

USE OF NIOBYUM PENTAOXIDE SYSTEM AS A PHOTOCATALYST: PHOTBLEACHING OF P-ROSANILINE HYDROCHLORIDE

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Abstract

The biggest consumers of water are textiles, tannery, electroplating and pulp and paper industries and these are also the most serious polluters of environment. Photocatalytic degradation has been considered to be an efficient process for degradation of organic pollutants, which are present in the effluents released by these industries. The photocatalytic bleaching of p-rosaniline hydrochloride was carried out on cationic dyes in the presence of niobium pentaoxide and was observed spectrophotometrically. The effect of various operating variables like pH, concentration of dyes, amount of semiconductor, light intensity, particle size, stirring, etc. was also observed on the efficiency of the reaction. A tentative mechanism has also been proposed for this photocatalytic bleaching.

Key words: wastewater treatment; photocatalytic bleaching; pararosaniline hydrochloride; niobium pentaoxide; semiconductor

1. INTRODUCTION

As we stepped into the twenty-first century, we are facing the challenge of purification of water and air resources. On one hand, we are enjoying the comforts and benefits that chemistry has provided to us, e.g. from drugs to dyes, from composites to computer chips, etc. On the other hand, we are facing with the problem of proper disposal of various products and byproducts of dye industries. In spite of many uses, the dyes are toxic and carcinogenic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. Coloured solution containing dyes from industrial effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the other hand, bleached dye solution is less toxic and almost harmless. Secondly, dye containing coloured water is of almost no use, but if this coloured solution is bleached to give colourless water, then it may be used for washing, cooling, irrigation and cleaning purpose. The photocatalytic bleaching seems to be quite promising and can provide a low cost method to solve this problem. The field of photocatalysis has been excellently reviewed by Ameta *et al.*. Photocatalytic degradation of cetylpyridinium chloride over TiO_2 has been reported by Singhal *et al.*. Similar photocatalytic reaction of xylydine ponceau and orange-G dyes by ZnO powder has been reported by Sharma *et al.*.

Yoneyama *et al.* studied the photocatalytic reduction of dichromate ions using WO_3 powder in acidic range. Costa *et al.* proposed the mechanism of gas phase degradation of cyclohexanol and methylcyclohexanol catalyzed by niobium pentaoxide and phosphite. Shyama and Arakawa have used zirconium dioxide as photocatalyst. A composite system of polycrystalline ZnO/TiO_2 and its photocatalytic activity was studied by Marci *et al.*. TiO_2 sol-gel deposited over glass and its application as a photocatalyst for water decontamination has been reported by Gelover *et al.*. Kako *et al.* suggested some preventive methods against catalytic poisoning of TiO_2 photocatalyst by H_2S . The effect of TiO_2 acidic pre-treatment on the photocatalytic phenol degradation was reported by Colon *et al.* whereas photodegradation of lignin from black liquor using a UV/TiO_2 system was investigated by Ksibi *et al.*. Enhanced efficiency of unsymmetrical versus symmetrical squaraine dyes sensitized nanocrystalline TiO_2 was reported by Alex *et al.*. Morwetz and Selli investigated the effect of iron species in photocatalytic degradation of azo dye in TiO_2 suspension. Kim *et al.* used ZnO coated TiO_2 nanoparticles for the flexible dye-sensitized solar cells. Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.*. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.*. Photocatalytic degradation of acid blue-62 over $\text{CuO}-\text{SnO}_2$ nanocomposite photocatalyst under simulated sunlight has been reported by Xia *et al.*. The photocatalytic bleaching of p-rosaniline hydrochloride in presence of niobium pentaoxide photocatalyst is being reported in the present

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investigation. Bleaching of some dyes using niobium pentoxide photocatalyst have been studied by Panwar et al..

