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Effect of transition metal ions on photoassisted bleaching of Reactive Yellow 86 by TiO_2

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ABSTRACT

The photocatalytic bleaching of textile azo dye Reactive Yellow 86 has been carried out in the presence of semiconductor TiO_2 *and the progress of reaction was observed spectrophotometrically.The effect of various operating parameters like pH, concentration of the dye, amount of photocatalyst and nature of photocatalyst on the efficiency of the reaction has been studied. Kinetic analysis of photodegradation reveals that the degradation follows approximately pseudo first order kinetics according to the Longmuir- Hinshelwood model. The optimum conditions for the degradation of Reactive Yellow 86 dye have been found as dye concentration* $2x10^{-5}M$*, pH= 7.5 and 0.25 g/100 ml catalyst dose. The effect of addition of transition metal ions (*Fe^{2+}*,* Cu^{2+}*,* Mn^{2+}*,* Zn^{2+}*,* Co^{2+}*,* Ag^{+}*) on photodegradation efficiency of* TiO_2 *have been investigated. It was observed that trace quantities of all the added metal ions increases the reaction rate to some extent. The increase in the photocatalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions on semiconductor surface. A tentative mechanism has been proposed.*

Key words: Azo dye, photodegradation, Semiconductor TiO_2, transition metal ions, Reactive Yellow 86.

INTRODUCTION

Azo dyes are versatile class of colored organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-). These are widely used in number of industries such as textile dying, food, leather, additive, cosmetic, paper, pharmaceutical industries etc.[1-2].

During dye production and textile manufacturing processes, a large quantity of waste water containing dyestuffs with intensive color and toxicity are introduced into the aquatic systems [3].These dyes do not decompose rapidly through natural processes and are resistant to aerobic degradation. The azo linkage is reduced to aromatic amines under anaerobic conditions that can be toxic and potentially carcinogenic [4-6].

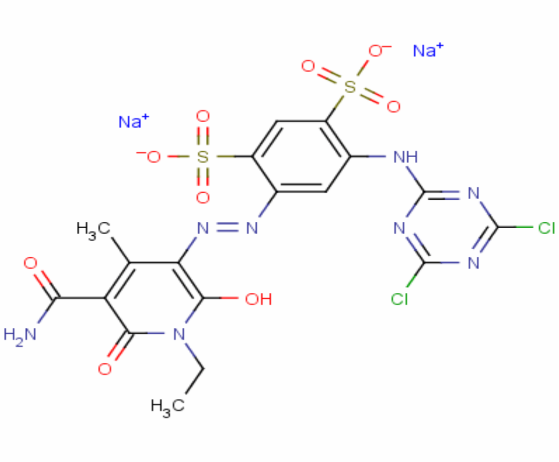
It is necessary to find an effective method of wastewater treatment in order to remove color from effluents. A number of physical and chemical techniques has been reported for the removal of dye compounds such as adsorption on activated carbon [7], biodegradation [8], ozonation [9] and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions [10,11], H_2O_2/UV processes [12] and semiconductor photocatalysis [13–15].

Advance oxidation processes are the methods in which very reactive species such as hydroxyl radicals ($^{\cdot}OH$) are produced. The hydroxyl radical is a powerful oxidant that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water [16,17], so it is able to degrade pollutants effectively[18,19].Among the AOPs heterogeneous photocatalytic oxidation using TiO_2 as photocatalyst has been extensively studied. TiO_2 is very effective, relatively inexpensive, easily available and chemically stable photocatalyst. The appropriate illumination of these particles produces excited-state high energetic electron and hole pairs (e^-/h^+). These pairs are able to initiate a wide range of chemical reactions that may lead to complete mineralization of organic and inorganic pollutants [20-23].

