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# Photodegradation of Fast Green by Using $SnO_2$ Quantum Dots/$TiO_2$ Nanoparticles Composite

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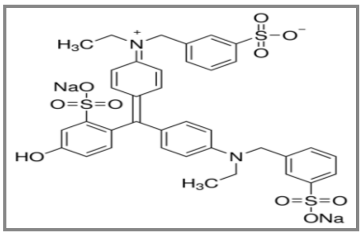
## ABSTRACT

*The photocatalytic degradation of fast green was studied under visible light using* $SnO_2$*-*$TiO_2$*. This composite was prepared by hydrothermal method using stannic chloride (hydrate) as precursor for* $SnO_2$ *quantum dots. It has more photocatalytic activity than titania nanopowder for degradation of fast green. The effect of various parameters like pH, the concentration of dye, amount of catalyst and light intensity on the rate of degradation was also studied. It can be a promising method for wastewater treatment.*

### Graphical Abstract



Structure of Fast green.

**Keywords:** Fast Green, Photocatalysis, Quantum dots, Nanoparticles.

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## INTRODUCTION

Water is the most important source for the life of all living organisms, but water is becoming polluted. Today, people are facing a major problem of water pollution. The industrial effluents are toxic sources of water pollution. Many industries are producing a large variety of harmful compounds through their effluents. Dyes are most common pollutants, which cannot be easily degraded. Although dyes are quite useful to us, but these are much harmful for human health also. Dye generates many diseases in human body like different types of tumor, allergic dermatitis, abdominal pain, vomiting, indigestion, trigger asthma, chromosomal damage, etc. There is an increasing demand of clean water all over the globe. Different types of method have been used for degradation of colored water but also require an urgent eco-friendly solution for treatment of waste water. AOPs are widely used for the removal or degradation of recalcitrant organic constituents from industrial and municipal waste water by oxidation through reactions with hydroxyl radicals ($^{\bullet}OH$). Photocatalysis is an efficient method for treatment of polluted water containing different organic contaminants.

The effluents from the textile, paper and food industries containing dye are strongly colored and have very harmful effects on living beings. Heterogeneous photocatalysis is an effective treatment method for the removal of dyes from industrial waste water. Synthetic dyes are used in a wide range of technologies, but their toxic nature generates demand for removal of dye from water [**1**]. Photocatalytic degradation has been found to be a very efficient process for minimization of organic pollutants. The photocatalyst is a substance, which is activated by absorbing a photon and is capable of accelerating a reaction [**2**].

Mandavgane *et al.,* [**3**] studied photocatalytic degradation of eosin Y by $TiO_2$ and ZnO catalysts in presence of UV light. The effect of operating conditions such as eosin Y initial pH, $H_2O_2$/COD ratio and the amount of catalyst loading on the removal efficiency was also evaluated. Paliwal *et al.,* [**4**] reported degradation of non-biodegradable methylene blue by using undoped and Co-doped bismuth ferrite as photocatalyst. The effect of different parameters like pH, concentration of dye, amount of photocatalyst and light intensity on the reaction rate was also studied.

Tanasa *et al.,* [**5**] prepared ZnO/$SnO_2$ nanocomposites by co-precipitation method. The structural properties of composite were evaluated by different techniques; XRD, UVDR, SEM, $N_2$ adsorption, and IR. It was used for photocatalytic degradation of eosin Y. As-prepared nanocomposites exhibit higher photocatalytic activity than a single semiconductor photocatalyst. ZnO can effectively improve the photocatalytic efficiency of $SnO_2$ under UV illumination.

Vattikuti *et al.,* [**6**] synthesized a zero-dimensional/two-dimensional binary $SnO_2$–ZnO quantum dots (QDs) deposited on the surface of graphitic carbon nitride (g-$C_3N_4$) nanosheets ($SnO_2$–ZnO QDs/g-$C_3N_4$ hybrid). They used an *in situ* co-pyrolysis approach to obtain high photoactivity for the degradation of pollutants and also for production of hydrogen under visible light irradiation. This hybrid showed excellent photocatalytic efficiency, where 99% rhodamine B dye degradation was achieved in 60 min. Du *et al.,* [**7**] prepared $SnO_2$ quantum dots anchored on $TiO_2$ nanospheres ($TiO_2$/$SnO_2$ composites) via a simple one-step hydrothermal process and used for photodegradation of methyl orange. The composite exhibited highly efficient degradation of methyl orange in 15 min under ultraviolet-visible light.

