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Photocatalytic Bleaching of Fast Green in Presence of Zinc Oxide as Photocatalyst

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Abstract: The photocatalytic bleaching of Fast Green on zinc oxide powder has been carried out in presence of light. The photocatalytic bleaching of dye was observed spectrophotometrically.

The effect of variation of different parameters like concentration of Fast Green, pH, amount of zinc oxide, and light intensity on the rate of photocatalytic bleaching was observed. A tentative mechanism for the photocatalytic bleaching of Fast Green has been proposed.

Keywords: Photocatalytic bleaching, Fast Green, Zinc Oxide, Dye, Semiconductor, Light intensity

I. INTRODUCTION

As we step into the twenty-first century, we are faced with the challenges of purification of our water and air resources. We are faced with the task of treating wastes generated during manufacturing processes and proper disposal of various products and by-products.

Popular treatment methods for eliminating dyes from wastewater stream suffer from many drawbacks¹. Photocatalytic degradation is found to be a very efficient process for bleaching of dye in which catalysts are semiconductor² particles under band gap excitation, the semiconductor particles act as short-circuited microelectrodes and initiate the oxidation and reduction process at adsorbed substrate³.

The photodecomposition of ZnO is thermodynamically favored because the anodic dissolution potential of ZnO (+0.65V vs, SCE) lies inside the semiconductor band gap and is more negative than the redox potential for water oxidation⁴.

Fast Green is used as a biological stain for coloring food, drugs, and cosmetics, it is, therefore, important to remove this dye from water resources.

II. MATERIALS AND METHODS

Fast Green (CDH) and Zinc oxide (CDH) were used in the present investigation. The dye solution of Fast Green was prepared in doubly distilled water.

0.0809 g of Fast Green (FCF) was dissolved in 100.0 mL of doubly distilled water so that concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This solution was further diluted. The optical density of this dye solution was determined with the help of a spectrophotometer ($\lambda_{\text{max}} = 630 \text{ nm}$).

Then it was divided into four parts -

- 1) The first beaker containing only dye solution was kept in dark,
- 2) The second beaker containing only dye solution was kept in sunlight,
- 3) 0.10 g of semiconductor zinc oxide was added to the third beaker containing dye solution and was kept in dark, and
- 4) 0.10 g of semiconductor zinc oxide was added to the fourth beaker containing dye solution and it was exposed to sunlight⁵.

These beakers were kept for 4 hours and then the optical density of solution in each beaker was measured with the help of a spectrophotometer.

It was observed that the solutions of first three beakers had the same optical density while the solution of the fourth beaker had a decrease in its initial value of optical density.

The above experiment confirms that the reaction between Fast Green (FCF) and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction.

III. RESULTS AND DISCUSSION

The photocatalytic bleaching of Fast Green was observed at ($\lambda_{max}=630nm$)⁶. The result for a typical run is given in Table 1 and graphically represented in Figure 1.

A. A Typical Run

TABLE I: A TYPICAL RUN

[Fast Green (FCF)] = $1.0 \times 10^{-5}M$

Light Intensity = 40.0 mW cm^{-2}

pH = 7.0

Zinc oxide = 0.20g

Time (min)	Optical Density (O.D)	1+log O.D
0.0	0.820	0.914
30.0	0.725	0.860
60.0	0.626	0.796
90.0	0.577	0.761
120.0	0.516	0.713
150.0	0.454	0.657
180.0	0.414	0.617
210.0	0.368	0.566

