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Photochemical and photocatalytic Studies of Cypermethrin under UV irradiation

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Abstract

The Photochemical and photo catalytic reactions have been studied under ultra violet light. The effect of pH, effect of concentration, effect of amount of semiconductor and effect of semiconductor, effect of intensity of light have been observed. The results obtained during the course of present investigations clearly indicate that the photolysis of Cypermethrin is fastest in the ultraviolet light in the presence of semiconductors. The reaction is much slow without catalysts. A tentative mechanism has been proposed for photochemical reaction.

Introduction

Calvert et al[1]. reported that ZnO can be used as photocatalyst for photochemical synthesis of hydrogen peroxide. Photoreduction of methylene blue on ZnO surface has been investigated by Barschchevski[2]. Frank and bard used TiO_2 for photocatalytic oxidation of cyanide sulphite[3]. Platinized TiO2 was used for photocatalytic decomposition of aqueous of acetic acid by Yoneyama et al[4]. The use of CdS as a photocatalyst in the dimerization of N-vinyl carbazole and in photocatalytic evolution of hydrogen from aqueous solution of sulphide has been reported by H.Ekabi et al[5]. Hettrich and Kisch[6] used CdS-ZnS as a photocatalyst for photodehydrodimerization of 2,5-dihydrofuran. Photocatalytic reduction of dicromate and photocatalytic oxidation of dichlorvos have been studied by Chen Shifu and Cao Gangye[7]. Photocatalytic degradation of organo phosphorous pesticides using thin film of TiO_2 has been studied by Zhao mangyue et al[8]. Photocatalytic degradation of an organophosphorous pesticide phosalone in aqeous suspensions of TiO_2 has been reported by N. Daneswar et al.[9-11].

Results and Discussion

10^{-1} M solution of Cypermethrin was prepared in water / methanol mix solvent as a stock solution. 50 ml 10^{-1}M solution was taken in measuring flask for each sample. Three different samples were prepared and two were kept in uv chambers and one was kept in dark.

It is observed that there is no reaction in case of sample -1 (In dark). The reaction was slow in case of sample-2 (in uv light without catalyst), whereas it precedes with a reasonable rate in case of sample-3(in uv light with catalyst). Observation of photochemical and photocatalytic reactions are reported in table - 1 and 2 respectively. A typical runs for photochemical and photocatalytic reactions are graphically presented in figure - 1 and 2.

Table-1: Photochemical reaction of Cypermethrin in presence of UV light

Time (Hour)	Abs	2+log Abs
0	0.225	1.3522
1	0.215	1.3324
2	0.206	1.3139
3	0.195	1.2900
4	0.184	1.2648
5	0.174	1.2405
6	0.161	1.2068
7	0.153	1.1847
8	0.144	1.1584
9	0.136	1.1335
10	0.128	1.1072
11	0.12	1.0792
12	0.114	1.0569
13	0.108	1.0334
14	0.103	1.0128
15	0.098	0.9912
16	0.093	0.9685
17	0.093	0.9685