Jangid *et al.,* [**8**] investigated photocatalytic degradation of Evans blue by $SrCrO_4$ in the presence of visible light. Strontium chromate was synthesized by precipitation method in a wet chemical process. The effect of various parameters such as pH, the concentration of dye, amount of semiconductor and light intensity on the rate of degradation was also studied. It was observed that strontium chromate has the highest catalytic activity in basic medium.

Paliwal *et al.,* **[9]** reported the degradation of malachite green using CuO/$Al_2O_3$ composite as a semiconductor. Alzahrani [**10**] synthesized magnetic nanoparticles coated with Ag using a co-precipitation method. As-fabricated Ag-doped magnetic nanoparticles were used for the degradation of eosin Y under UV-lamp irradiation. The fabricated magnetic nanoparticles coated with Ag (MNPs) were characterized by different techniques such as SEM, TEM, EDX, and XRD analysis.

Gupta *et al.,* [**11**] used barium chromate powder as a photocatalytst to degrade eosin yellow. The rate of decomposition was affected by different parameters like pH, concentration of dye, amount of photocatalyst and intensity of light. The reaction proceeded through oxidation by hydroxyl radicals as confirmed by specific scavenger, 2-propanol.

Martins *et al.,* [**12**] synthesized a composite of $TiO_2$ (P25) and N-doped carbon quantum dots (P25/NCQD) by using a hydrothermal method. It was then used as catalyst for the photooxidation of

NO under UV and visible light irradiation. Photodegradation ratio of methylene blue was found to be increased from 68 to 91% on 1 h UV irradiation.

## MATERIALS AND METHODS

**Synthesis of $SnO_2$QD-$TiO_2$:** $SnO_2$ QD-$TiO_2$ was synthesized as reported earlier [13].

**Photocatalytic Process:** The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of fast green dye (Figure 1). A stock solution of dye (1.0 x $10^{-3}$ M) was prepared by dissolving (0.0808 g) of dye in 100 mL doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics model 335), and the desired pH of the solution was adjusted by addition of standard 0.1 N sulfuric acid and 0.1 N sodium hydroxide solutions. The reaction mixture containing 0.10 g photocatalyst ($TiO_2$ or $SnO_2$-$TiO_2$) was exposed to a 200 W tusngten lamp. About 3 mL aliquot was taken out at an interval of 10 min and absorbance (A) was measured at $\lambda_{max}$ = 620 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM 201). The absorbance of the solution was measured at various time intervals with the help of a spectrophotometer (Systronics Model 106). It was observed that the absorbance of the solution decreases with increasing time of exposure, which indicates that the concentration of fast green dye decreases with increasing time.

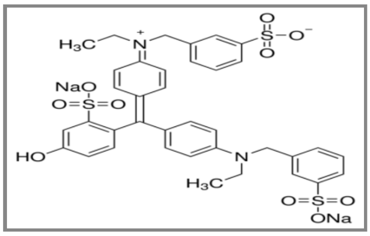

**Figure 1.** Structure of Fast green.

## RESULTS AND DISCUSSION

The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{slope} \qquad ...(1)$$

**Typical run:** Typical run is graphically represented in figure 2 and rate constant of $TiO_2$ and $SnO_2$-$TiO_2$composite was determined as 3.83 x $10^{-5}$ and 5.11 x $10^{-5}$sec$^{-1}$, respectively. pH = 7.0,[Fast Green] = 7.00 x $10^{-6}$M, amount of semiconductor = 0.10 g and light intensity = 50.0 mWcm$^{-2}$.

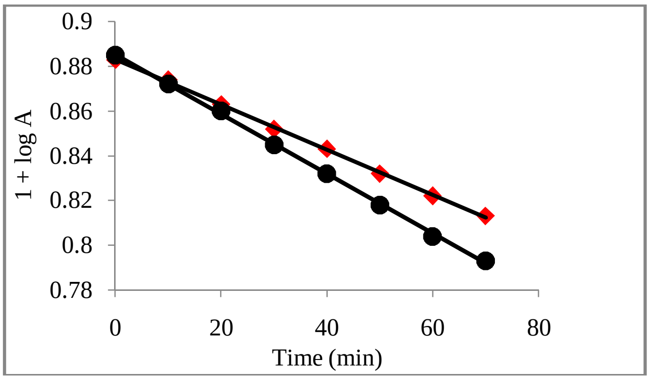

**Figure 2.** Typical runs.

### Effect of Parameters

**pH variation:** The effect of variation of pH was studied in the range 5.0-8.5 and the results are presented in figure 3. It was observed the rate of degradation increases with an increase in pH up to 7.0, but it decreases with a further increase in pH. An electron from conduction band is abstracted by dissolved oxygen to generate $O_2^{\bullet -}$. An increase in the rate of photocatalytic degradation of dye with the increase in pH may be due to the availability of more $O_2^{\bullet -}$ radicals. A decrease in the rate of photocatalytic degradation of the dye may be due to the fact that fast green is present in its anionic form, which will experience a force of repulsion with the negatively charged surface of the semiconductor due to absorption of more OH ions on the surface of the photocatalyst. [Fast Green] = 7.00 x $10^{-6}$M, Amount of semiconductor = 0.10 g and light intensity = 50.0 mWcm$^{-2}$.