The aim of this work to asses the photocatalytic treatment of mono azo dye Reactive Yellow 86(MF: $C_{19}H_{14}Cl_2N_8Na_2O_9S_2$, MW: 862.27) selected due to its toxicity, carcinogenic in nature as well as its presence in wastewater of several industries such as textile dying, printing, tannery etc.[scheme.1]

Two main aspects are studied: The first one was the optimization of the operational conditions for the removal of dye by means of spectrophotometric method to measure optical density. All the possible significant factors are investigated such as dye concentration, pH, amount of catalyst, nature of catalyst. The second aspect is the influence of dissolve transition metal ions on photocatalytic properties of TiO_2.In photocatalysis addition of metal ions to a semiconductor can change the photocatalytic process by changing the semiconductor surface properties. It creates new trapping sites on semiconductor surface to inhibit electron–hole recombination during illumination, thereby enhance the rate of photocatalytic reaction [24-28]. On irradiation, electron migrates on metal where it becomes trapped and electron – hole recombination is suppressed. The hole is then free to diffuse on the semiconductor surface where oxidation of organic species can occur.

Structure



Scheme 1. Reactive Yellow 86

EXPERIMENTAL SECTION

Materials

For the present studies the commercially available azo dye Reactive Yellow 86 obtained from Charbhuja processors Ltd., Bhilwara and the photocatalyst titanium dioxide (Merck, 99% purity) were used. For photocatalytic degradation 0.001M (0.862g/L) stock solution of dye Reactive Yellow 86 was prepared in double distilled water. Aqueous solutions of desired concentrations were prepared from the stock solution. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

Procedure and Analysis

To carry out the photochemical reaction 100 ml of dye solution of desired concentration (2x 10^{-5}M) was taken in 250 ml round bottom flask and appropriate amount of solid TiO_2 catalyst (0.25 g) was added to it. The mixture was then irradiated under light using 2 x 200 W Tungsten lamps (Sylvania Laxman) to provide energy to excite TiO_2 loading. To ensure thorough mixing of TiO_2 catalyst, oxygen was continuously bubbled with the help of aerator. A water filter was used to cut off thermal radiation. The pH was measured with pH meter (Systronics, 106).

About 3 ml aliquot of the dye solution was withdrawn after a specific time interval and its absorbance was measured using spectrophotometer (Schimadzu, UV- 1700 pharmaspec) at 419 nm after filtration through a G-3 sintered glass crucible. The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of inorganic ions such as sulphate and nitrate were tested by standard procedure. The evolution of CO_2 was tested by passing the evolved gas during the reaction into lime water. The result of photocatalytic bleaching of Reactive Yellow 86 is graphically presented [Fig-1,Table-1]

Table 1: A TYPICAL RUN

Reactive Yellow 86 = 2x10^{-5} M **TiO_2** = 0.25 g
λ max = 419 nm **pH**= 7.5.

Time	**O.D**	**1+log O.D**
0	0.405	0.607
30	0.366	0.563
60	0.331	0.519
90	0.305	0.484
120	0.278	0.444
150	0.255	0.406
180	0.230	0.361
210	0.208	0.318
240	0.188	0.274

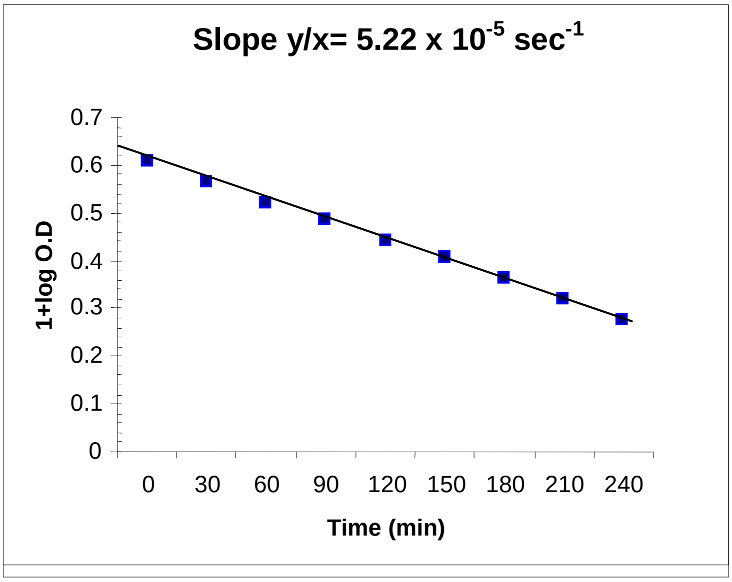


Fig.1- A plot showing a typical run of photochemical degradation of Reactive Yellow 86 observed at 419 nm under optimum conditions