2. EXPERIMENTAL DETAILS

Degradation of pararosaniline hydrochloride using niobium pentoxide

A 0.0305 g of p-rosaniline hydrochloride was dissolved in 100.0 ml of doubly distilled water so that the concentration of the dye solution was 1.0×10^{-3} M. This solution was used as stock solution. The photocatalytic degradation of p-rosaniline hydrochloride was observed on a 50 ml dye solution (5.00×10^{-6} M), which was prepared in doubly distilled water, and adding 0.10 g niobium pentoxide (photocatalyst). Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp. The intensity of light at various distances from the lamp was measured with the help of a Solarimeter (SM CEL 201). A water filter was used to cut out the thermal radiations. A digital pH meter was used to measure the pH of solution. The desired pH of solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The progress of the reaction was monitored spectrophotometrically by measuring the optical density (O.D.) of the dye solution at various time intervals. Controlled experiments were also carried out to confirm that the reaction is neither photochemical nor thermal, but it is photocatalytic.

3. RESULTS AND DISCUSSION

The results of a typical run are graphically represented in Fig. 1. The plot of $\log O.D.$ v/s exposure time is a straight line. This indicates that the photocatalytic degradation of p-rosaniline hydrochloride in presence of niobium pentoxide follows pseudo first order kinetics and the rate constant for this reaction was determined using the expression $k = 2.303 \times \text{slope}$.

A Typical Run

(Progress of the Photocatalytic reaction)