$$k = 6.55 \times 10^{-5} (\text{sec}^{-1})$$

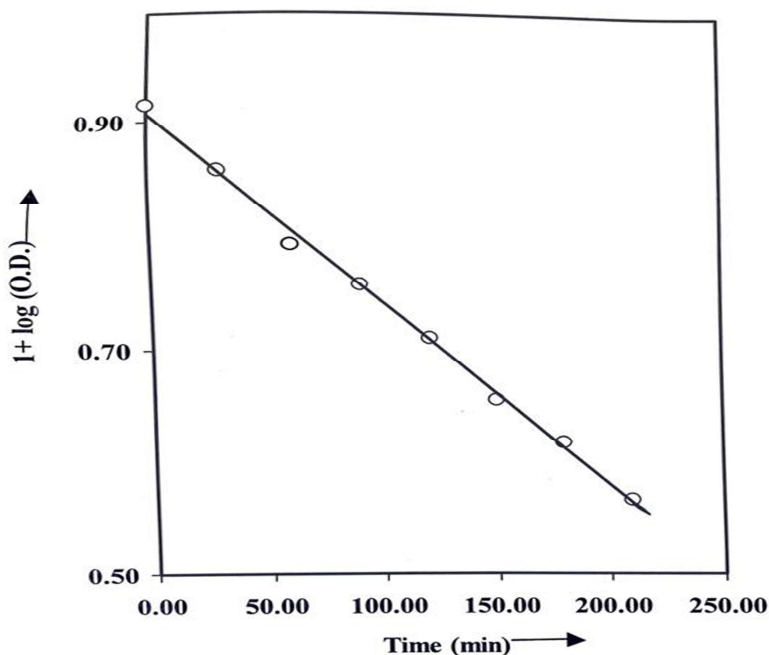


Fig. 1: A typical run

It was observed that the optical density of Fast Green (FCF) solution in presence of semiconductor was much low as compared to sample without semiconductor at the same time intervals. It means that the rate of this photocatalytic degradation is favorably affected by a semiconductor in the case of Fast Green (FCF). The plot of log O.D. v/s time was linear and hence this reaction follows pseudo-first order kinetics. The rate constant of this reaction was determined by the expression (1).

B. Effect of pH Variation

The pH of the solution is likely to affect the bleaching of the dye⁷. The effect of pH on the rate of bleaching of dye solution was investigated in the pH range (5.0 - 8.5). The results are reported in Table II and graphically presented in Figure 2.

TABLE II: EFFECT OF pH

[Fast Green (FCF)] = 1.0×10^{-5} M
 Light Intensity = 40.0 mW cm^{-2}

Zinc oxide = 0.20g

pH	$k \times 10^5$ (sec^{-1})
5.0	3.38
5.5	3.65
6.0	3.75
6.5	4.70
7.0	6.55
7.5	6.08
8.0	3.59
8.5	1.21

