PHOTOCATALYTIC DEGRADATION OF TRIFLURALIN; HERBICIDE USING NANO-SIZED THERMO-CHEMICALLY SYNTHESIZED TIO_2 UNDER VISIBLE LIGHT

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ABSTRACT

Mesoporous anatase titanium dioxide (TiO_2) semiconductor heterogeneous photocatalyst powder with high specific area were synthesized by using cetyltrimethylammoniumbromide (CTAB) as a directing and performing agent via hydrothermal process in a facile and reproducible way. The phase state and crystallite size of the as-synthesized TiO_2 nanoparticlres were characterized by the X-Ray Diffraction pattern; (XRD), Transmission Electron Micrtoscopy (TEM) and UV-Visible spectroscopy techniques. Band gap energy (E_{bg}) of TiO_2 was obtained, spectrophotometrically. Heterogeneous photocatalytic degradation of triflualin; herbicide using TiO_2 as a photocatalyst was carried out in a Batch Reactor. The observed kinetic data revealed that photodegradation of trifluralin in aqueous solution using titanium dioxide followed first order kinetics. Increase in the light intensity as well as in time resulted in the enhancing of the rate of degradation of trifluralin.

Keywords: Nanosize, Photocatalysis, Thermochemical, Titanium Dioxide, Trifluralin

I. INTRODUCTION

The residual pesticides in food/ water are very toxic for animals as well as plants; therefore, their degradation is very serious problem. To achieve economy, photo catalytic degradation method can be applied. There are numerous type of photo catalyst are available. Among these Nanostructured titania (TiO_2) possess an immense range of applications e.g. in the field of optics [1], electrical insulation [2], photovoltaic solar cells [3], electrochromic displays [4], antibacterial coatings [5]. Since the Photocatalytic activity of TiO_2 is influenced by crystal size, crystal structure, crystallinity and surface hydroxylation the synthesis of phase pure nanorcystalline anatase TiO_2 is challenging [6], [7], [8], [9] and [10]. Among three crystalline phases of TiO_2 (Anatase, Rutile and Brookite), anatase exhibits the highest photocatalytic activity. In the present investigation, hydrothermal method has been adopted for the preparation of mesoporous anatase TiO_2 nanoparticles by using

Cetyltrimethylammoniumbromide (CTAB). Herbicide such as trifluralin, yellow orange colored crystals is chosen for photocatalytic degradation due to its wide solubility in solvents like acetone, chloroform, ethyl acetate and high stability even to hydrolysis at pH 3-9 at 52ºC. Photocatalytic degradation of trifluralin is carried out in the presence of TiO_2 as a photocatalyst by using a Batch Reactor.

II.MATERIAL AND METHODS

It is categorized into three parts:

2.1 Synthesis of TiO_2 Nanoparticles:

Titanium Dioxide Nanoparticles with high specific surface area has been prepared by using Cetyltrimethylammoniumbromide (CTAB) as a directing agent via hydrothermal process. A known amount (about 1 gm) of TiO_2 was treated with conc^n HCl and the reaction mixture was strongly heated to eliminate excess of the acid. The residue was mixed with CTAB and H_2O to make the final composition Ti^{+4}: CTAB: H_2O=1:(0.05, 0.10, 0.15 and 0.20): 100). After stirring for 30 minutes, the resulting mixture was aged at room temperature for 12 hours and then was heated in an autoclave at 100ºC for hydrothermal treatment. The resulting powders was cooled at room temperature, washed with water and ethanol and finally dried at 120 ºC overnight. The as-prepared samples were calcined in a furnace at 400 ºC for 6 hours to improve crystallinity. Different samples were prepared by varying the molarities of surfactant (CTAB) in solution.

2.2 Characterization of the Nanoparticles:

Synthesized TiO_2 Nanoparticles were characterized by the Transmission Electron Microscopy (TEM) (Fig.1), X-Ray Diffraction Pattern (XRD) (Fig.2) and UV-Visible Spectroscopy (Fig.3).

