

# Degradation of P-Rosaniline hydrochloride using a novel nano-sized photo catalyst BaWO<sub>4</sub> - An Aid to Environmental Remediation

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**Abstract:** There are many methods for removing these water pollutants like thermal dehydration, adsorption by charcoal etc. One of the most eco-friendly method is the use of photo catalytic process. The present work describes the photo catalytic bleaching of P-Rosaniline hydrochloride in the presence of photo catalyst BaWO<sub>4</sub> and the progress of the reaction is monitored. The effects of operating variables like pH, concentration of dye, amount of semiconductor and light intensity on the rate of bleaching was observed and a tentative mechanism is proposed.

## 1. Introduction:

Water is one of the fundamental requirements of life and any undesired addition any substance leads to its contamination and it become unfit for human use. The effluent from dyeing, textile and chemical industries pollute the water. Heterogeneous photo catalysis has emerged as a promising technique for removal of these pollutants. An additional reason for advocating heterogeneous photo catalysis is that it fits the green environment postulates.

Synthesis and characterization of CeFeO<sub>3</sub> photo catalyst used in photo catalytic bleaching of Gentian Violet was suggested by Ameta et al [1]. Use of Zirconium phosphate as photo catalyst in photo bleaching of some dyes was reported by Panwar et al [2] while enhanced photo degradation of Azure-b by co-precipitated NiS-ZnS (1:5) was investigated by Sharma et al [3]. Phenol photo degradation on platinized TiO<sub>2</sub> photo catalysts related to charge carrier dynamics was carried out by Emilio et al [4]. Dye-sensitized photo-oxidation of thiourea by singlet oxygen was reported by Vaidhya et al [5]. Photo assisted bleaching of dyes utilizing TiO<sub>2</sub> and visible light was carried out by Gary et al [6] while UV-induced photo catalytic degradation of azo dyes by organic-capped ZnO nano crystals immobilized onto substrate was suggested by

Comparelli et al [7]. Treatment of bleaching effluent from the pulp and paper industry by photo catalytic oxidation was investigated by Toor et al [8].

Photo catalytic degradation of Acid Red G by Bismuth titanate in three-phase fluidized bed photo reactor was reported by Liu Hong et al[9]. Sol-Gel Developed CdS Nanoparticles for Photo catalytic Degradation of Alizarin Red was carried out by Patil et al[10] while effect of factors on decolorization of azo dye Methyl orange was studied by Liu et al[11]. Photo catalytic degradation of textile dye X3B by heteropolyoxometalate acids was carried out by Hu et al[12]. Photo catalytic degradation of phenol in aqueous solution by titanium dioxide coupled with magnetic field was studied by Yun-Hai et al[13] while UV/TiO<sub>2</sub> photo catalytic degradation of xanthene dyes was investigated by Pereira et al[14]. Disdier et al [15] studied effect of employing platinized TiO<sub>2</sub> catalysts on photo catalytic reactions while adsorption of Amido black 10 B onto cross linked chitosan (a polysaccharide) was studied by Yang et al [16]. A photo assisted bleaching of dyes utilizing TiO<sub>2</sub> and visible light was carried out by Epling et al [17]. Photo catalytic oxidation of organophosphorous pesticides using ZnO was reported by Fadaei et al[18]. Cheng et al [19] investigated hydrothermal preparation of uniform nanosize rutile and anatase particles. Photo catalytic decolorization of Remazol Red RR in aqueous ZnO suspensions was studied by Akyol et al [20]. TiO<sub>2</sub>-assisted photocatalytic degradation of azo dyes in aqueous solution, kinetic and mechanistic investigations was carried out by Konstantinou et al [21]. Modified titanium dioxide photocatalysts for the enhanced photodegradation of organic substrates was investigated by Ranjit et al. It is observed that no attention is paid on binary semiconductor BaWO<sub>4</sub> for the purpose of purification of water although it is found to act more precisely as compared to other semiconductors. Thus the present research work incorporated BaWO<sub>4</sub> as a photocatalyst.

## 2. Experimental:

A stock solution of P-Rosaniline hydrochloride (BDH) ( $0.0809 \text{ g}/250 \text{ ml}=1 \times 10^{-3} \text{ M}$ ) was prepared in doubly distilled water. The photo catalytic degradation of P-Rosaniline hydrochloride was initiated by adding  $0.10 \text{ g}$  of  $\text{BaWO}_4$  (Sigma Aldrich) to the dye solution. Irradiation was carried out keeping whole assembly exposed to a  $200\text{W}$  tungsten lamp (Philips). The intensity of light at various distances from the lamp was measured with the help of solarimeter (CEL201). The pH of the solution was measured by a digital pH meter (Henna imported pen type). The desired pH of the solution was obtained by the addition of prestandardized HCl and NaOH solutions. The progress of the reaction was followed by recording optical density at regular time intervals using a spectrophotometer (Systronics 106).