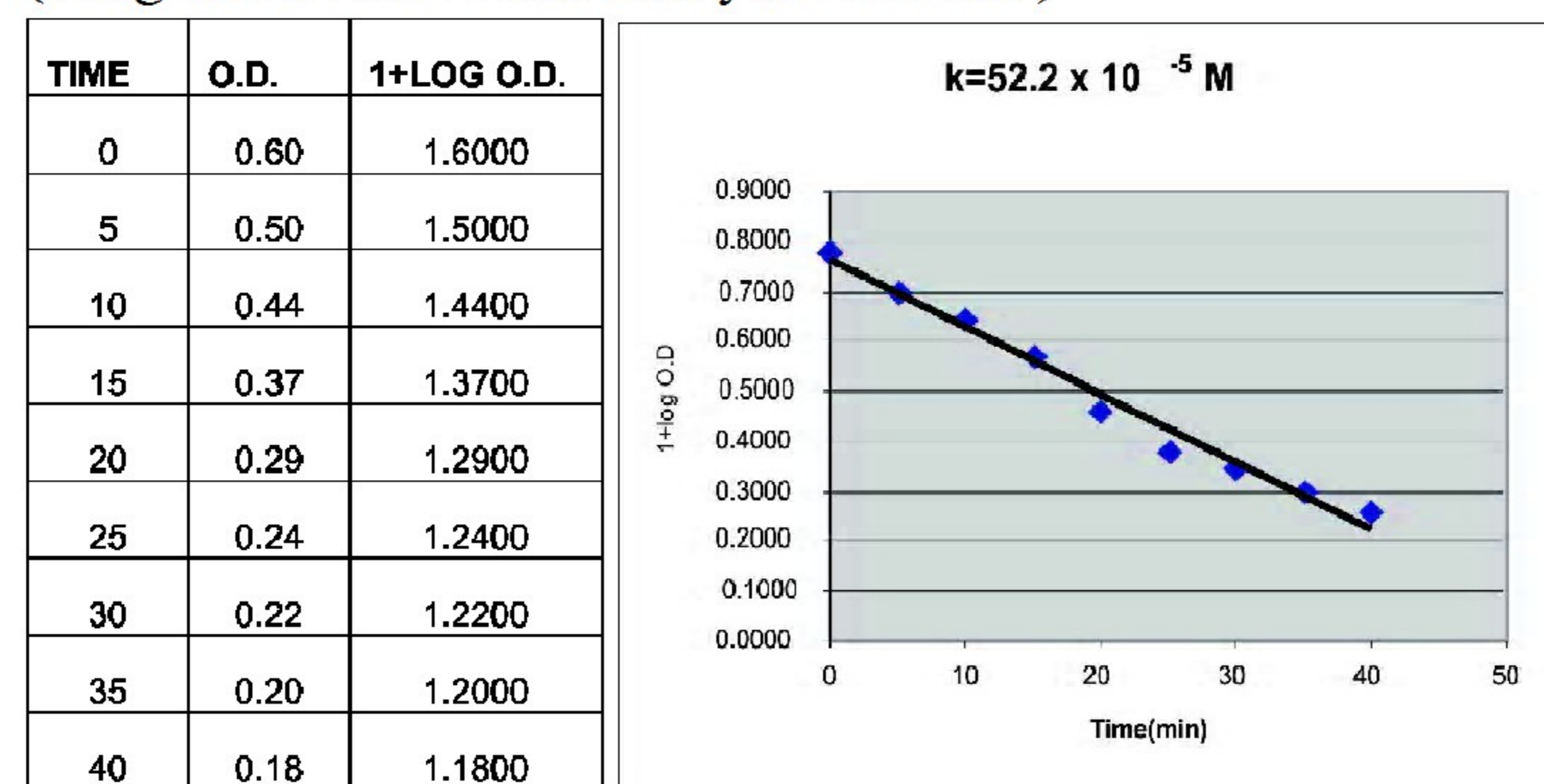


Fig. 1. Variation of dye concentration with time of exposure. Conditions: [P-Rosaniline hydrochloride] = 5.00×10^{-6} M, pH = 8.5, Niobium pentoxide = 0.10 g and light intensity = 37.0 mW cm^{-2}

Effect of the pH

The effect of pH on photocatalytic degradation was also investigated. The results are reported in Table 1 and are graphically presented in Fig. 2.

It was observed that with an increase in pH, the rate of photocatalytic degradation of the dye increases from 6.00 to 8.50. On further increasing the pH, a decrease in the rate of photocatalytic bleaching was observed. This behaviour can be explained on the basis that as the pH of the solution increases, more OH^- ions are available. OH^- ions will generate more OH^\cdot radicals by combining with the hole of the semiconductor and these