materials and Methods

Reference analytical standards of Dicamba (Purity 99.2%), Imazethapyr (Purity 99.9%), Metsulfuron-methyl (Purity 98.9%) and Clodinafop-propargyl (Purity 98.8%) were obtained from Sigma Aldrich. The test items of Dicamba 400 g/L SC, imazethapyr 100 g/L SL, Metsulfuron-methyl 20 WG and Clodinafop-Propargyl 240g/L EC) were purchased from local market. The test soil (Loamy sand) was collected from Hakimpet in Rangareddy district, Telangana. Acetonitrile, Water HPLC grade, Ortho Phosphoric acid AR grade, Sodium hydroxide AR grade, Titanium tetrachloride, AR grade, Ferric nitrate, AR grade, Ferric chloride, GR grade, Ethylene diamine tetra acetic acid AR grade, Ferric nitrate, AR grade were obtained from the Merck India limited. Distilled water was purified by using the Stone-fin. Shimadzu High Performance Liquid Chromatograph system equipped with LC-20 ATvp pump and SPD-20A UV/VIS CTO-20A Column oven using LC soluition software. pH meter supplied by M/s. Digisun Electronic, Hyderabad 500 482.Volumetric flasks, pipettes, measuring cylinder and glass columns - All 'A' grade glassware supplied by M/s.Borosil Glass and Glassware Mumbai, India and Sartorious -BSA 2245-CW analytical balance, capable of weighing 0.01 mg (Table 1).

Table 1. *HPLC Separation parameters*

Parameters	Dicamba	Imazethapyr	Metsulfuron-methyl	Clodinafop-propargyl
Column oven Temperature	30°C	30°C	30°C	30°C
Column	Phenomenex C18 (25 cm x 4.6 mm i.d x 5µm particle size.)	Phenomenex C18 (25 cm x 4.6 mm i.d x 5µm particle size.)	Phenomenex C18 (25 cm x 4.6 mm i.d x 5µm particle size.)	Nucleosil C18 (250 mm, 4.0 mm x 5µm particle size)
Volume injected	20 µL			
Flow rate	1.0 mL/min	1.0 mL/min	1.0 mL/min	2.0 mL/min
Wave length (nm)	220	230	254	305
Mobile Phase	Acetonitrile HPLC water (0.1% H_3PO_4)	Acetonitrile pH 3.0 adjusted with H_3PO_4 milli-Q water	Acetonitrile pH 4.0 adjusted with H_3PO_4 milli-Q water	Acetonitrile pH 3.0 adjusted with H_3PO_4 milli-Q wate
Mobile Phase ratio (% v/v)	50 : 50	50 : 50	50 : 50	60 : 40
Retention time in minutes (approximate)	7.1	5.9	5.2	5.5
Instrument	HPLC	Shimadzu High Performance Liquid Chromatograph system		
	Pump	LC-10 ATvp		
	Column oven	CT0-20A		
	Detector	SPD-10AV - vp UV Detector		
	Software	LC Solution		

Experimental Procedure

Preparation of TiO_2 nanoparticles. The TiO_2 nanoparticles was prepared by adding drop wise 4 mL of Titaniumtetrachloride ($TiCl_4$) in 100 mL distilled water containing 1% Hydrochloric acid (HCl) at 5°C and was ultrasonicated for 1 hour at 80°C and kept for 16 hours at 80°C in a thermostat controlled oven

$$TiCl_4 + 2H_2O \rightarrow TiO_2 \quad + 4HCl$$

The obtained white precipitate was washed in distilled water 8 times by using refrigerated centrifuge and finally washed with methanol. The methanol was decanted and the precipitate (TiO_2 nanoparticles) was dried at 120°C for 4 hours.

Preparation of $FeTiO_2$ nanoparticles. $FeTiO_2$ nanoparticles was prepared by adding drop wise 100 mL boiling solution of Iron nitrate [100 mL containing 0.0473 g $Fe(NO_3)_3{\cdot}9H_2O$] into a 100 mL boiling distilled water contained 2 g TiO_2 nanoparticles. Both the solutions were mixed by sonicating at 100°C for 30 min, according to the following chemical equation:

$$TiO_2(aqua) + Fe(NO_3)_3 \cdot 9H_2O(aqua) \rightarrow Fe\text{–}TiO_2$$

The obtained brown coloured $FeTiO_2$ nanoparticles was washed in distilled water 5 times by using refrigerated centrifuge and finally washed with methanol. The $FeTiO_2$ nanoparticles were dried at 120°C for 4 hours after decanted the methanol.