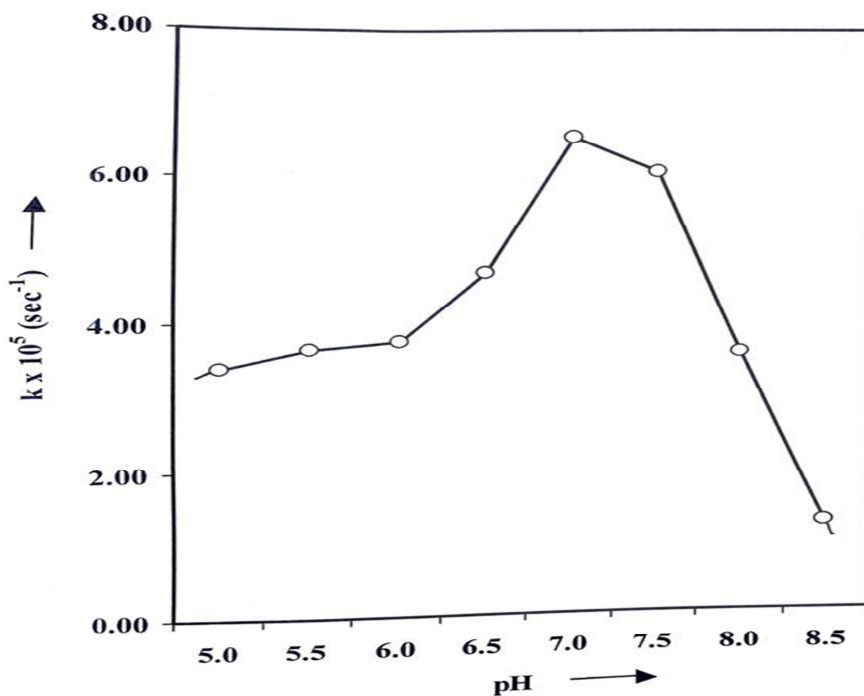


Fig. 2: Effect of pH

It was observed that with increase in the pH of medium, the rate of photocatalytic bleaching of Fast Green (FCF) increases up to pH 7.0 and a further increase in pH value will decrease the rate of photocatalytic bleaching. This can be explained on the basis that as the pH of medium was decreased below 7.0, then the surface of the semiconductor remains positively charged due to adsorption of H^+ ions, and the dye also loses its anionic behavior and hence, there is a corresponding decrease in the rate of bleaching due to coulombic repulsion between positively charged semiconductor surface and propagated dye molecule. Above pH 7.0, hydroxyl ions are more in the solution and these hydroxyl ions will adsorb on the semiconductor surface, making it negatively charged. Thus, there will be a coulombic repulsion between negatively charged semiconductor surface and anionic dye. This is reflected in the decrease in rate of photobleaching of the dye on increasing pH above 7.0.

C. Effect of Fast Green (FCF) Concentration

Effect of variation of dye concentration was also studied by taking a different concentration of Fast Green (FCF). The results are tabulated in Table III and graphically represented in Figure 3

Table III: Effect Of Fast Green Concentration

pH = 7.0

Zinc oxide = 0.20g

Light Intensity = 40.0 mW cm⁻²

[Fast Green (FCF)] = 1.0 x 10 ⁻⁵ M	k x 10 ⁵ (sec ⁻¹)
0.5	3.43
1.0	6.55
1.5	5.08
2.0	2.99
2.5	2.13
3.0	1.79