OH^\cdot are considered responsible for the photocatalytic bleaching. After a certain pH value, more OH^- ions in the bulk will retard the approach of the dye molecules towards the semiconductor surface in the desired time limit due to the decrease in the movement of the large dye molecules. This will result in a decrease in the rate of photocatalytic bleaching of p-rosaniline hydrochloride. The participation of OH^\cdot radicals in the reaction was confirmed by carrying out the reaction in presence of oxalate ions, which act as hole (h^+) scavenger through the following reaction.

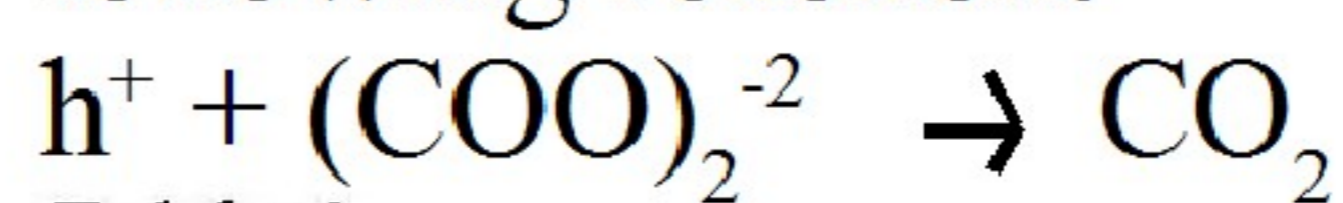


Table 1

Effect of pH on the rate of photocatalytic degradation of p-rosaniline hydrochloride

pH	$k \times 10^5 (\text{s}^{-1})$
6.0	21.9
6.5	22.3
7.0	30.7
7.5	34.5
8.0	48.4
8.5	52.2
9.0	52.2
9.5	52.6
10.0	52.2