## 3. Result and Discussion:

The photo catalytic degradation of the dye is observed at  $\lambda_{\text{max}} 544\text{nm}$ . The results of typical run is graphically represented in Figure 1. The plot of  $1 + \log \text{O.D.}$  versus time was found to be a straight line. This indicates that the photo catalytic degradation of dyes in presence follows pseudo first order kinetics and the rate constant was determined using the expression

$$k = 2.303 \times \text{slope.}$$

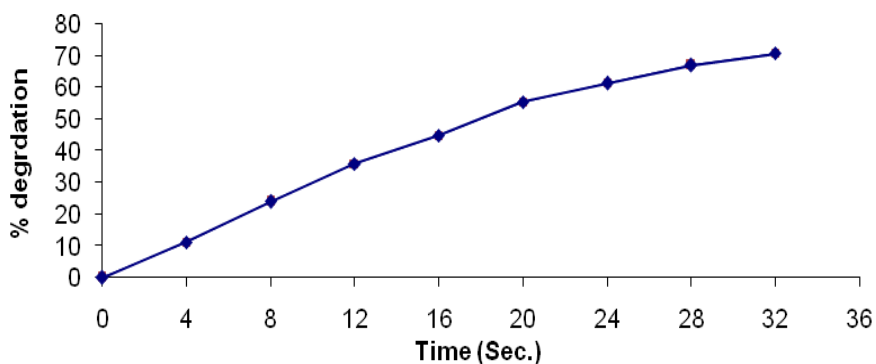


Fig.1- A Typical Run

Participation of free radical  $\text{OH}^*$  was confirmed by use of scavenger. This free radical is strong enough to break different bonds like C-H, C-N, C=N, N-H, C=C etc. The process slows down

with due course of time because it is difficult to convert N atoms in N compounds. Controlled experiments were carried out to prove that the reaction is a photo catalytic degradation process.

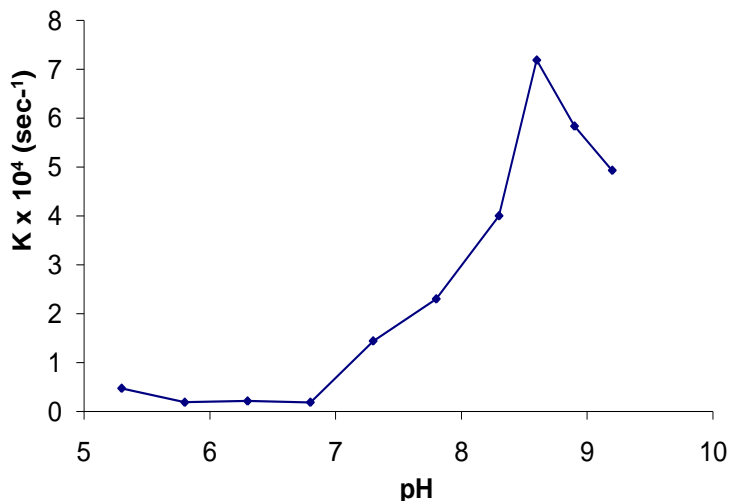
### **3.1 Effect of pH**

The effect of pH on photo catalytic degradation of P-Rosaniline hydrochloride was investigated (pH 5.3 to 9.5) keeping other parameters constant. Experimental data are given in table-1 and figure-2.

Table-1: Effect of pH

[P-Rosaniline hydrochloride] =  $1 \times 10^{-5}$  M, amount of semiconductor = 0.16 g, intensity = 37 mW/cm<sup>2</sup>.