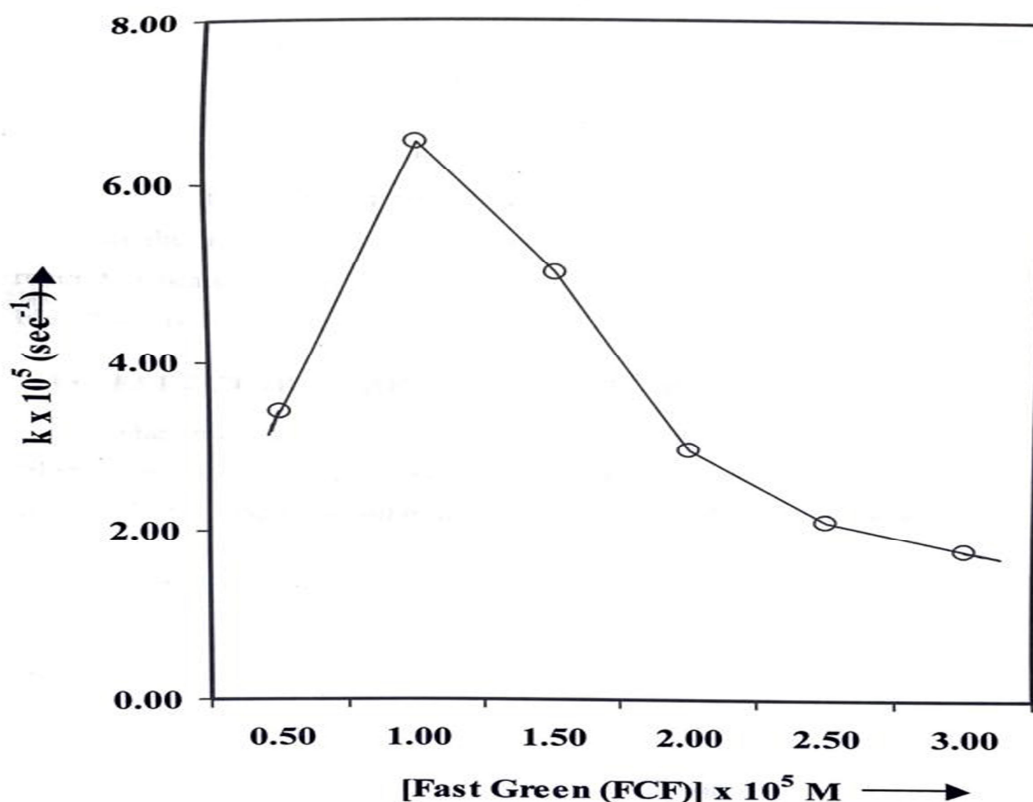


Fig.3: Effect of Fast Green (FCF) concentration

It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye. It may be due to the fact that as the concentration of Fast Green (FCF) was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with an increase in the concentration of the dye further. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic bleaching of Fast Green (FCF).

D. Effect of Amount of Semiconductor

The amount of semiconductor is also likely to affect the process of dye bleaching. Different amounts of photocatalysts were used and the results are reported in Table IV and graphically represented in Figure 4

TABLE IV: EFFECT OF AMOUNT OF SEMICONDUCTOR

[Fast Green (FCF)] = 1.0×10^{-5} M

pH = 7.0

Light Intensity = 40.0 mW cm^{-2}

Amount of Semiconductor (g)	$k \times 10^5 \text{ (sec}^{-1}\text{)}$
0.04	3.80
0.08	4.52
0.12	5.36
0.16	5.82
0.20	6.55
0.24	6.58
0.28	6.53