RESULTS AND DISCUSSION

Control experiments (in absence of photocatalyst, oxygen and light) confirm the necessity of photocatalyst, oxygen and light to follow the photocatalytic path for the photobleaching of dye. The photocatalytic degradation of Reactive Yellow 86 was studied at 419 nm. The optimum conditions for the removal of dye is [Dye] = 2.0 × 10^{-5}M, pH = 7.5, TiO_2 = 0.25g. The rate of reaction (k) was determined using the expression:

Rate (k) = 2.303 × Slope
= 5.22×10^{-5} sec^{-1}

The plot of *1+log Abs* was found to be straight line suggesting that bleaching of dye by TiO_2 follows a pseudo first order rate law.

The effect of variation in reaction parameters has been studied like pH, concentration of the dye, amount of catalyst, nature of photocatalyst and presence of transition metal ions.

Effect of variation in pH

The pH of the reaction medium has a significant effect on the surface properties of TiO_2 catalyst. The effect of pH on photocatalytic bleaching of Reactive Yellow 86 with TiO_2 was investigated in the pH range of 6.0 to 9.0 under visible light source, reported in Fig -2. It was found that the rate of photocatalytic bleaching increases with an increase in pH up to 7.5. Thereafter there is an adverse effect on the rate of reaction on increasing pH further. This observation can be explained on the basis that as the pH of solution increases, more OH^- ions are available. These OH^- ions will generate more $^{\bullet}OH$ radicals by combining with the hole of the semiconductor. The hydroxyl radical is an extremely strong, non selective oxidant [E^0= +3.06], which leads to the partial or complete mineralization of several organic chemicals.

After a certain pH value, more OH^- ions will make the surface of semiconductor negatively charged and is retarded the approach of dye molecules toward the semiconductor surface due to repulsive force between semiconductor surface and anionic (Reactive Yellow 86, having sulphonic groups in its structure) dye molecule. This will result into a decrease in rate of photocatalytic bleaching of dyes.

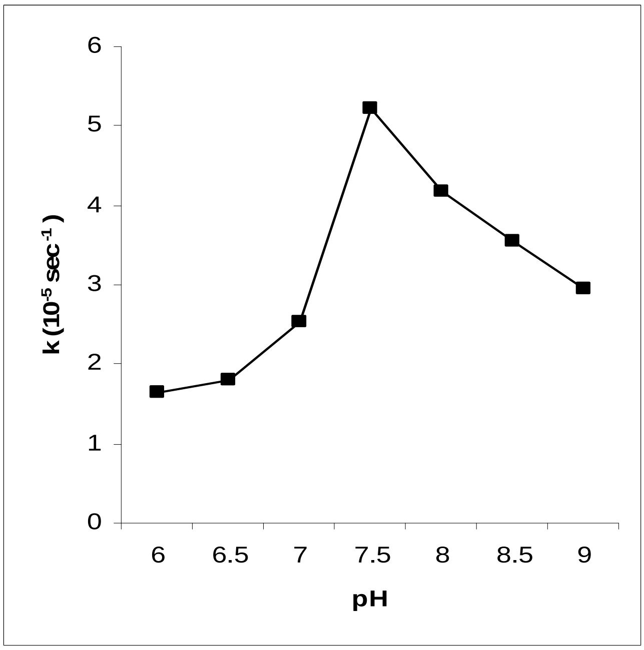


Fig.2: Effect of pH on the photocatalytic bleaching of Reactive Yellow 86 by TiO_2, Reactive Yellow 86 = 2×10^{-5} M, TiO_2 = 0.25 g

Effect of amount of catalyst [TiO_2]

The effect of amount of photocatalyst on the degradation kinetics of Reactive Yellow 86 was investigated employing different concentrations of the TiO_2 varying from 0.10 to 0.40g/ 100ml. It was observed that the rate of dye decolourization increases with increasing catalyst level up to 0.25g and beyond this, the rate of reaction becomes almost constant (Fig.3).