2.3 Photodegradation Study:

Photocatalytic degradation of trifluralin was carried out in the presence of TiO_2 as a photocatalyst by using Batch Reactor. 100 ml of 10^{-4} M trifluralin solution in water was taken in beaker and it was mixed with 1 gm of synthesized TiO_2 TABLE 1, the same was stirred and irradiated by 100W or 200W electric bulb, kept 30 cm above the liquid level in the beaker. Each time, 5ml sample was drawn out from the reaction vessel at an interval of 10 minutes. The absorbance of the samples at λ_{max} = (nm) were noted using a U.V./Visible Spectrophotometer (EI, Model: 312). The concentration of trifluralin at intervals of time was estimated by comparing the observed absorbance with the standard curve drawn between the absorbance versus concentration of the pesticide TABLE 2. The effect of the light intensity on the kinetics of photodegradation of the pesticide was also studied.

III. RESULTS AND DISCUSSION

3.1 Characterization of TiO_2 nanoparticles:

TEM Analysis:

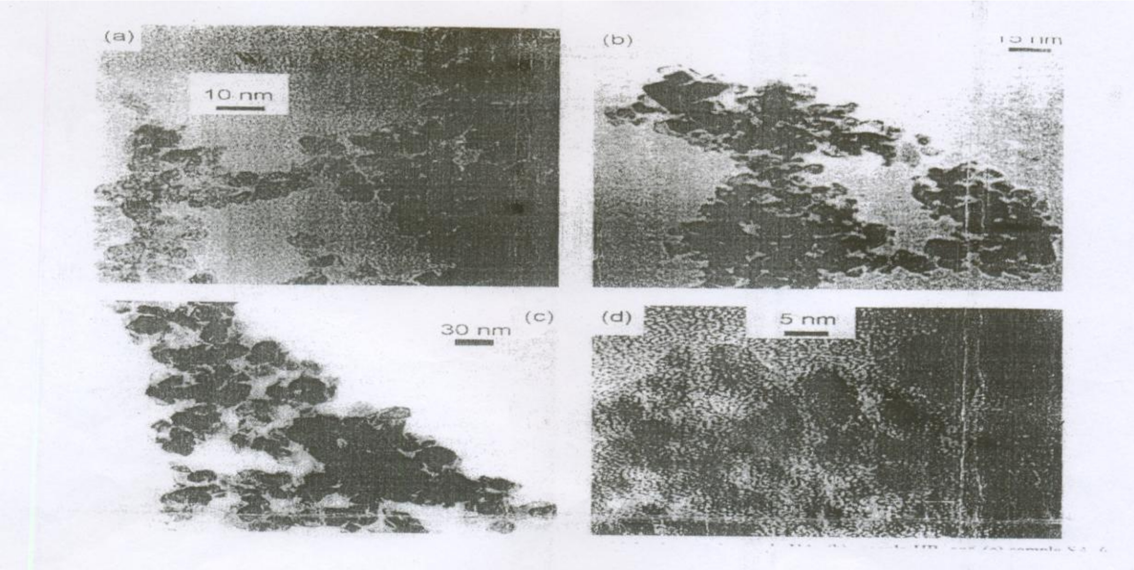

Fig. 1 TEM images of TiO_2 nanoparticles synthesized by hydrothermal process using different amounts of CTAB in Ti^{+4}+CTAB+H_2O solutions during synthesis

(a) Ti^{+4} : CTAB : H_2O = 1 : 0.10 : 100

(b) Ti^{+4} : CTAB : H_2O = 1 : 0.15 : 100

(c) Ti^{+4} : CTAB : H_2O = 1 : 0.20 : 100

(d) Ti^{+4} : CTAB : H_2O = 1 : 0.05 : 100

XRD analysis:

The observed XRD pattern at θ= 14º, 18.5 º, 21.5 º, 28 º, 29.5 º, 30 º, 34.5 º, correspond to the miller indices for the crystal planes: (110), (101), (111), (211), (220), (002) and (301) respectively, suggest the anatase phase of nanocrystalline structure TiO_2.