<b>pH</b>	<b>K x 10<sup>4</sup>(sec<sup>-1</sup>)</b>
5.3	0.472
5.8	0.187
6.3	0.213
6.8	0.185
7.3	1.44
7.8	2.30
8.3	4.00
<b>8.6</b>	<b>7.19</b>
8.9	5.84
9.5	4.93



**Fig.2-Graph between K and pH**

It was observed that as pH increases, the rate of degradation of the dye increases (up to pH 8.6). It can be explained that as the pH increases, the concentration of  $\text{OH}^-$  ions increases. The  $\text{OH}^-$  ions combine with the holes of semiconductor and generate  $\text{OH}^*$  radicals which are responsible for dye degradation. Above pH 8.6, on increasing the pH of the medium, the rate of degradation decreases as more  $\text{OH}^-$  ions make the surface of semiconductor negatively charged and this retards the approach of dye molecules towards the semiconductor surface due to neutral nature of dye molecules. This will result into a decrease in the rate of photo catalytic bleaching of dyes.

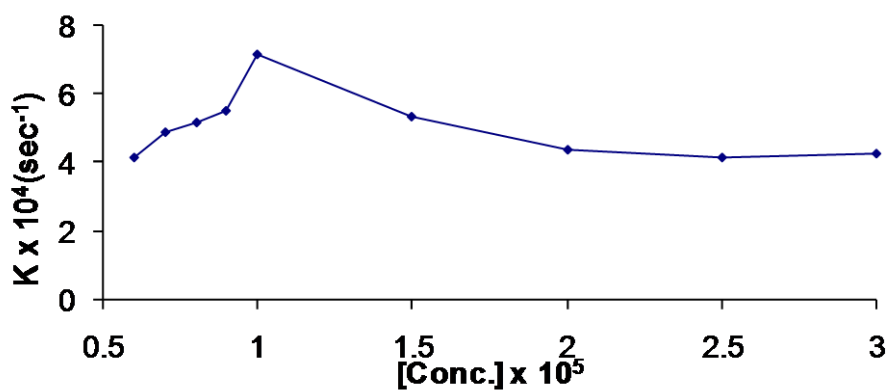
### ***3.2 Effect of Concentration of dye***

Concentration of the dye plays an important role in degradation and so the effect was studied by taking different concentrations of dye ( $0.6 \times 10^{-5}$  to  $3.0 \times 10^{-5}$ ) and keeping all other factors constant. The results are tabulated in Table-2 and figure-3.

Table 2: Effect of concentration of dye

pH = 8.6, intensity of light =  $37 \text{ mW/cm}^2$ , amount of semiconductor = 0.16 g.

[Conc.] x 10 <sup>5</sup> M	K x 10 <sup>4</sup> (sec <sup>-1</sup> )
0.6	4.18
0.7	4.87
0.8	5.15
0.9	5.51
<b>1.0</b>	<b>7.19</b>
1.5	5.36
2.0	4.40
2.5	4.18
3.0	4.28



**Fig.3-Graph between K and concentration of dye**

From the data, it is evident that the rate of photo catalytic degradation increases with increasing concentration of the dye (upto  $1.0 \times 10^{-5}$  M). This is because as the concentration of dye increases, more dye molecules are available for excitation and so there is an increase in the rate. The rate of photo catalytic degradation was found to decrease with an increase in the concentration further. Here, the dye starts acting as a filter to the incident light and does not permit the desired light intensity to reach the semiconducting particles thus decreasing the rate of the photo catalytic bleaching of dye.

### 3.3 Effect of amount of semiconductor

Amount of semiconductor affects the degradation of dye. Thus the effect is studied by varying the amount (0.04 g to 0.22 g) and all other factors were kept constant. The results are given in Table-3 and figure-4.

Table 3: Effect of amount of semiconductor:

[P-Rosaniline hydrochloride] =  $1 \times 10^{-5}$  M, intensity = 37 mW/cm<sup>2</sup>, pH = 8.6

Amount of semiconductor (g)	K x 10 <sup>4</sup> (Sec <sup>-1</sup> )
0.06	2.93
0.08	3.21
0.12	3.38
0.14	3.83
<b>0.16</b>	<b>7.19</b>
0.18	3.68
0.20	3.63
0.22	3.49