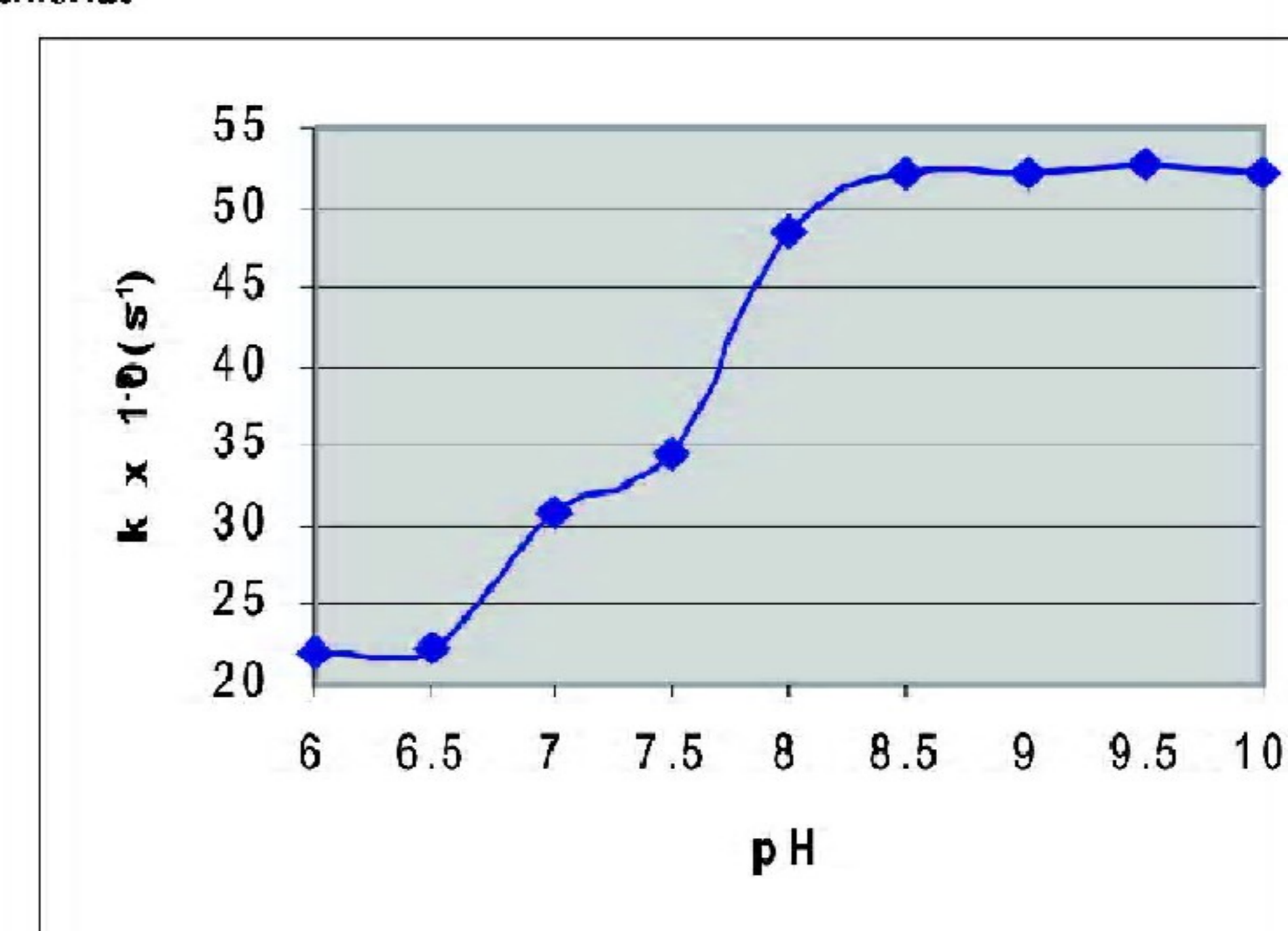


Fig. 2. Effect of pH on the rate of photocatalytic degradation of p-rosaniline hydrochloride. Conditions: [P-Rosaniline hydrochloride] = 5.00×10^{-6} M, Niobium pentoxide = 0.10 g and light intensity = 37.0 mW cm^{-2}

Effect of the p-rosaniline hydrochloride concentration

The effect of variation of dye concentration was also studied by taking different concentrations of p-rosaniline hydrochloride. The results are tabulated in Table 2 and graphically presented in Fig. 3.

From the data presented, it is clear that the rate of photocatalytic degradation increases with increasing concentration of the dye (up to 5.0×10^{-5} M). This may be attributed to the fact that as the concentration of p-rosaniline hydrochloride was increased, more dye

molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. Further increase in the concentration of the dye (i.e. above 5.00×10^{-5} M) resulted in a decrease in the rate of reaction. This may be explained on the basis that at higher concentrations, the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconducting particles and thus, the rate of the photocatalytic bleaching of p-rosaniline hydrochloride decreases.

