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Use of Solar Energy in Removal of Quinaldine Red from Effluents Using PbS as Semiconductor

INDERJEET YADAV and SHIPRA BHARDWAJ*
Department of Chemistry, M.P. Government Postgraduate College
Chittorgarh-312 001, India
E-mail: sidsidsmart@yahoo.co.in

Quinaldine red was removed in presence of sunlight from industrial effluents using Pbs as semiconductor. The reaction was found to follow pseudo first order rate law. Effect of variation of factors like pH, concentration of dye, amount of semiconductor, intensity of light, *etc*. were studied and a tentative mechanism is also proposed.

Key Words: Solar energy, Quinaldine red, Semiconductor, PbS.

INTRODUCTION

The kinetics of photo bleaching Aber chrome 540 in various solvents was carried out by Rappon and Syuitski[1]. Photocatalytic bleaching of Orange G by ZnO perticulate system was reported by Sharma *et al.*[2]. The chemistry of SO_2 and NO_2, Zn and ZnO powder has been reported by Rodrigenez *et al.*[3] photochromic behaviour of potassium hexacyanoferrate (II)-phenolphthalein system was observed by Ameta *et al.*[4] and Datta *et al.*[5]. Various semiconductors are used for bleaching purpose but PbS is less reported due to its less reactive nature. In present studies an attempt has been made to remove quinaldine red dye from effluents using PbS as semiconductor.

EXPERIMENTAL

The stock solution of quinaldine red dye was prepared in distilled water and diluted as required. The pH of the solutions were determined using pH meter (Hena imported pen type). Solution of the dye was taken in a beaker and known amount of PbS was added and finally covered with water filter to avoid the heat reaction. The solution was irradiated by visible tungsten lamp and the optical density (O.D.) was recorded spectrophotometrically (systronics spectrophotometer).

RESULTS AND DISCUSSION

The plot of 1 + log O.D. was found straight line suggesting that bleaching of dye by PbS follows pseudo first order rate law. Rate constant were calculated by graphs as follows: -K = 2.303 × slope. A typical run is given in Fig. 1 (Table-1).

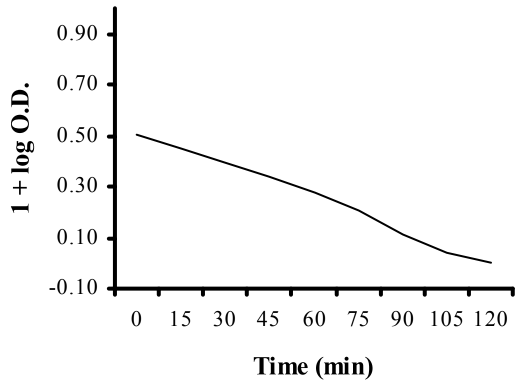

Fig. 1. A typical run

TABLE-1
[Quinaldine red] = 6.00 × 10^{-5} M; PbS= 0.12 g
Intensity = 37.0 mW cm^{-2}; pH = 5.5

Time (min)	O.D.	1 + log O.D.
0	0.32	0.51
15	0.28	0.45
30	0.25	0.40
45	0.22	0.34
60	0.19	0.28
75	0.16	0.20
90	0.13	0.11
105	0.11	0.04
120	0.10	0.00

Effect of pH variation: The effect of pH variation was studied. It was found that as pH is raised, the rate of photo-catalytic bleaching increases. It attains a maximum value at pH 5.5. After that, if pH is raised, the rate decreases. Increase in pH increases the number of H^+ ions in acidic medium. When a hole is generated by semiconductor, electron is added to H^+ ion converting it into $OH_2^{\bullet}$ free radical in presence of oxygen. This free radical is responsible for the bleaching of dye as proved by use of scavanger. The effect of pH variation is given in Table-2.

Effect of concentration of quinaldine red: Keeping all other factors constant, the concentration of dye was changed and its effect on rate of bleaching was studied. The data are summarized in Table-3.