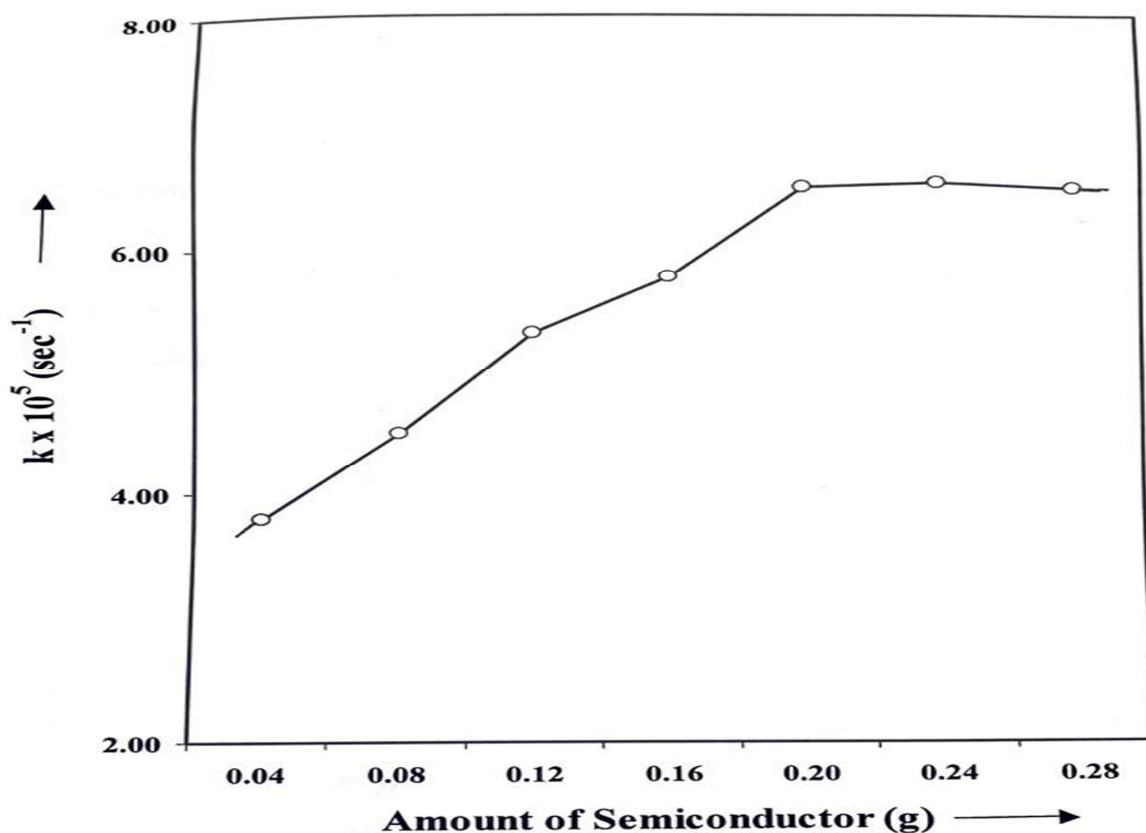


Fig. 4: Effect of amount of semiconductor

It has been observed that the rate constant of photobleaching of Fast Green (FCF) increases with an increase in the amount of semiconductor but ultimately, it becomes almost constant after a certain amount. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductor 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 Fast Green (FCF). 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, once the complete bottom of the reaction vessel is covered by the photocatalyst⁸. It may be also confirmed on the basis of geometry of the reaction vessel. This was observed by taking reaction vessels of different dimensions. the point of saturation was shifted to higher value; when vessels of larger capacities were used. A reverse trend was observed when vessels of smaller capacities were used.

E. Effect of Light Intensity

To observe the effect of intensity of light on the photocatalytic bleaching of Fast Green (FCF), light sources of different wattage were used or the distance between the light source and the exposed surface area was varied⁹. The intensity of light at each distance was measured by suryamapi (CEL Model SM 201). The results obtained are reported in Table V and graphically represented in Figure 5

TABLE V: EFFECT OF LIGHT INTENSITY

[Fast Green (FCF)] = $1.0 \times 10^{-5}M$

Zinc oxide = 0.20g

pH = 7.0

Intensity of light (mW cm ⁻²)	k x 10 ⁵ (sec ⁻¹)
20.0	5.04
30.0	5.73
40.0	6.55
50.0	7.09
60.0	7.63
70.0	8.17