Characterization. The Characterization of $FeTiO_2$ nanoparticles by Scanning Electron Microscopy (SEM) (Indian Institute of Technology, Chennai - facility) for the quantitative determination and elemental composition of Fe/Ti ratio presented in Figure 1 indicates the Fe content was 0.5 % and Ti, O and Fe are the elemental compositions. The size of the particle was observed to be 15-18 nm by scanning Transmission Electron Microscopy (TEM) (Indian Institute of Technology, Chennai - facility) as presented in Figure 2.

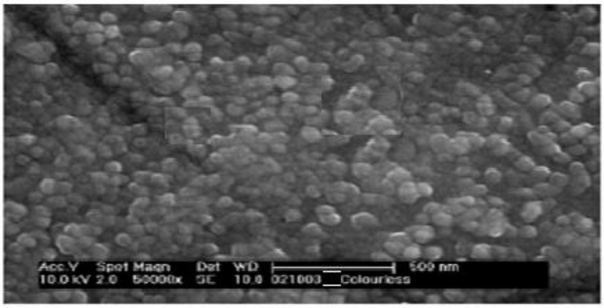

Figure *1*
SEM Image of $FeTiO_2$ nanoparticles

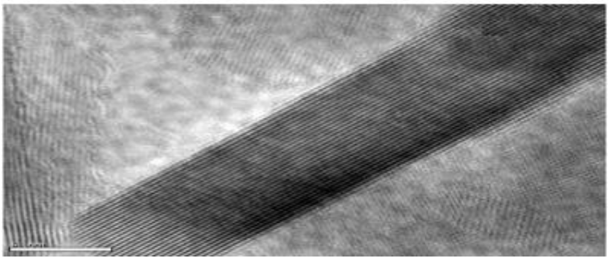

Figure 2.
TEM Image of $FeTiO_2$ nanoparticles

Preparation of standard stock solutions. The stock solutions of reference analytical standards were prepared by weighing around 10 mg of dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl of known purity into each of different 10 mL volumetric flasks using an analytical balance having accuracy of 0.01 mg. The content of each flask were dissolved using HPLC grade acetonitrile and made up to the mark.

Preparation of formulation solutions of herbicide. The required quantity of herbicide formulation (Dicamba 400 g/L SC, imazethapyr 100 g/L SL, Metsulfuron-methyl 20 WG and Clodinafop-Propargyl 240g/L EC) were weighed into each of different 50 mL volumetric flasks. The content was dissolved in Milli-Q water and made upto the mark (Table 2).

Table 2
Dose applications of herbicides

Formulation	Application Dosage	Weight of formulation
Dicamba 480 g/L SL	2 L product/ha	40 mg product / Kg
Imazethapyr 100 g/L SL	1 L product/ha	20 mg product / Kg
Metsulfuron-methyl 20 WG	60 g a.i/ha	1.5 mg product/ Kg
Clodinafop-Propargyl 240g/L EC	75 g a.i/ha	2mg product/ Kg

Preparation of calibration solutions. Calibration solutions were prepared by diluting aliquots of the herbicide stock solution into each of separate volumetric flask in acetonitrile for linearity determination. The concentration used for dicamba and imazethapyr were 2.0, 1.0, 0.5, 0.1, 0.05 and 0.01 mg/L, while for metsulfuron-methyl and clodinafop-propargyl the concentration were 5.0, 2.0, 0.5, 0.1, 0.05 and 0.01 mg/L.

Recovery and limit of quantification. Recovery studies were conducted by fortifying three different concentrations of each herbicide at 0.03, 0.15 and 0.3 µg/g levels in loamy sand soil. Three replicates determinations were made at each concentration level along with two controls. Based on the recovery study the limit of quantification is established.