This may be due to the fact that, initially the increase in the amount of catalyst increases the number of active sites on the TiO_2 surface that in turn increases the number of $^{\bullet}OH$ and $O_2^{\bullet -}$ radicals. After a certain level of catalyst availability with the same concentration of dye, further dye molecules are not available for adsorption. The additional catalyst particles therefore are not involved in the catalytic activity. Hence the degradation remains constant.

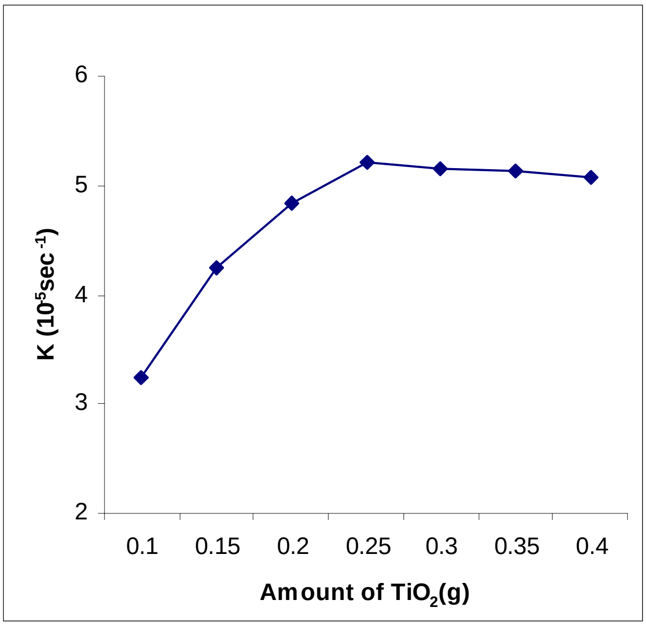


Fig.3: Effect of catalyst concentration [TiO_2] on the photocatalytic bleaching of Reactive Yellow 86, Reactive Yellow 86 = 2x 10^{-5}, pH= 7.5

Effect of concentration of Dye [Reactive Yellow 86]

The effect of substrate concentration on the degradation of Reactive Yellow 86 was studied at different concentrations varying from 1.0×10^{-5} M to 4.0×10^{-5} M at fixed concentration of TiO_2=0.25 g, pH=7.5.The highest efficiency was observed at lower concentration, which decreases with the increase in substrate concentration from 1.0×10^{-5} M to 4.0×10^{-5} M (*Fig-5*). This may be due to the fact that with the increase in initial concentration of the dye, while the irradiation period and catalyst dose are kept constant, more dye molecules are adsorbed onto the surface of TiO_2. Thus, an increase in the number of substrate ions accommodating in interlayer spacing inhibits the action of the catalyst, which thereby decreases the number of reactive $^{\bullet}OH$ and $O_2^{\bullet -}$ free radicals attacking the dye molecules and photodegradation efficiency.