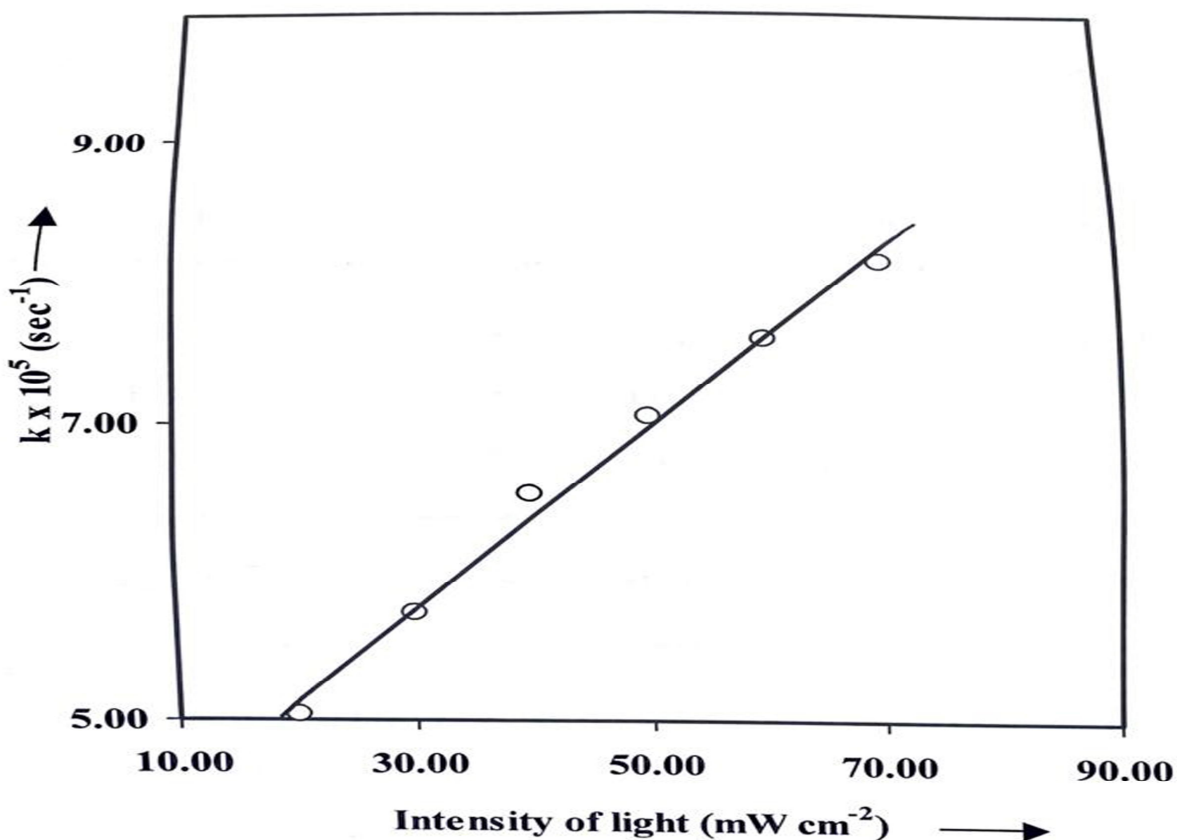
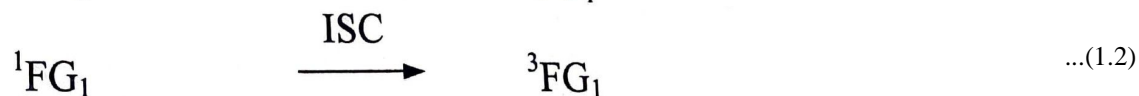
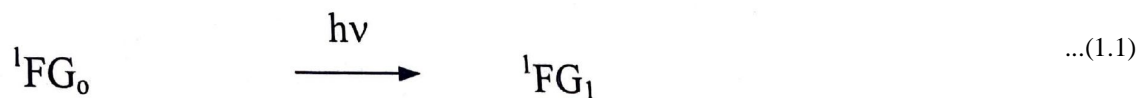


Fig. 5: Effect of light intensity

The result given in Table V indicates that 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. A linear behavior between light intensity and rate of reaction was observed.

IV. MECHANISM

On the basis of these observations, a tentative mechanism for photocatalytic bleaching of Fast Green (FCF) may be proposed.



When the solution of Fast Green (FCF) was exposed to light, in presence of a semiconductor, initially the dye molecules are excited to first excited singlet state. Then these excited singlet molecules are transferred to triplet state through intersystem crossing (ISC). The triplet dye may donate its electron to the semiconductor and the Fast Green (FCF) becomes positively charged. The dissolved oxygen of solution will pull on electron from the conduction band of semiconductor; thus, regenerating semiconductor and $\text{O}_2^{\cdot-}$ is formed. In acidic medium, oxygen ion radical reacts with proton to form HO_2^{\cdot} radical. This radical reduces the positively charged Fast Green (FCF) molecules in leuco form (FGH) regenerating oxygen molecules. The participation of HO_2^{\cdot} ion radical as an active species was confirmed by carrying out the reaction in presence of HO_2^{\cdot} , ion scavenger e.g. 2-propanol. Where the reaction rate was drastically retarded¹⁰.

V. CONCLUSION

- 1) An optimum rate of photocatalytic bleaching of Fast Green (FCF) was observed at pH = 7
- 2) Optimum rate of photocatalytic bleaching was observed at concentration $1.0 \times 10^{-5} \text{M}$
- 3) The rate constant of photobleaching of Fast Green (FCF) increases with an increase in the amount of semiconductor but it becomes almost constant after certain amount.
- 4) A linear behavior between light intensity and rate of photocatalytic bleaching was observed.

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