Effect of humic acid content. To investigate the effect of humic acid content on the decontamination of herbicide in soil, soil samples were added humic acid (prepared by dissolving 100 mg of Humic acid in 0.1M NaOH solution and diluted with 1000 mL distilled water) by varying the concentration of 0, 10, 20, 30 and 50 mg/Kg in soil without varying the concentration of the $FeTiO_2$ and without changing pH of soil. The soil samples were spread by hand to get 5 mm layer thickness in a glass tray and sprayed with aqueous solution of herbicide formulation which is dissolved in 50mL distilled water for 1Kg soil by using 1L High density polyethylene bottle sprayer and kept in an oven at 110°C for 2 hours to evaporate the water molecules. The glass trays were exposed to sun light from morning 8 a.m. to evening 5 p.m. in the month of February, 2015. Three replicates were maintained for each soil.

***Effect of* $\mathbf{p^H}$** . To investigate the effect of p^H on the decontamination of herbicide in soil, p^H of soil samples were adjusted to p^H 4.0, 6.5, 8.0 and 9.7 using an aqueous solution of H_2SO_4 or an aqueous solution of NaOH with constant $FeTiO_2$ concentration without the addition of Humic acid in soil. The soil was spread by hand to get 5mm layer thickness in a glass tray and sprayed with aqueous solution of herbicide formulation. This was prepared by dissolved in 50mL distilled water for 1kg soil. and kept in an oven at 110°C for 2 hours to evaporate the water molecules. The glass trays were exposed to sun light from morning 8 a.m. to evening 5 p.m. in the month of February, 2015. Three replicates were maintained for each soil.

Effect of moisture content. To investigate the effect of moisture content on the decontamination of herbicide in soil, soil samples were added water to vary the moisture content 0, 20, 30, 40 and 50 mL/Kg with constant $FeTiO_2$ concentration and without the addition of humic acid. The soil was spread by hand to get 5mm height in a glass tray and sprayed with aqueous solution of herbicide formulation. This was prepared by dissolved in 50mL distilled water for 1kg soil and kept in an oven at 110°C for 2 hours to evaporate the water molecules and then added 0, 20, 30, 40 and 50 mL/Kg water. The glass trays were exposed to sun light from morning 8 a.m. to evening 5 p.m. in the month of February, 2015. Three replicates were maintained for each soil. Experimental design for photocatalytic decontamination of herbicide in soil is presented in Table 3.

Table 3. *Experimental design for photocatalytic decontamination of herbicide in soil*

No.	Type of Experiment	Type of soil	Amount of $FeTiO_2$ loaded (wt %)	pH Value of Soil	Amount of Humic acid (mg/Kg)	Moisture content (mL/Kg)
1	Effect of Humic acid	Loamy sand	0.6	6.82	5, 10, 20, 30 and 40	Not added
2	Effect of soil pH	Loamy sand	0.6	4.0, 6.5, 8.0 and 9.7	Not added	Not added
3	Effect of moisture content	Loamy sand	0.6	6.82	Not added	0, 20, 30, 40 and 50

Results and discussion

Linearity

The methods were found to be linear with acceptable correlation coefficient when tested in the range 2.0 - 0.01 mg/L for dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl. The Limit of Detection (LOD) is established as 0.01 mg/L based on 3:1 peak to noise height ratio. Statistical parameters for linearity such as Correlation Coefficient (r) and the linear regression equation (Y = mX + C) were done by plotting different concentration of calibration solutions versus observed were of calibration solutions were presented in Table 4. Calibration curve was presented in Figure 3.

Table 4. *Calibration details - dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl.*

Concentration (mg/L)	Peak area of dicamba (µV-sec)	Peak area of imazethapyr (µV-sec)	Peak area of metsulfuron-methyl (µV-sec)	Peak area of clodinafop-propargyl (µV-sec)
2	42361	45385	43758	38854
1	21451	22787	21241	19484
0.5	10765	11023	11089	10052
0.1	2058	2105	2254	1987
0.05	1012	1087	1148	1003
0.01	189	221	244	198