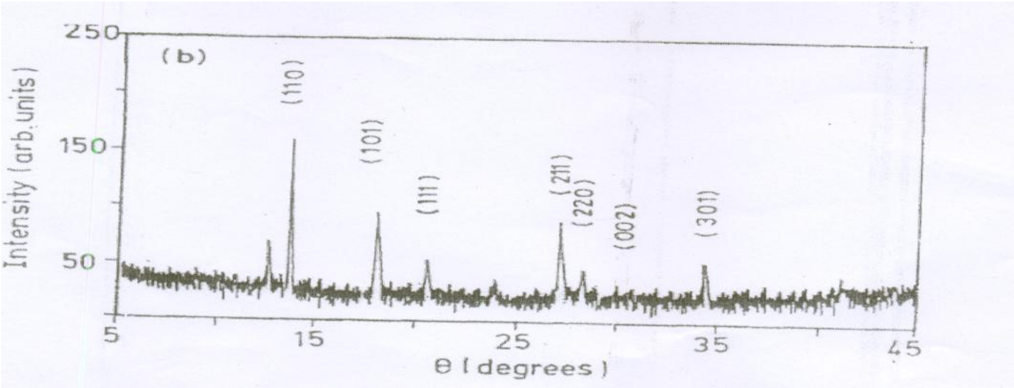

Fig. 2 XRD patterns of TiO_2 nanoparticles synthesized by hydrothermal process

3.2 Photocatalytic Degradation:

Determination of λ_{max} for trifluralin & Preparation of Standard Curve:

Table-1 Values of absorbance as a function of wavelength for 100ppm Trifluralin

Wavelength (λ)/nm	Absorbance
400	1.12
410	1.31
420	1.28
480	1.10
500	0.71
540	0.32
620	0.12

Table-2 Values of Absorbance versus concentration (in ppm) for Trifluralin solutions at λ_{max} = 410nm

Concentration of [Trifluralin]X10^{-4} M	Absorbance
0.1	0.18
0.2	0.37
0.3	0.51
0.4	0.68
0.5	0.85
0.6	1.01
0.7	1.15
0.8	1.26
0.90	1.38
1.00	1.48

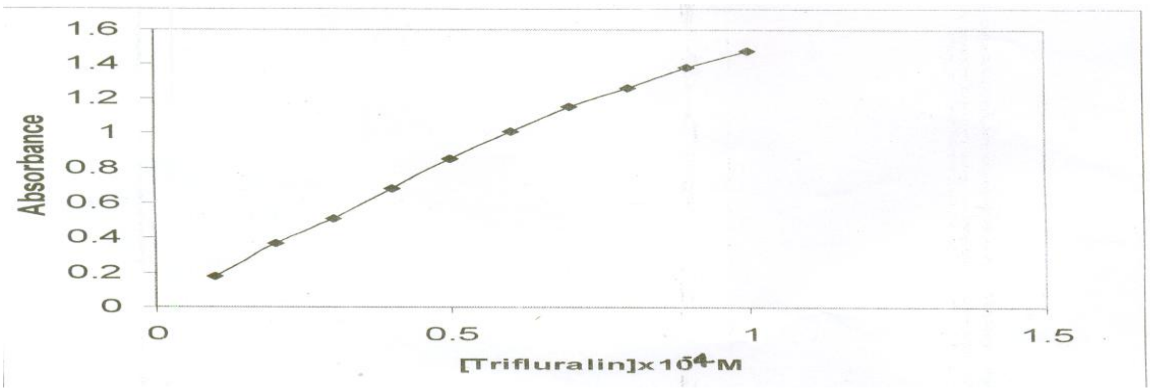

Fig.3 Plot of absorbance as a function of concentration of trifluralin at (λ_{max}) = 410nm

3.3 Photodegradation Study:

Values of absorbance and concentration of trifluralin at (λ_{max}) = 410 nm solutions versus reaction time under visible light from tungsten filament lamp (100W and 200W) have been given in TABLE-3.