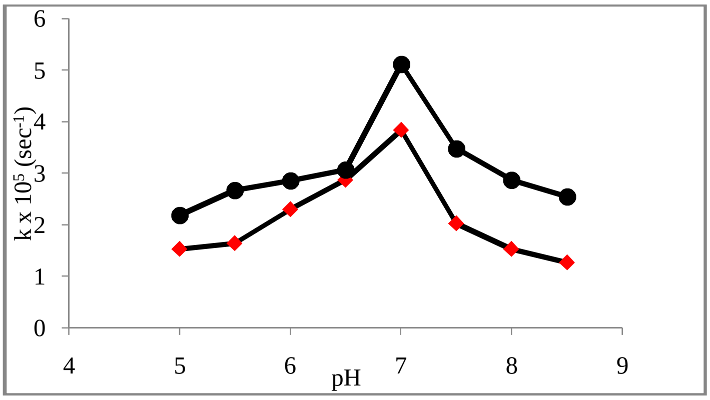

**Figure 3.** Variation of pH.

**Dye concentration variation:** The effect of dye concentration on the photocatalytic degradation of fast green was observed in the range of 3.0 x $10^{-6}$ to 1.0 x $10^{-6}$ M and results are reported in figure 4. It was observed that the dye degradation increases with increasing dye concentration, but after 7.0 x $10^{-6}$ M concentration, the rate of photocatalytic degradation decreases. Here, the dye will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel. pH = 7.0, Amount of semiconductor = 0.10 g and light intensity = 50.0 mWcm$^{-2}$.

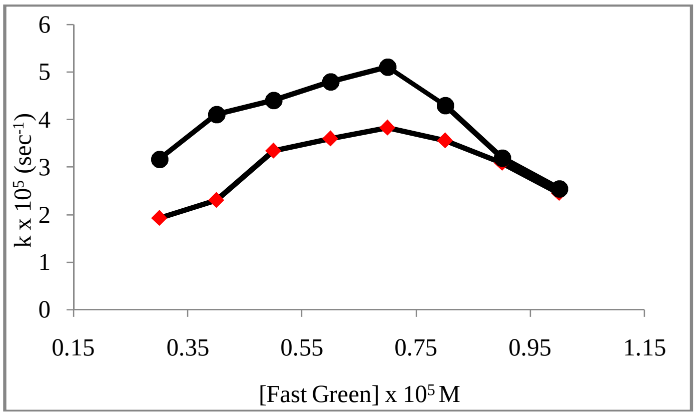

**Figure 4.** Variation of dye concentration.

**Amount of photocatalyst variation:** The effect of variation of the amount of photocatalyst on the rate of dye degradation has been studied in the range from 0.02 to 0.14 g. The results of effect of amount of semiconductor on rate constant are represented in figure 5. It was observed that as the amount of photocatalyst was increased, the rate of photocatalytic activity increases. The rate of degradation was optimum at 0.10 g of the semiconductor, beyond which (0.10 g), it showed a declining behavior. Because after this value, an increase in the amount of photocatalyst will only increase the thickness of the photocatalyst layer and not the exposed surface area. This was confirmed by taking reaction vessels of different dimensions. This decline may be due to the fact that excessive amount of photocatalyst may create hindrance and blocks light penetration. It may be also be due to electron-hole recombination as multi layers are formed, which are quite close to each other, making recombination easier. pH = 7.0, [Fast Green] = 7.00 x $10^{-6}$ M and light intensity = 50.0 $mWcm^{-2}$.