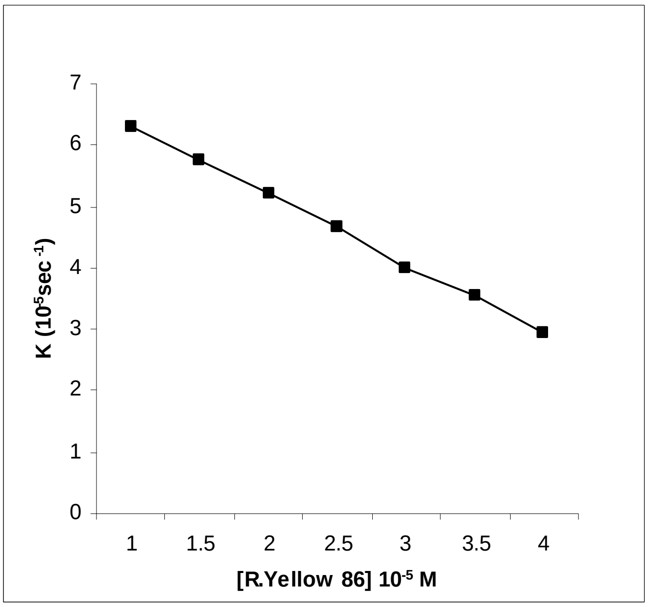


Fig.4: Effect of Reactive Yellow 86 concentrations on photocatalytic bleaching of Reactive Yellow 86 by TiO_2, TiO_2 = 0.25 g, pH= 7.5

Effect of nature of semiconductor photocatalyst

Keeping all the factors identical the effect of the nature of the photocatalyst on photocatalytic bleaching of Reactive Yellow 86 was studied by using different photocatalyst such as TiO_2, ZnO, SnO_2, and Fe_2O_3. It was observed that under visible light irradiation, the rate of photobleaching of Reactive Yellow 86 decreases with the increase in the band gap of semiconductor (Fig.6). The rate of photobleaching of Reactive Yellow 86 is found to be decreasing in the following order;

$Fe_2O_3 > TiO_2 > ZnO > SnO_2$

Fe_2O_3 having 2.2 eV band gap energy, is more efficient photocatalyst in visible region as compare to ZnO and SnO_2 having large band gap energy.

It can be explained on the basis that the semiconductor oxides having λmax > 400 nm absorb more efficiently in visible region.

Table-2

Reactive Yellow 86 = 2x 10^{-5} M **semiconductor**= 0.25 g

pH= 7.5

Semiconductor	Band Gap Energy (eV)	K (10^{-5} sec^{-1})
TiO_2	3.2	5.22
ZnO	3.4	3.79
SnO_2	3.6	1.15
Fe_2O_3	2.2	7.86

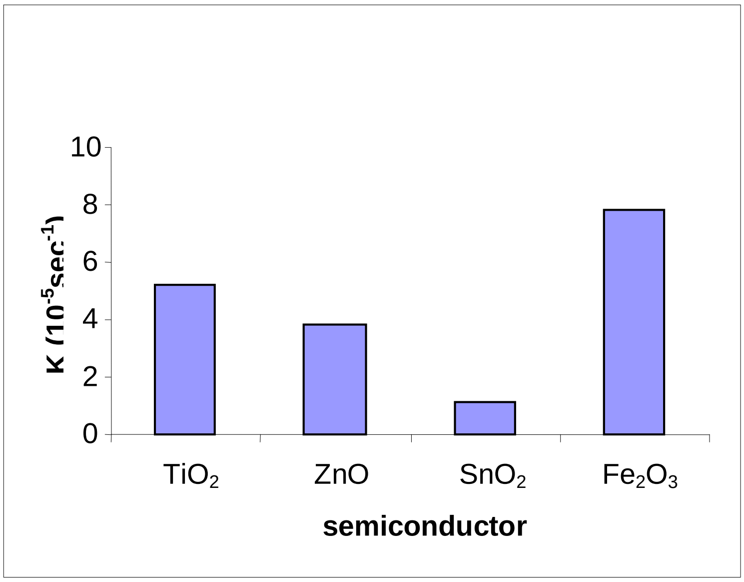


Fig.5: Effect of nature of semiconductor photocatalyst on photocatalytic bleaching of Reactive Yellow 86 for 180 min.

Effect of transition metal ions on photocatalytic bleaching of R.Yellow 86 by TiO_2
The effect of addition of transition metal ions (M^{n+}= Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ag^{+}) photodegradation efficiency of TiO_2 has been investigated, and results are reported in fig. (6).The result shows that the trace quantities of all the added metal ions enhance the rate of photocatalytic bleaching of Reactive Yellow 86 to some extent.