Table 2
Effect of concentration of p-rosaniline hydrochloride on the rate of photocatalytic degradation

[Rosaniline hydrochloride] $\times 10^{-5}$ M	k $\times 10^4$ (s ⁻¹)
4.2	29.6
4.4	34.2
4.6	45.3
4.8	45.7
5.0	52.2
5.2	26.5
5.4	24.6

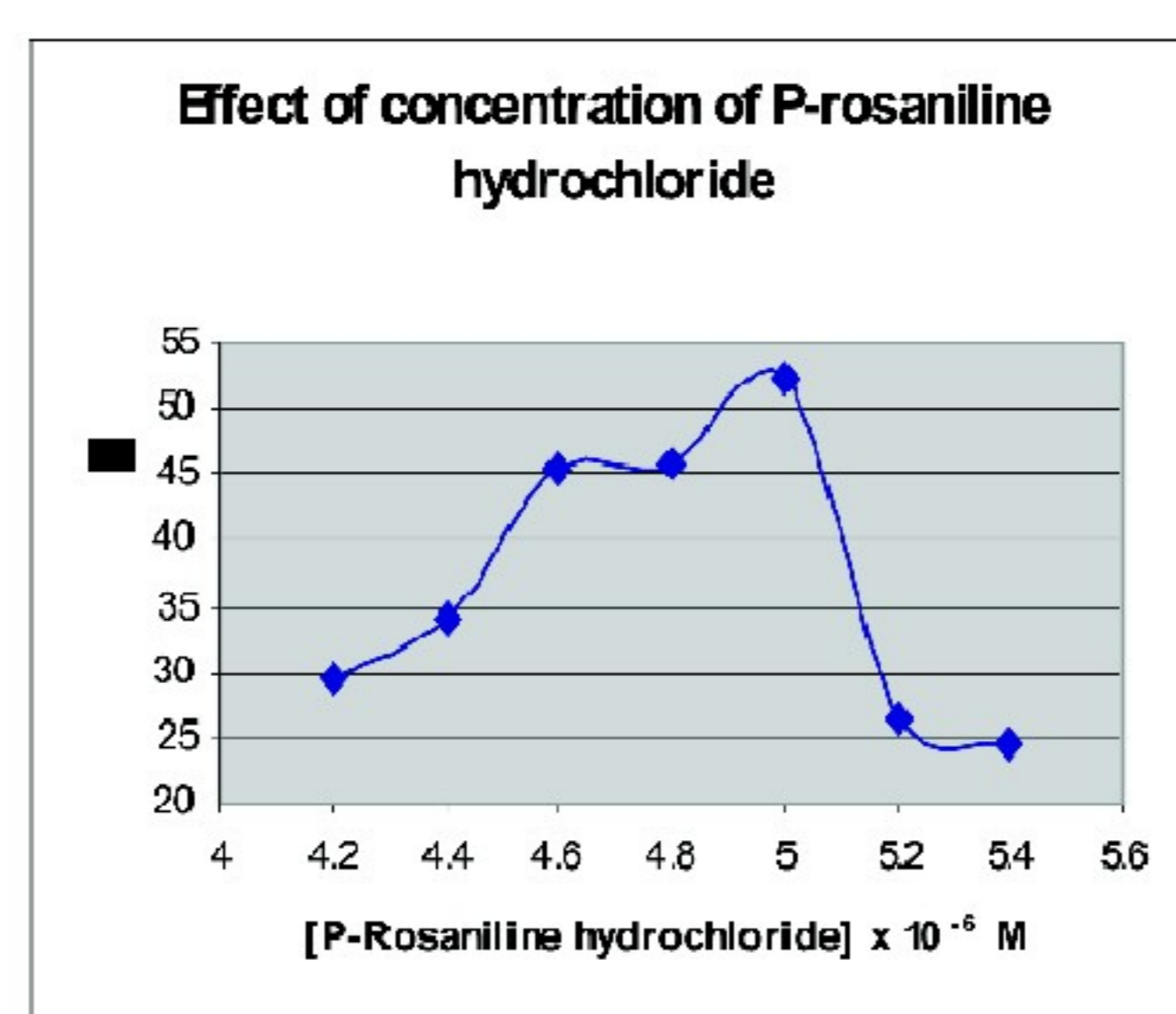


Fig. 3. Effect of concentration of p-rosaniline hydrochloride on the rate of photocatalytic degradation. Conditions: Light intensity = 37.0 mW cm⁻², Niobium pentaoxide = 0.10 g and pH = 8.5