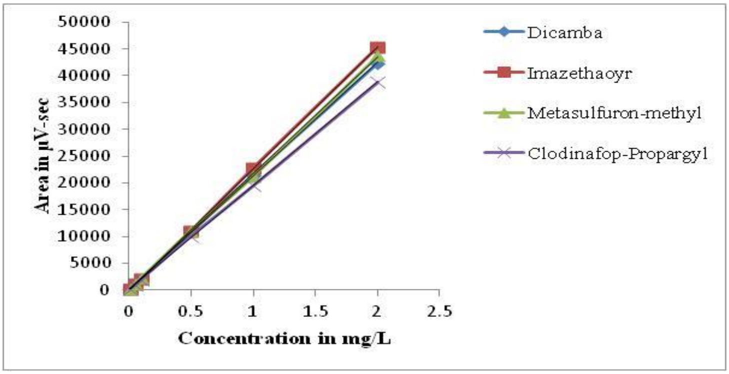

Figure 3 *Calibration curve of dicamba, imazethapyr, metsulfuron-methyl and clodinafop-propargyl*

Recovery

The methods were observed in precision with a acceptable range < 20 % of RSD when injected 10 x LOQ recovery sample five times consecutively into the HPLC. The method had an acceptable recovery range (70 - 110 %) for herbicide in loamy sand soil. The Limit of Quantification (LOQ) is established as 0.03 mg/L from 10:1 peak to noise height ratio. The statistical parameters for recovery such as mean recovery percentage, standard deviation (SD), percentage of relative standard deviation (% RSD) and Horwitz Limit were presented in Table 5.

Table 5. *Recovery details of Herbicide in loamy sand soil*

Type of Soil	Statistical parameters	Compound Name			
		Dicamba	Imazethapyr	Metsulfuron-methyl	Clodinafop-propargyl
Loamy sand	Mean	92.31	90.24	94.58	91.89
	SD	2.03	1.74	1.21	2.45
	% RSD	2.19	1.93	1.27	2.67

Effect of p^H

On 0 hour soil sample analysis from each p^H of soil with constant 2,4-D concentration showed that the residue value of dicamba were 30.12 µg/g, 30.09

µg/g, 30.12 µg/g, 30.13 µg/g for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. Dissipation of 2,4-D went to 9.54 µg/g, 8.29 µg/g, 5.92 µg/g, 1.28 µg/g on 36th hour for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. On 63rd h the 2, 4-D got complete degradation for p^H 8.0 and p^H 9.7 but p^H 4.0 and p^H 6.5 soils got complete degradation on 90th hour.

On 0 hour soil sample analysis from each pH of soil with constant imazethapyr concentration showed that the residue value of imazethapyr were 21.12 µg/g, 21.14 µg/g, 21.13 µg/g, 21.16 µg/g for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. Dissipation of imazethapyr went to 5.89 µg/g, 4.23 µg/g, 3.33 µg/g, 2.96 µg/g on 18 h for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. On 54th hour, imazethapyr got complete degradation for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 soil.

On 0 hour soil sample analysis from each pH of soil with constant metsulfuron-methyl concentration showed that the residue value of metsulfuron-methyl were 0.208 µg/g, 0.204 µg/g, 0.211 µg/g, 0.209 µg/g for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. Dissipation of metsulfuron-methyl went to 0.079 µg/g, 0.102 µg/g, 0.096 µg/g, 0.092 µg/g on 18th hour for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. On 36th hour, metsulfuron-methyl got complete degradation for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 soil.

On 0 hour soil sample analysis from each p^H of soil with constant clodinafop-propargyl concentration showed that the residue value of clodinafop-propargyl were 0.224 µg/g, 0.221 µg/g, 0.223 µg/g, 0.225 µg/g for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. Dissipation of clodinafop-propargyl went to 0.069 µg/g, 0.094 µg/g, and 0.104 µg/g, 0.092 µg/g on 18th hour for p^H 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 respectively. On 54th hour, clodinafop-propargyl got complete degradation for pH 4.0, p^H 6.5, p^H 8.0 and p^H 9.7 soils.