The increase in the photocatalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions. On irradiation, electron migrates on metal where it becomes trapped and electron – hole recombination is suppressed. The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur. ***(**Scheme 2)*

As the surface of catalyst particles is negatively charged and hence, it permits more metal ions to get adsorbed on the TiO_2 particles surface and as consequence, the surface of semiconductor will become positively charged. As reactive Yellow 86 dye is anionic dye, so it will face more electrostatic attraction with cations (M^{n+}) adsorbed on the semiconductor surface.

The electron from TiO_2 conduction band is transferred to metal ion to convert it into its lower oxidation state, in turn transfer this electron to oxygen molecule. Thus prevent electron-hole recombination. At the same time , the positively charged vacancies(h^+) remaining in the valence band of TiO_2 can extract electron from hydroxyl ions in the solution to produce the hydroxyl radicals(($^{\bullet}OH$). These hydroxyl radicals oxidize the dye molecule into colorless products.

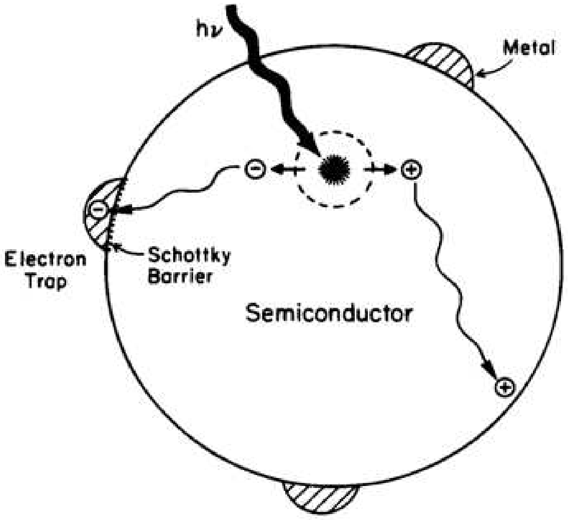
$$H^+ + H_2O_{(ads)} \longrightarrow {}^{\bullet}OH + H^+$$

$$H^+ + 2OH^- \longrightarrow {}^{\bullet}OH + OH^-$$

The concentration of transition metal ions is very small and large concentrations are detrimental.

Metal modification

$^{1}\mathrm{Dye} + h\nu \longrightarrow 1\mathrm{Dye}_1$ (singlet excited state)
$^{1}\mathrm{Dye}_1 \longrightarrow {}^{3}\mathrm{Dye}_1$ (triplet excited state)
$\mathrm{TiO_2} \longrightarrow \mathrm{TiO_2}^{*}\,(h^{+}_{vb} + e^{-}_{cb})$
$\mathrm{M}^{n+} + e^{-} \longrightarrow \mathrm{M}^{(n-1)+}$
$\mathrm{M}^{(n-1)+} + \mathrm{O_2} \longrightarrow \mathrm{M}^{n+} + \mathbf{O_2}^{\cdot -}$
$\mathrm{TiO_2}^{*}\,(h^{+}_{vb}) + \mathrm{OH}^{-} \longrightarrow \mathrm{TiO_2} + {}^{\bullet}\mathrm{OH}$
$^{3}\mathrm{Dye}_1 + {}^{\bullet}\mathrm{OH} \longrightarrow$ Degradation of the dye