Concentration = 0.1 M; pH = 3,0 ; Temp.=305 K ; Wavelength = 275 nm

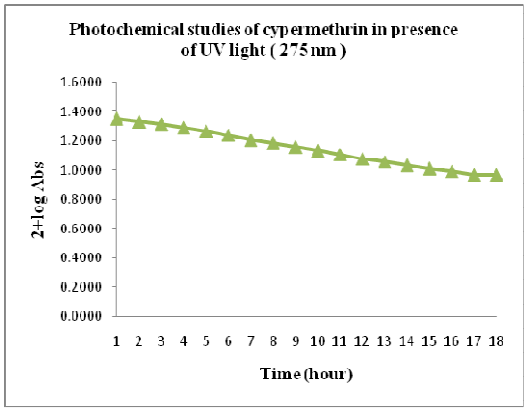

Fig. 1

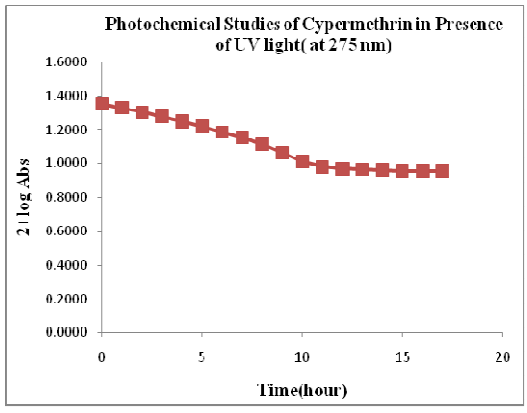

Fig. 2

Table-2: Photocatalytic reaction of Cypermethrin in presence of UV light

Time (Hour)	Abs	2+log Abs
0	0.225	1.3522
1	0.215	1.3324
2	0.206	1.3139
3	0.195	1.2900
4	0.184	1.2648
5	0.174	1.2405
6	0.161	1.2068
7	0.153	1.1847
8	0.144	1.1584
9	0.136	1.1335
10	0.128	1.1072
11	0.120	1.0792
12	0.114	1.0569
13	0.108	1.0334
14	0.103	1.0128
15	0.098	0.9912
16	0.093	0.9685
17	0.093	0.9685

Concentration = 0.1 M pH = 3,0
Temp.= 305 K Amount of CdS = 0.200 gm.

Effect of pH

The effect of different pH of the medium was investigated by maintaining different pH in acidic range only as the solution became turbid in basic medium. The results are reported in table - 3 and graphically presented in figure – 3.

Table – 3: Effect of pH on the rate of photocatalytic reactioin in UV light

pH	Absorbance
1.0	0.200
2.0	0.220
3.0	0.225
4.0	0.234
5.0	0.240
6.0	0.248
7.0	0.260
8.0	0.267

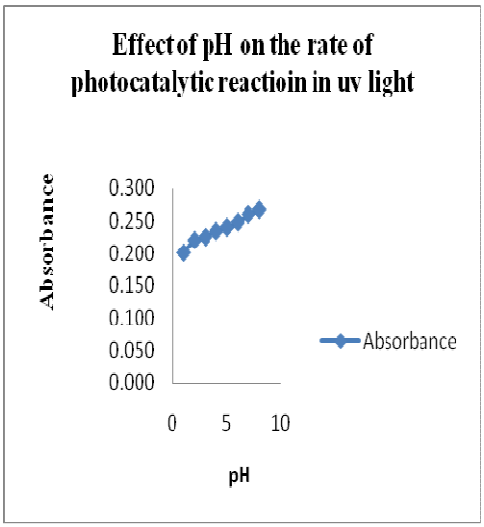

Fig.3

Concentration = 0.1 M Temp.= 305 K Wavelength = 275 nm

It has been observed that the rate of photocatalytic reaction of Cypermethrin decreases on increasing pH. This behavior can be explained on the basis that at higher pH values more OH radicals will be produced.

Effect of Semiconductors

Four semiconductors with different band gaps were selected to photocatalyes this reaction. These are CdS, TiO_2, ZnO, ZnS The results are summarized in table – 4.

It is evident from the observed results that the semiconductor with band gap lower than 3.0 ev is more effective in driving this reaction in presence of uv radiations, because their max falls in the uv range of Cypermethrin . The order of effectiveness of photo catalysts used in the present investigation is Cds › TiO_2 › ZnO › ZnS This order has direct correlation with the order of their band gaps which is ZnS › ZnO › TiO2 › CdS. Therefore, CdS will absorb more efficiently in the uv range as compared to other semiconductors.