The p^H of the soil plays an important role in the studies on the photodegradation of herbicide, since it influences the surface-charge properties of the catalyst TiO_2 thus governing the rate of reaction. It can be concluded from results that the rate of the decontamination of metsulfuron-methyl and clodinafop-propargyl appewered to be greater at soil p^H 4.0 and p^H 9.7 than at soil p^H 6.5 and p^H 8.0 but for dicamba and imazethapyr the rate greater at soil p^H 8.0 and p^H 9.7 than at soil p^H 4.0 and p^H 6.5. The $FeTiO_2$ surface is positively charged in acidic media ($p^H < 6.5$), whereas it is negatively charged under alkaline conditions ($p^H > 8.0$). Under acidic or alkaline conditions, more H^+ or OH^- ions were produced in soil, and these ions would be able to facilitate the photocatalytic reactions of herbicides. Kinetic parameters such as rate constant (k), $DT_{50,}$ and DT_{90} for effect of pH on dissipation were presented in Table 6.

Effect of humic acid content

On 0 hour soil sample analysis from each concentration of humic acid added soil with constant dicamba concentration showed that the residue value of dicamba were 30.09 µg/g, 30.08 µg/g, 30.09 µg/g, 30.11 µg/g, and 30.06 µg/g for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively.

Table 6
Kinetic parameters for effect of p^H on decontamination of herbicide in soil under direct sunlight.

Kinetic parameters	**pH**			
	p^H 4.0	p^H 6.5	p^H 8.0	p^H 9.7
Dicamba				
DT_{50} (h)	16.67	14.80	13.42	7.90
DT_{90} (h)	55.37	49.17	44.58	26.24
k (1×10^{-3} h^{-1})	41.6	46.8	51.7	87.8
Imazethapyr				
DT_{50} (h)	10.73	9.22	7.55	6.75
DT_{90} (h)	35.64	30.61	25.07	22.43
k (1×10^{-3} h^{-1})	64.6	75.2	91.9	102.7
Metsulfuron-methyl				
DT_{50} (h)	10.59	16.18	12.76	11.44
DT_{90} (h)	35.18	53.73	42.40	38.01
k (1×10^{-3} h^{-1})	65.5	42.9	54.3	60.6
Clodinafop-propargyl				
DT_{50} (h)	13.08	15.89	17.79	15.50
DT_{90} (h)	43.46	52.80	59.11	51.48
k (1×10^{-3} h^{-1})	53.0	43.6	39.0	44.7

The residues of dicamba dissipated to 7.98 µg/g, 7.03 µg/g, 8.24 µg/g, 8.92 µg/g, and 9.77 µg/g on 36 h for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively.

On 72nd hour, the 2,4-D concentration degraded to near the LOQ level for all concentration of humic acid added soil respectively and got complete degradation on 90th hour. The comparatively high degradation is observed for 10 mg/Kg humic acid added soil. The decrease of degradation on further increase of humic acid content is observed.

On 0 hour soil sample analysis from each concentration of humic acid added soil with constant imazethapyr concentration showed that the residue value of imazethapyr were 21.15 µg/g, 21.12 µg/g, 21.14 µg/g, 21.11 µg/g, and 21.13 µg/g for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. The residues of imazethapyr dissipated to 4.68 µg/g, 6.23 µg/g, 6.45 µg/g, 6.73 µg/g, and 6.92 µg/g on 18 h for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. On 36th hour, the imazethapyr concentration degraded to near the LOQ level for all concentration of humic acid added soil respectively and got complete degradation on 54th hour. The comparatively high degradation is observed for 0 mg/Kg humic acid added soil. The addition of humic acid content decreases the degradation imazethapyr.

On 0 hour soil sample analysis from each concentration of humic acid added soil with constant metsulfuron-methyl concentration showed that the residue value of metsulfuron-methyl were 0.197 µg/g, 0.201 µg/g, 0.199 µg/g, 0.202 µg/g, and 0.201 µg/g for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. The residues of metsulfuron-methyl dissipated to 0.092 µg/g, 0.088 µg/g, 0.074 µg/g, 0.034 µg/g, and 0.038 µg/g on 18th hour for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. On 27h the metsulfuron-methyl concentration degraded to near the

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LOQ level for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg humic acid added soil respectively and got complete degradation on 36th hour. The comparatively high degradation is observed for 30 mg/Kg humic acid added soil. The addition of humic acid content increases the degradation of metsulfuron-methyl.