Scheme 2. Metal-modified semiconductor photocatalyst particle

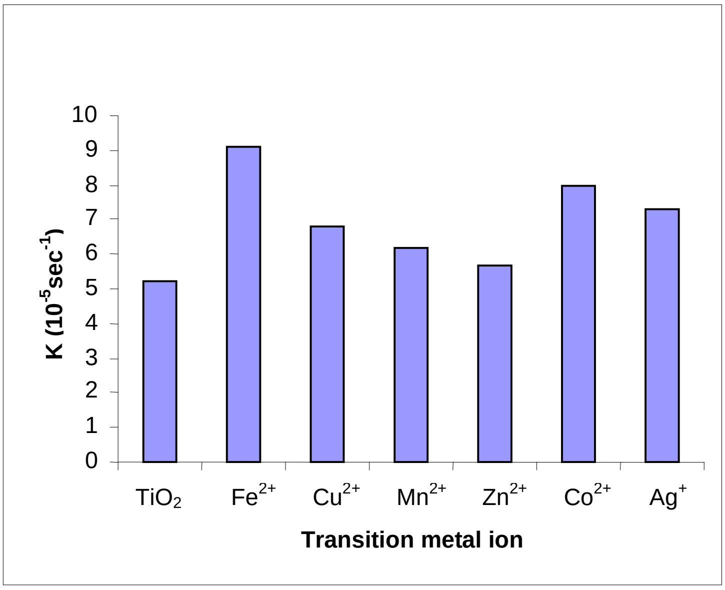


Fig. 6: Effect of transition metal ions (M^{n+}) on photocatalytic bleaching of R.Yellow 86 by TiO_2, Reactive Yellow 86 = 2x 10^{-5} M, TiO_2 = 0.25 g, M^{n+} = $1x10^{-5}$M, pH= 7.5

Mechanism:

Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of photons with energy equal to, or greater than the band gap energy of the semiconductor (3.2 ev for anatase), producing electron–hole (e-/h+) pairs.

$$\mathbf{TiO_2 + \mathit{hv} \longrightarrow TiO_2^* + h^+ (vb) + e^-(cb)} \tag{1}$$

Where *cb* is conduction band and *vb* is valence band.

The photo produced holes and electrons may migrate to the particle surface, where the holes can react with surface-bound hydroxyl groups (OH^-) and water molecules to form hydroxyl radicals ($^{\bullet}OH$).

$$\mathbf{h^+ + OH^- \longrightarrow {}^{\bullet}OH} \tag{2}$$
$$\mathbf{h^+ + H_2O \longrightarrow {}^{\bullet}OH + H^+} \tag{3}$$

The electrons in conduction band react with the adsorbed oxygen molecules to form super oxide ions ($O_2^{\bullet -}$).

$$\mathbf{e^- + O_2\ (ads.) \longrightarrow O_2^{\bullet -}\ (ads.)} \tag{4}$$

Super oxide ions ($O_2^{\bullet -}$) is reduced by H^+, accounting for hydroperoxyl radical ($HO_2^{\bullet}$) and hydroxyl radical production.

$$\mathbf{O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}} \tag{5}$$
$$\mathbf{2\,O_2^{\bullet -} + 2\,H^+ \longrightarrow 2\,{}^{\bullet}OH + O_2^{\bullet}} \tag{6}$$

$HO_2^{\bullet}$, $^{\bullet}OH$ and $O_2^{\bullet}$ are strong oxidizing species and they react with dye molecules to oxidize them.

In the second pathway where a dye absorbs radiation of suitable wavelength and excited to its first singlet state followed by intersystem crossing to triplet state.

$$\mathbf{{}^1Dye_0 \xrightarrow{\mathit{hv}} {}^1Dye_1\ (singlet\ excited\ state)} \tag{7}$$
$$\mathbf{{}^1\,Dye_1 \longrightarrow {}^3Dye_1\ (triplet\ excited\ state)} \tag{8}$$

The excited dye may be oxidize to product by highly reactive hydroxyl radical ($^{\bullet}OH$).

$$\mathbf{{}^3Dye_1 + {}^{\bullet}OH / HO_2^{\bullet} / O_2^{\bullet -} \longrightarrow Colourless\ End\ Products\ (Degradation)} \tag{9}$$

The participation of $^{\bullet}OH$ radical as an active oxidizing species was confirmed using its scavenger, i.e. 2-propanol, where the rate of bleaching was drastically reduced. After continuous irradiation the formation of CO_2, sulphate ions and nitrate ions in bleached dye solution show that there is total destruction of organic compounds in this process. The end products are simple molecules and harmless to the environment.