Effect of the amount of semiconductor

The amount of semiconductor is also likely to affect the rate of photocatalytic degradation of p-rosaniline hydrochloride. Different amounts of photocatalyst (niobium pentaoxide) were used and the results are summarized in Table 3 and graphically presented in Fig.4. It was observed that as the amount of semiconductor increased, the rate of photodegradation of p-rosaniline hydrochloride also increased, but ultimately the reaction rate become constant after a certain amount (0.10 g) of semiconductor. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increased, but after a certain limit (a point of saturation), if the amount of niobium pentaoxide was further increased, there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of p-rosaniline hydrochloride because any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel. This behaviour was confirmed by using reaction vessels of different dimensions and taking several solutions of different dye concentrations.

Table 3
Effect of amount of semiconductor on the rate of photocatalytic degradation of p-rosaniline hydrochloride

Amount of semiconductor(g)	K ₁ $\times 10^5$ (S ⁻¹)
0.06	40.3
0.08	41.5
0.10	52.2
0.12	41.1
0.14	40.7

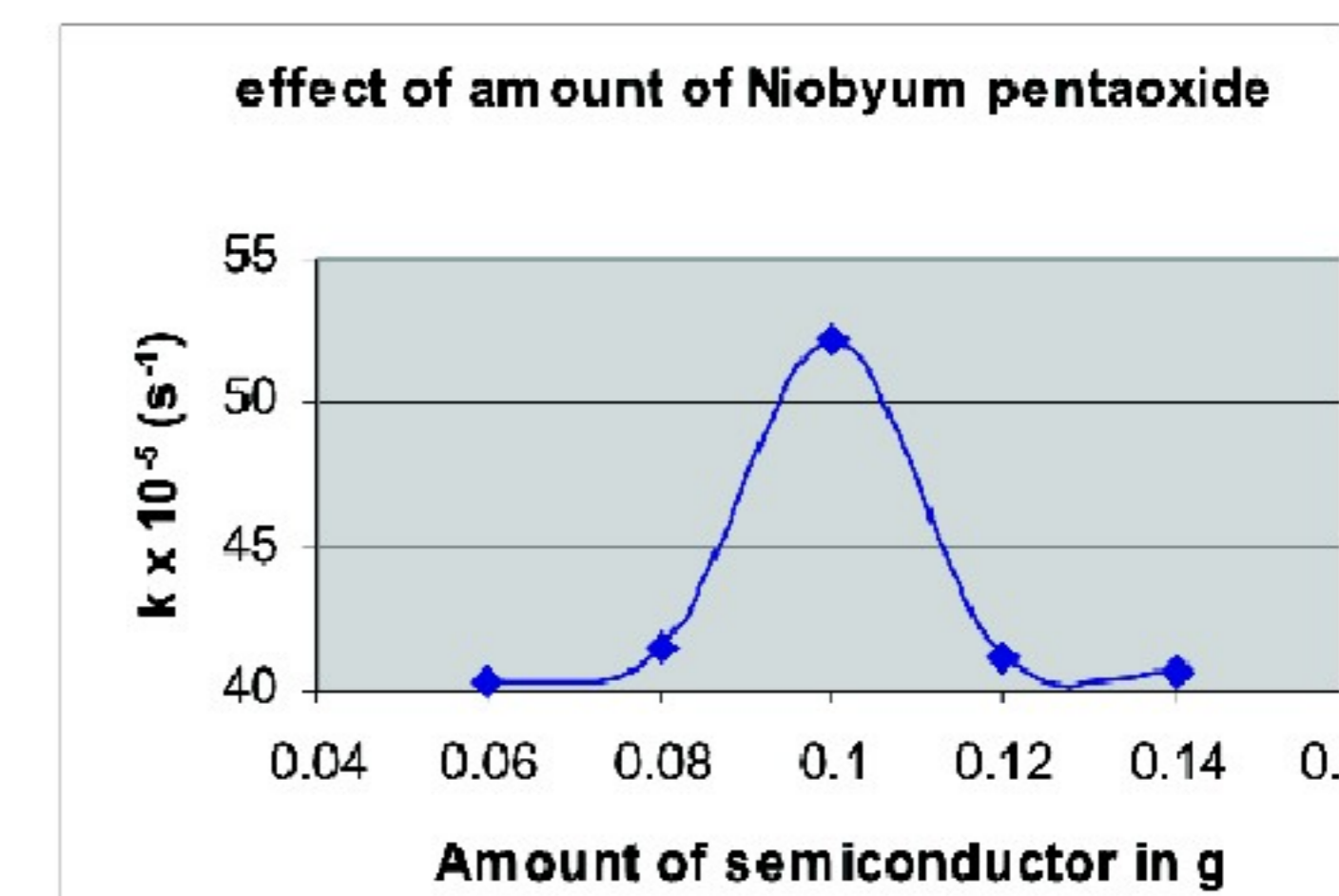


Fig. 4. Effect of amount of semiconductor on the rate of photocatalytic degradation of p-rosaniline hydrochloride. Conditions: [P-Rosaniline hydrochloride] = 5.00×10^{-6} M, pH = 8.5 and light intensity = 37.0 mW cm⁻²

Effect of the light intensity

The effect of the variation of light intensity on the rate was also investigated and the observations are reported in the Table 4 and graphically presented in Fig.5

The results indicate that the bleaching action was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. An almost linear dependence between the light intensity and rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Table 4
Effect of light Intensity on the rate of photocatalytic degradation of p-rosaniline hydrochloride

Intensity(mW cm ⁻²)	K ₁ $\times 10^5$ (S ⁻¹)
23	26.5
27	28.4
30	37.2
37	52.2

Niobium pentaoxide = 0.10 g and pH = 8.5.