On 0 hour soil sample analysis from each concentration of humic acid added soil with constant clodinafop-propargyl concentration showed that the residue value of clodinafop-propargyl were 0.221 µg/g, 0.225 µg/g, 0.223 µg/g, 0.222 µg/g, and 0.224 µg/g for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. The residues of clodinafop-propargyl dissipated to 0.089 µg/g, 0.081 µg/g, 0.078 µg/g, 0.062 µg/g, and 0.084 µg/g on 18th hour for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg, 30 mg/Kg and 40 mg/Kg humic acid added soil respectively. On 36h the clodinafop-propargyl concentration degraded to near the LOQ level for 0 mg/Kg, 10 mg/Kg, 20 mg/Kg and 40 mg/Kg humic acid added soil respectively and got complete degradation on 54th hour. The comparatively high degradation is observed for 30 mg/Kg humic acid added soil. The addition of humic acid content increases the degradation of clodinafop-propargyl from 0 to 30 mg/Kg.There is no increase on further addition of humic acid. Kinetic parameters such as rate constant (k), DT_{50}, and DT_{90} for effect of humic acid dissipation were presented in Table 7.

Table 7. *Kinetic parameters*

	Humic acid content				
Kinetic parameters	0 mg/Kg Humic acid content	10 mg/Kg Humic acid content	20 mg/Kg Humic acid content	30 mg/Kg Humic acid content	40 mg/Kg Humic acid content
Dicamba					
DT_{50} (h)	15.68	14.47	16.27	16.94	18.10
DT_{90} (h)	52.07	48.08	54.06	56.28	60.13
k (1 x 10^{-3} h^{-1})	44.2	47.9	42.6	40.9	38.3
Imazethapyr					
DT_{50} (h)	9.15	10.00	10.18	10.30	10.50
DT_{90} (h)	30.40	33.23	33.82	34.22	34.88
k (1 x 10^{-3} h^{-1})	75.7	69.3	68.1	67.3	66.0
Metsulfuron-methyl					
DT_{50} (h)	15.21	14.29	12.88	11.00	12.57
DT_{90} (h)	50.52	47.49	42.78	36.55	41.77
k (1 x 10^{-3} h^{-1})	45.6	48.5	53.8	63.0	55.1
Clodinafop-propargyl					
DT_{50} (h)	14.92	14.21	12.59	9.78	15.12
DT_{90} (h)	49.56	47.22	41.82	32.49	50.24
k (1 x 10^{-3} h^{-1})	46.5	48.8	55.1	70.9	45.8

Effect of moisture content

On 0 hour soil sample analysis of soil with constant dicamba concentration and different moisture content showed that the residue value of dicamba were 30.09 µg/g, 30.11 µg/g, 30.07 µg/g, 30.09 µg/g, and 30.07 µg/g for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. The residues of dicamba dissipated to 7.98 µg/g, 6.01 µg/g, 5.02 µg/g, 4.88 µg/g, and

4.83 µg/g on 36th h for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. On 72nd hour the dicamba concentration degraded to near the LOQ level for all soil with addition of moisture content and got complete degradation on 90th hour. The comparatively high degradation is observed for 40 mL/Kg and 50 mL/Kg moisture content in soil. The addition of moisture content increases the degradation of dicamba from 0 to 40 mg/Kg. There is no increase on further addition of moisture content.

On 0 hour soil sample analysis of soil with constant imazethapyr concentration and different moisture content showed that the residue value of imazethapyr were 21.15 µg/g, 21.11 µg/g, 21.14 µg/g, 21.15 µg/g, and 21.14 µg/g for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. The residues of imazethapyr dissipated to 4.68 µg/g, 4.26 µg/g, 3.98 µg/g, 3.26 µg/g, and 3.28 µg/g on 18th hour for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. On 36th hour the imazethapyr concentration degraded to near the LOQ level for all soil with addition of moisture content and got complete degradation on 90th hour. The comparatively high degradation is observed for 30 mL/Kg moisture content in soil. The addition of moisture content increases the degradation of imazethapyr from 0 to 30 mg/Kg. There is no increase on further addition of moisture content.