Table-3 Values of absorbance and concentration of trifluralin as a function of time (λ_{max}) = 410 nm

	100 W		200 W	
Time (hr)	**Absorbance**	**[Trifluralin] X 10^{-4}M**	**Absorbance**	**[Trifluralin] X 10^{-4}M**
	1.41	1.00	1.41	1.00
	1.28	0.77	1.25	0.73
	1.16	0.69	1.15	0.62
	1.10	0.65	1.02	0.58
	1.03	0.60	0.91	0.52

Photodegradation rate constant (k) for trifluralin was calculated using the first order reaction integral expression-

K= (2.303/t). log (C_0/C_t) --------------(1)

Or log (C_0/C_t) = k. t / 2.303 -------------- (2)

Where, C_0 = initial concentration of trifluralin and C_t = concentration at time'tʼ.

The rate constant (k) was obtained from the slope of the plot b/w log (C_0/C_t) and time (t).

The values of log (C_0/C_t) as a function of time for trifluralin are given in TABLE-4 and the corresponding plot in Fig.4.

Table - 4 Values of log (C_o/C_t) as a function of time for trifluralin solution C_o=1x10^{-4}M

	100 W		200 W	
Time (hr)	**C_tx10^{-4}M**	**log (C_o/C_t)**	**C_t x10^{-4}M**	**log (C_o/C_t)**
2	0.74	0.026	0.70	0.031
4	0.67	0.070	0.63	0.091
6	0.65	0.096	0.60	0.126
8	0.60	0.123	0.54	0.180

The observed kinetic data reveal that photodegradation of trifluralin in aqueous solution using photocatalyst titanium dioxide follow first order kinetics. It is evident from the linear plots of log (C_0/C_t) versus time(hrs) as given in Fig.4 that increase in the light intensity results in the enhancing of the rate of degradation of trifluralin.

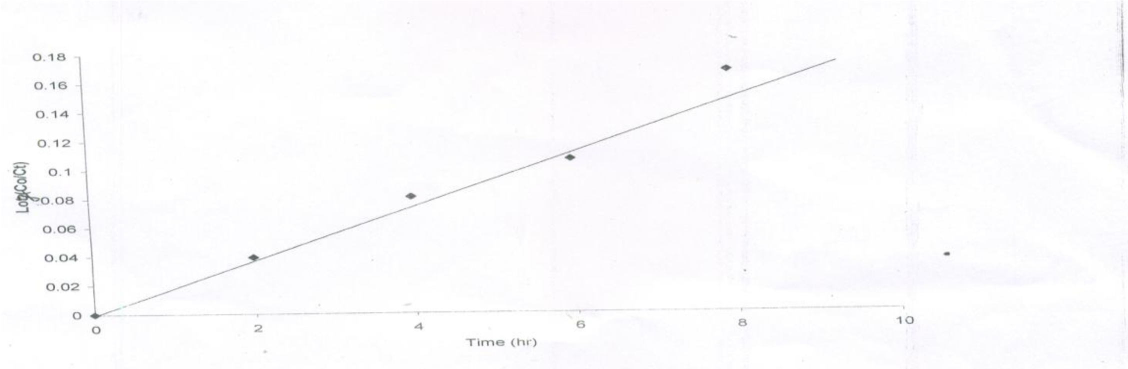

Fig. 4 Plot of log [C_o/C_t] as a function of time (hrs) for trifluralin using radiation from 200W tungsten filament bulb

The values of reaction rate constant (k) are given in TABLE-5.

Table – 5 Values of photodegradation rate constant (k) for trifluralin at varying intensity of radiation

Bulb Wattage/Watt	**Rate constant/k (hr^{-1})**
100	0.034
200	0.061

IV. CONCLUSION

The observed kinetic data reveal that photodegradation of trifluralin in aqueous solution using photocatalyst titanium dioxide follow first order kinetics. Increase in the light intensity as well as in time results in the enhancing of the rate of degradation of trifluralin.

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