Table- 4: Photoccatalytic reaction of Cypermethrin with different semiconductors in presence UV light

Time (Hour)	CdS		TiO_2		ZnS		ZnO	
	Abs	2+logAbs	Abs	2+logAbs	Abs	2+logAbs	Abs	2+logAbs
0	0.197	1.2945	0.197	1.2945	0.197	1.2945	0.197	1.2945
1	0.185	1.2672	0.186	1.2695	0.187	1.2718	0.188	1.2742
2	0.172	1.2355	0.175	1.2430	0.176	1.2455	0.178	1.2504
3	0.160	1.2041	0.161	1.2070	0.166	1.2201	0.168	1.2253
4	0.143	1.1549	0.153	1.1847	0.154	1.1875	0.159	1.2014
5	0.127	1.1033	0.142	1.1523	0.144	1.1584	0.148	1.1732
6	0.114	1.0582	0.129	1.1100	0.134	1.1271	0.139	1.1430
7	0.101	1.0060	0.117	1.0699	0.122	1.0864	0.132	1.1206
8	0.091	0.9593	0.106	1.0239	0.110	1.0414	0.122	1.0870
9	0.082	0.9157	0.094	0.9728	0.101	1.0043	0.113	1.0530
10	0.071	0.8536	0.085	0.9279	0.091	0.9590	0.102	1.0069
11	0.064	0.8062	0.076	0.8795	0.083	0.9191	0.094	0.9730
12	0.062	0.7924	0.069	0.8366	0.074	0.8707	0.085	0.9285
13	0.062	0.7924	0.064	0.8062	0.066	0.8195	0.076	0.8799
14	0.062	0.7924	0.062	0.7924	0.064	0.8062	0.069	0.8370
15	0.061	0.7853	0.062	0.7924	0.062	0.7924	0.064	0.8062
16	0.061	0.7853	0.061	0.7853	0.062	0.7924	0.062	0.7924
17	0.061	0.7853	0.061	0.7853	0.061	0.7853	0.062	0.7924

Concentration = 0.1 M, pH = 3.0, Temp.= 305 K, Wavelength = 275 nm

Effect of of Amount of Semiconductor

The amount of semiconductor also affects the rate of this reaction, and therefore, different amount of photocatalysts were used to observe it. The results are reported in table – 5 and graphically presented in figure – 5.
The above data clearly indicates that the increase in the amount of semiconductor, the rate of

reaction increases and it reaches a maxima for a particular amount of semiconductor. On further increasing the amount of semiconductor, no remarkable change in the rate constant was observed.

Table 5: Effect of amount of semiconductor on the rate of photocatalytic reaction in UV light

Wt. of semiconductor(CdS) in gms.	Absorbance (after 10 hrs.)
0.050	0.122
0.100	0.115
0.150	0.108
0.200	0.103
0.250	0.107
0.300	0.120
0.350	0.125
0.400	0.131