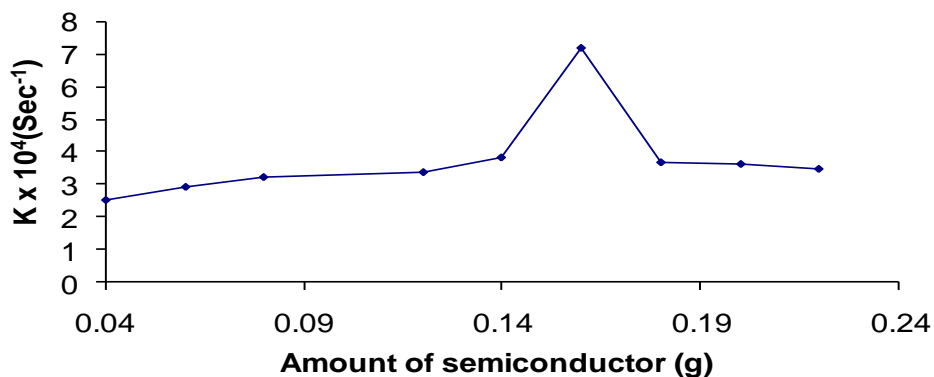


Fig.4-Graph between K and amount of semiconductor

It was observed that up to certain loading (0.16g), photo catalytic degradation rate increases and then with further loading, the rate decreases. It may be explained as that with increase in amount more area of photo catalyst is exposed to the photons to generate OH\* free radicals resulting in increased rate. Further increases in amount, produces greater amount of free radical thus crowding forces them to recombine resulting in decrease in the rate of degradation.

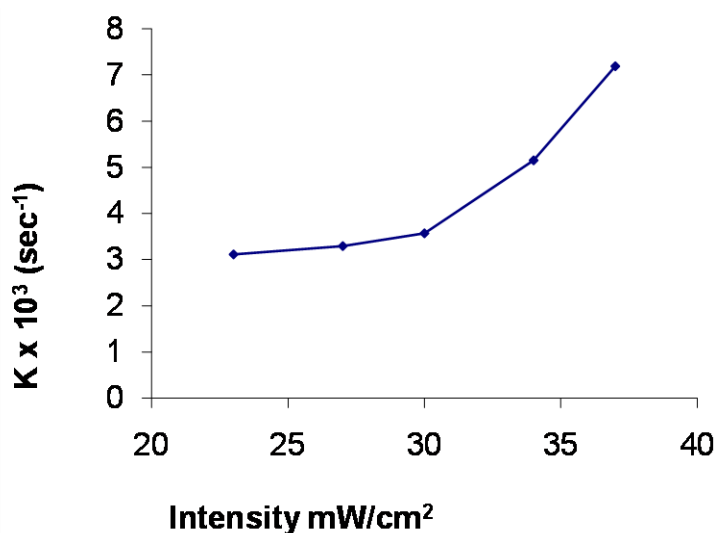
### 3.4. Effect of light intensity

The effect of the variation of light intensity on the rate was also investigated (23 to 37 mW/cm<sup>2</sup>) and the observations are reported in the Table-4 and figure-5.

Table 4: Effect of intensity of light

[P-Rosaniline hydrochloride] = 1 x 10<sup>-5</sup>M, pH = 8.6, amount of semiconductor = 0.16 g.

Intensity mW/cm <sup>2</sup>	K x 10 <sup>4</sup> (Sec <sup>-1</sup> )
37	7.19
34	5.15
30	3.57
27	3.29
23	3.11



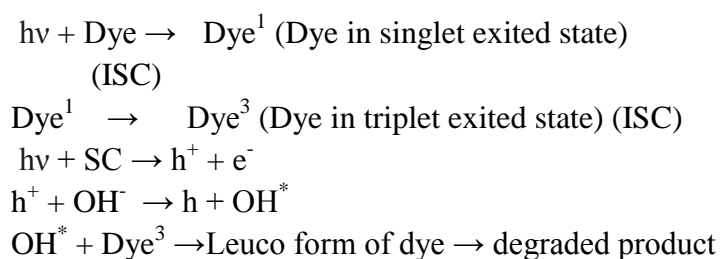
...Fig-5 Graph between K and



The results indicate that bleaching action is accelerated as the intensity of light increases because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder.

#### 4. Mechanism

On the basis of the experimental observations, a tentative mechanism for photocatalytic bleaching of P-Rosaniline hydrochloride is given as:



Here ISC stands for inter system crossing and SC stands for semiconductor

When the solution of dye is exposed to light in the presence of semiconductor, initially, the dye molecules are excited to singlet state. Then these singlet molecules are transferred to the triplet state through intersystem crossing (ISC). The triplet state may donate an electron to semiconductor. On the other hand, the semiconductor gets excited by absorbing photon and an electron is excited from its valence band to conduction band leaving behind a hole. The hole abstracts an electron from  $\text{OH}^-$  ion generating  $\text{OH}^*$  free radical. These  $\text{OH}^*$  free radicals will oxidize the dye molecules into colorless products. The participation of  $\text{OH}^*$  radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger where the reaction rate was drastically reduced.

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