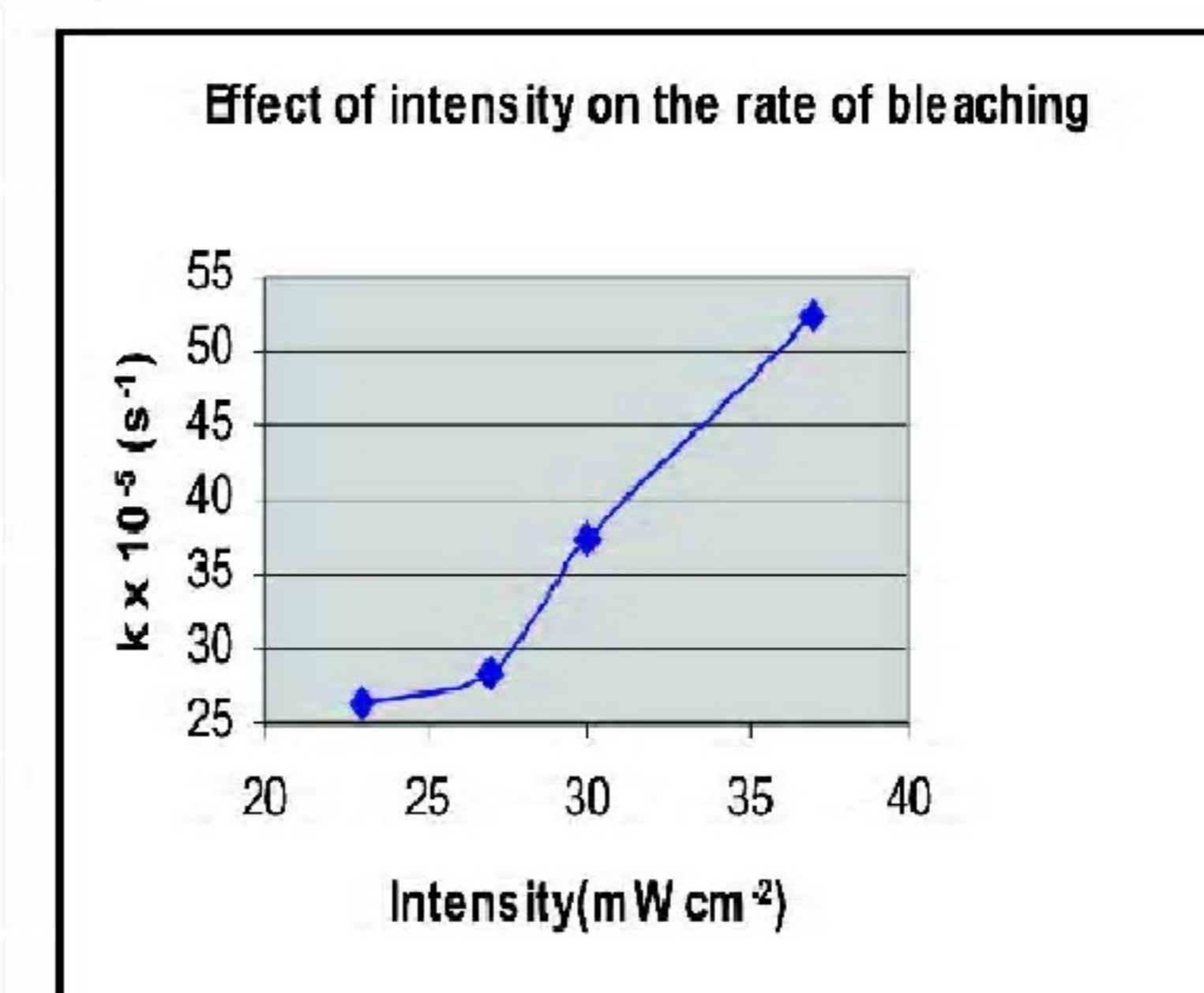
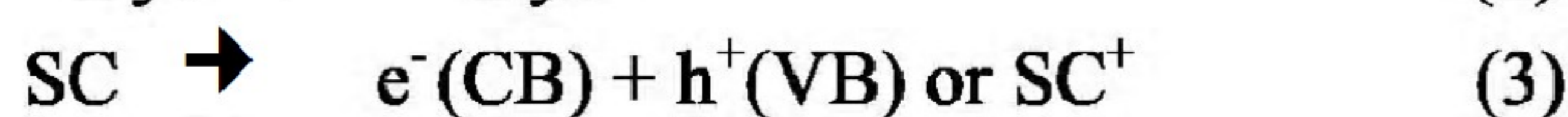


Fig. 5. Effect of light Intensity on the rate of photocatalytic degradation of p-rosaniline hydrochloride. Conditions: [P-Rosaniline hydrochloride] = 5.00×10^{-6} M,

MECHANISM

On the basis of the experimental observations, a tentative mechanism for photocatalytic bleaching of p-rosaniline hydrochloride may be proposed as—



The dye (p-rosaniline hydrochloride) absorbs radiation of suitable wavelength and it is excited to its first singlet state followed by intersystem crossing

(ISC) to triplet state (Eq. 1 and 2). On the other hand, the semiconducting niobium pentoxide (SC) also utilized the incident light energy to excite its electron from valence band to conduction band (Eq. 3), thus leaving behind a hole. This hole may abstract an electron from the OH⁻ ions to generate OH[·] radicals (Eq. 4). The excited dye may be oxidized to products by OH[·] radicals (Eq. 5). The participation of OH[·] radicals as an active oxidizing species was confirmed using its scavenger.

4. CONCLUSION

The photocatalytic decolourization of p-rosaniline hydrochloride over niobium pentoxide provides an ecofriendly method for degradation of the dye. The photocatalytic process may be utilized for the treatment of effluents from dyes and printing industries. The decolourization efficiency increases with increasing in pH, attaining maximum value at pH 8.50. The photocatalytic degradation of follows pseudo first order kinetics. The principal oxidizing species responsible for the dye decolourization is the hydroxyl radicals (OH[·] radical).

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