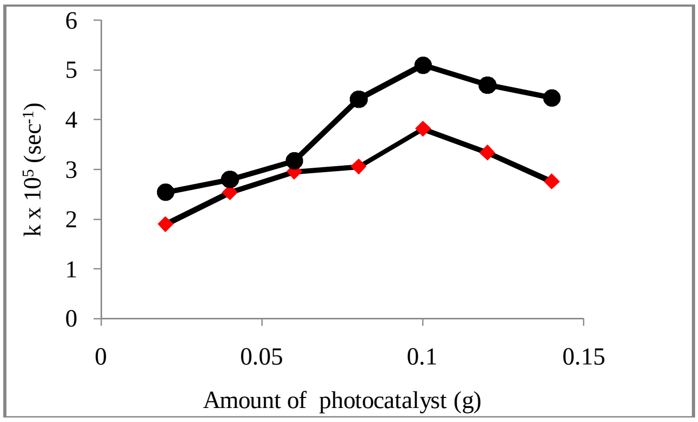

**Figure 5.** Variation of photocatalyst.

**Light intensity variation:** The effect of light intensity variation on the rate of photocatalytic degradation was studied in the range of 20.0 to 70.0 $mWcm^{-2}$ by varying the distance between the light source and exposed surface area. The results are shown in figure 6. It was observed that photocatalytic degradation of fast green increasing with increase in light intensity. The maximum rate was observed at 50.0 $mWcm^{-2}$ for degradation of fast green. On further increasing the intensity above 50.0 $mWcm^{-2}$, there was a decrease in the rate of photodegradation. There may be some thermal effects or side reactions above this limit and therefore, higher intensities were avoided. pH = 7.0, [Fast Green] = 7.00 x $10^{-6}$ M, and amount of semiconductor = 0.10 g.

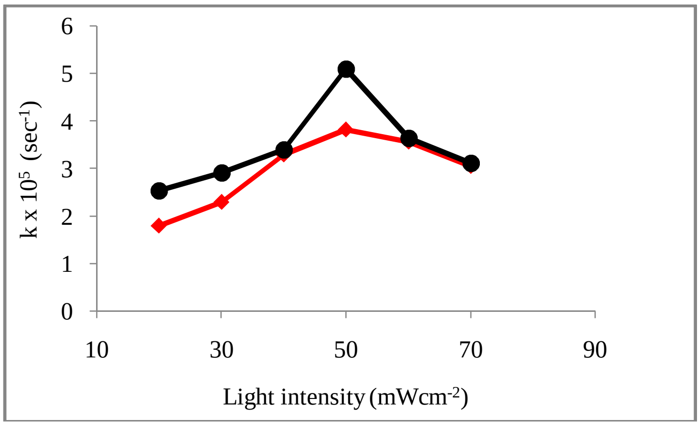

**Figure 6.** Variation of light intensity.

There was no effect on the rate of photocatalytic degradation of fast green in presence of hydroxyl radical scavengers, which indicates that hydroxyl radical is not active oxidizing species. The other possibility is oxidation by$O_2^{\bullet -}$ anion radical as optimum condition was found at 7.0.

**Mechanism:** On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of fast green (FG) may be proposed as:

$$^{1}FG_{0} \xrightarrow{h\nu} {}^{1}FG_{1} \qquad \ldots (2)$$

$$^{1}FG_{1} \xrightarrow{ISC} {}^{3}FG_{1} \qquad \ldots (3)$$

$$SC \xrightarrow{h\nu} SC\ (h^{+})\ (VB) + SC\ (e^{-})(CB) \qquad \ldots (4)$$

$$SC\ (e–)\ (CB) + O_2 \longrightarrow O_2^{\bullet -} \qquad \ldots (5)$$

$$O_2^{\bullet -} + {}^{3}FG_{1} \longrightarrow \text{Leuco FG} \qquad \ldots .(6)$$

$$\text{Leuco FG} \longrightarrow \text{Products} \qquad \ldots .(7)$$

Fast green is excited from its ground state by absorbing light intensity of a suitable wavelength to give its first excited singlet state. It undergoes intersystem crossing to corresponding triplet state of fast green to gain stability. $TiO_2/SnO_2$ composite also absorbs light to excite an electron from its valence bond to conduction band leaving behind a hole in valence band. Electron in conduction band can be abstracted by dissolved oxygen to generate an oxidant, $O_2^{\bullet -}$ anion radical. This oxygen molecule anion radical oxidizes triplet state of fast green to its leuco form, which in unstable and ultimately degrades to final smaller products.

## APPLICATION

Quantum dots find numerous applications in diode lasers, amplifiers, photocatalysis, photovoltaic devices, displays, photo detectors, solar cells, etc.

## CONCLUSION

$TiO_2/SnO_2$ composite has been successfully prepared by hydrothermal method. It was used to carry out the photocatalytic degradation of fast green under visible light in the presence of $SnO_2$ QDs decorated $TiO_2$ as a photocatalyst. It was observed that the $SnO_2$ QDs-$TiO_2$composite was having more photocatalytic activity than titania nanopowder alone for degradation of fast green. There was a 33.4 % increase in photocatalytic activity of titania on decorating it with $SnO_2$ QDs. This will prove to be a promising eco-friendly method for waste water treatment.

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