On 0 hour soil sample analysis of soil with constant metsulfuron-methyl concentration and different moisture content showed that the residue value of metsulfuron-methyl were 0.197 µg/g, 0.201 µg/g, 0.199 µg/g, 0.202 µg/g, and 0.201 µg/g for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. The residues of metsulfuron-methyl dissipated to 0.092 µg/g, 0.088 µg/g, 0.074 µg/g, 0.034 µg/g, and 0.038 µg/g on 18thh for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. On 27th hour, the metsulfuron-methyl concentration degraded to near the LOQ level for all soil with addition of moisture content and got complete degradation on 36th hour. The comparatively high degradation is observed for 40 mL/Kg moisture content in soil. The addition of moisture content increases the degradation of metsulfuron-methyl from 0 to 40 mg/Kg. There is no increase on further addition of moisture content.

On 0 hour soil sample analysis of soil with constant clodinafop-propargyl concentration and different moisture content showed that the residue value of clodinafop-propargyl were 0.221 µg/g, 0.224 µg/g, 0.223 µg/g, 0.222 µg/g, and 0.224 µg/g for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. The residues of clodinafop-propargyl dissipated to 0.089 µg/g, 0.079 µg/g, 0.072 µg/g, 0.045 µg/g, and 0.049 µg/g on 18 h for 0 mL/Kg, 20 mL/Kg, 30 mL/Kg, 40 mL/Kg and 50 mL/Kg moisture content in soil respectively. On 36th hour the clodinafop-propargyl concentration degraded to near the LOQ level for 0 mL/Kg, 20 mL/Kg, and 30 mL/Kg moisture content in soil respectively and got complete degradation on 54th hour. The comparatively high degradation is observed for 40 mL/Kg moisture content in soil. The addition of moisture content increases the degradation of clodinafop-propargyl from 0 to 40 mg/Kg. There is no increase on further addition of moisture content. Kinetic parameters such as rate constant (k), $DT_{50,}$ and DT_{90} for effect of moisture content on dissipation were presented Table 8.

Table 8. *Kinetic parameters for effect of moisture content on decontamination of herbicide in soil under direct sunlight*

Moisture Content (%)				**Kinematic Parameters**		
Replication 1	Replication 2	Replication 3	Mean	DT50 (h)	DT90 (h)	k (1 x 10-3 h-1)
Dicamba						
13.5	12.9	12.1	11.9	15.7	52.1	44.2
44.9	42.9	40.0	39.4			
51.2	53.6	57.5	58.4			
Imazethapyr						
8.70	8.00	4.80	4.80	9.60	30.4	75.7
28.8	26.7	15.8	16.1			
80.1	86.4	146	143			
Metsulfuron-methyl						
14.3	13.5	7.0	7.5	15.2	50.5	45.6
47.6	44.9	23.2	24.9			
48.3	51.2	99.0	92.6			
Imazethapyr						
13.9	12.8	7.80	8.20	14.9	49.6	46.5
46.1	42.4	25.9	27.3			
49.9	54.4	88.7	84.4			

Conclusions

The p^H of the soil plays an important role in the studies on the photodegradation of herbicide, since it influences the surface-charge properties of the catalyst TiO_2 thus governing the rate of reaction. It can be concluded from results that the rate of the decontamination of metsulfuron-methyl and clodinafop-propargyl papered to be greater at soil p^H 4.0 and p^H 9.7 than at soil p^H 6.5 and p^H 8.0 but for dicamba and imazethapyr the rate greater at soil p^H 8.0 and p^H 9.7 than at soil p^H 4.0 and p^H 6.5. The $FeTiO_2$ surface is positively charged in acidic media ($p^H < 6.5$), whereas it is negatively charged under alkaline conditions ($p^H > 8.0$). Under acidic or alkaline conditions, more H^+ or OH^- ions were produced in soil, and these ions would be able to facilitate the photocatalytic reactions of herbicides. In presence of humic acid photo catalytic degradation of herbicides very fast in loamy sand soil. The addition of moisture content increases the degradation of herbicides in loamy sand soil.

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