The rate of photocatalytic bleaching was found to increase with increase in the concentration of quinaldine red (Table-3). This may be explained that the rate of reaction is directly proportional to the molar concentration of reacting species and it will be up to optimum concentration of quinaldine red (concentration 6.00×10^{6} M). If more concentration of dye is taken, it imparts a darker colour to the solution and may act as filter to the incident light reaching the semiconductor surface. As a consequence, the rate of photocatalytic bleaching of quinaldine red decreases.

TABLE-2
[Quinaldine red] = 6.00×10^{-5} M
Intensity = 37.0 mW cm^{-2};
PbS = 0.12 g

pH	$K_1 \times 10^4$ (s^{-1})
4.0	2.25
4.5	3.35
5.0	4.55
5.5	17.74
6.0	7.09
6.5	7.68
7.0	5.62
7.5	6.30
8.0	3.54

TABLE-3
PbS = 0.12 g; pH = 5.5
Intensity = 37.0 mW cm^{-2}

[Quinaldine red] × 10^{-5} M	$K_1 \times 10^4$ (s^{-1})
1.0	10.39
2.0	9.04
4.0	12.33
6.0	17.74
8.0	13.31
10.0	12.33
12.0	10.39
14.0	9.04

Effect of amount of PbS: The amount of PbS was varied and its effect on bleaching was studied whose results are summarised in Table-4. It was found that up to a limited amount, the rate of photo-bleaching increases. It may be due to more surface area available of semiconductor to catch hold the light and generate the excited states. After a limit, rate of bleaching may decrease due to the interference of molecules of PbS. The abundance of molecules interferes in the pathway of other molecules gaining the excited state, thus resulting decrease in bleaching.

Effect of intensity on rate of bleaching: The effect of intensity of light on rate of bleaching was studied by keeping the reaction mixture at different places below the lamp. The data are given in Table-5.

The rate of photocatalytic bleaching increases as the intensity increases. It may be explained on basis of number of excited molecules. As more intensity of light falls on PbS molecules, more number of molecules get excited which in turn may bleach more dye molecules, thus the rate of bleaching was found increasing with increase in intensity of light.

TABLE-4
[Quinaldine Red] = 6.00×10^{-5} M
pH = 5.5; Intensity = 37.0 mW cm^{-2}

Amount of semiconductor (g)	$K_1 \times 10^4$ (s^{-1})
0.04	4.33
0.06	7.43
0.08	8.67
0.10	10.32
0.12	17.74
0.14	6.52
0.16	3.96

TABLE-5
[Quinaldine Red] = 6.00×10^{-5} M pH = 5.5; Weight of Semiconductor = 0.12 g

Intensity (mW cm^{-2})	$K_1 \times 10^4$ (s^{-1})
37.0	17.74
30.0	12.80
27.0	8.87
23.0	5.22

On the basis of above studies carried out, mechanism is proposed of bleaching of the dye through its degradation by lead sulphide particles.

$$^1Dye_0 \xrightarrow{h\nu} {}^1Dye_1 \text{ (Singlet excited state)}$$
$$^1Dye_1 \xrightarrow{ICS} {}^3Dye_1 \text{ (Triplet excited state)}$$
$$Sc \longrightarrow e^- + h^+ \text{ or } Sc^+$$
$$e^- + O_2 \longrightarrow O_2^{\bullet -}$$
$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$$
$$O_2^{\bullet} + 3Dye \longrightarrow Leucodye \rightarrow Products$$

Dye absorbs the light and gets excited to singlet state. This inter-system crossing, gets converted to triplet state. On the other hand the semi-conductor gets excited by absorbing light and an electron is excited from valance band to conduction band leaving behind a hole. This electron in presence of O_2 gets attached to H^+ ion generating $HO_2^{\bullet}$ free radical. The dye is now being bleached from this free radical producing luco base.

The participation of $HO_2^{\bullet}$ radical is confirmed by the use of scavanger, which stops the bleaching reaction completely.

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