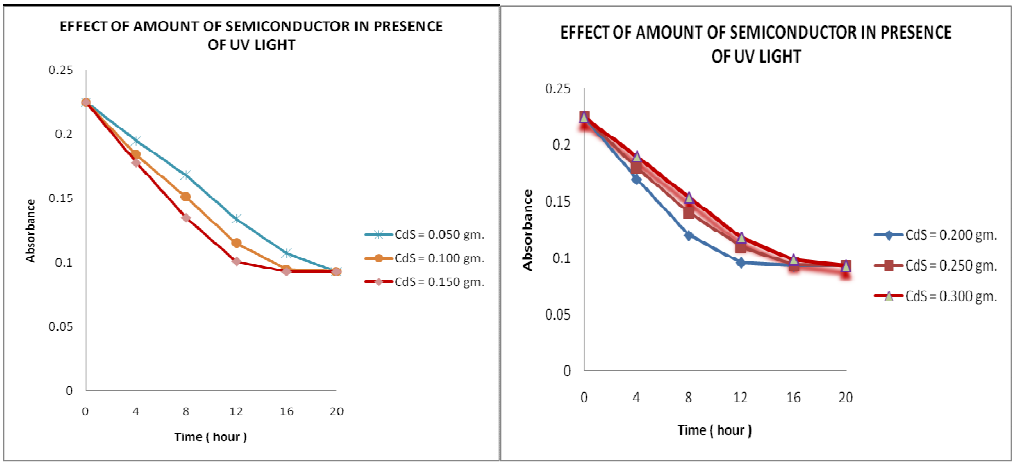

Fig.5

Effect of Intensity of Light

The effect of light intensity on the rate of photocatalytic reactions of Cypermethrin was also observed. The light intensity was varied by changing the distance between the light source and the exposed surface of semiconductor. The results are reported in table – 6 and graphically presented in figure – 6.

It was observed that there is increase in the rate of reaction as the intensity of incident light was increased. This may be explain on the basis that with the increase in light intensity, more photons

will be available for excitation and therefore, more electron hole pairs will be generated in the semiconductor resulting into enhanced rate of reaction.

Table – 6: Effect of intensity of light on the rate of photocatalytic reaction in UV light

Time (hour)	Absorbance		
	Distance		
	18 Inches	14 Inches	10 Inches
0	0.197	0.197	0.197
1	0.192	0.190	0.185
2	0.188	0.178	0.172
3	0.171	0.168	0.160
4	0.160	0.152	0.143
5	0.150	0.145	0.127
6	0.138	0.130	0.114
7	0.130	0.118	0.101
8	0.117	0.105	0.091
9	0.106	0.095	0.082
10	0.093	0.081	0.071
11	0.080	0.075	0.064
12	0.082	0.072	0.062
13	0.074	0.070	0.062
14	0.070	0.066	0.062
15	0.066	0.063	0.061
16	0.064	0.062	0.061
17	0.063	0.061	0.061
18	0.062	0.061	0.061
19	0.062	0.061	0.061
20	0.061	0.061	0.061

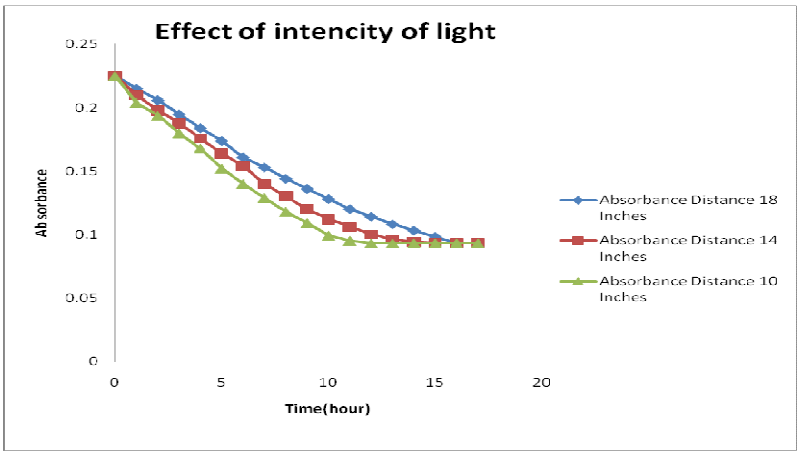

Fig. 6

The results obtained during the course of present investigations clearly indicates that the photolysis of Cypermethrin is fastest in the ultraviolet light in the presence of semiconductors. The reaction is much slow without catalyst.

Materials and Methods

Cypermethrin is soluble in water and methanol so all the solutions are prepared in mix sovent. A 200 w uv lamp was used for irradiating the reaction mixture. A sample was kept at 10 Inches from the light source. The intensity of light was measured with the help of solarimeter surya mapi (CEL 201) in terms of wcm^{-2}. The pH of the solutions was measured by a pH meter(Systronic model 324) . The disired pH of the solution was adjusted by addition of previous standardised NaOH and perchloric acid solutions.Solutios were always centrifuged before measuring the absorbance. The progress of the reaction was recorded by measuring the absorbance at different time intervals of irradiations with the help of a systronic uv/vis spectrophotometer 118 model.

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