The whole process can be summarized as:

$$\underset{\text{(R. Yellow 86)}}{C_{19}H_{14}Cl_2N_8Na_2O_9S_2} \xrightarrow{{}^{\bullet}OH\ /\ HO_2^{\bullet}\ /O_2^{\bullet-}} \text{Intermediates}$$

$$\longrightarrow CO_2 + NO_3^{-} + SO_4^{2-} + H^{+} + Na^{+} + H_2O + Cl^{-}$$

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REFERENCES

[1] M Dakiky; I Nemcova; *Dyes Pigments*, **2000**, 44,181.
[2] N Daneshvar; D Salari; AR Khataee. *J. Photochem. Photobiol. A*, **2003**,
[3] 157,111.
[4] MA Brown; SC De; C Vito. *Rev. Environ. Sci.Technol*., **1993**, 23, 249.
[5] S Sandhya; S Padmavathy; K Swaminathan; YV Subrahmanyam; S N Kaul. *Process Biochemistry*, **2005**, 40, 885-890.
[6] K Golka; S Kopps; ZW Myslak. *Toxicology Letters*, **2004**,151, 203-210.
[7] A Gnanamani; M Bhaskar; R Ganga; G Sekaran; S Sadulla. *Chemosphere*, **2004**, 56, 833-841.
[8] I Safarik; K Nymburska; M Safaikova. *J. Chem. Tech. Biotechnology,* **1997**, 69,1.
[9] AT More; A Vira; S Fogel. *Environ. Sci. Technol* , **1989**, 23, 403.
[10] YM Slokar; AM Le Marechal. Dyes Pigments, **1998,** 37, 1160.
[11] WG Kuo. *Wat. Res*.,**1992**, 26, 881.
[12] C Morisson; J Bandara; J Kiwi; A Lopez. *J. Adv. Oxid. Technol*,**1996,** 1, 160.
[13] I Arslan; T Akmehmet; T Tuhkamen. *Environ. Technol*, **1999**, 20, 921.
[14] H Lachheb; E Puzenat; A Houas; M Ksibi; E Elaloui; C Guillard; JM Herrmann. *Appl. Catal. B: Environ*., **2002**, 39, 75.
[15] I K Konstantinou; TA Albanis; *Appl. Catal. B: Environ*., **2004,** 49, 1.
[16] 15. F Zhang; J Zhao; T Shen; H Hidaka; E Pellizzetti; N Serpone. *Appl.Catal. B: Environ.*, **1998,**15, 147.
[17] M Muruganandham; M Swaminathan. *Dyes Pigments*, **2007**, 72 , 137.
[18] MS Lucas; JA Peres. *Dyes Pigments*, **2006,** 71, 235.
[19] IBS Will; JEF Moraes. *Sep. Purif. Technol.*, **2004**, 34, 51.
[20] H Zheng; X Xiang. *Spectrosc. Spectr. Anal. 24*, **2004**, 726.
[21] L Zou; B Zhu. *J. Photochem. Photobiol. A: Chemistry*, **April 2008**,196 (1), 24.
[22] J Saien; S Khezrianjoo. *J. Hazardous Materials*, **2008,** 157 (2-3), 269.
[23] L Lhomme; S Brosillon; D Wolbert. *Chemosphere*, **2008**, 70(3), 381.
[24] W Baran; A Makowaski; W Wardas. *Dyes and Pigments***, 2008**, 76, 226.
[25] M Zhou; J Yu; B Cheng. *J. Haz. Mat.*, **2006**,137(3)1838-1847.

[26] 25. J Yang; D Li; Z Zhang; Q Li; H Wang. *J. Photochem. Photobiol. A: Chem.*, **2000.** 137, 197–202.
[27] 26. MW Xu; SJ Bao; XG Zhang. *Materials Letters* ,**2005**, 59(17), 2194-2198.
[28] 27. C Sahoo; AK Gupta; A Pal. *Dyes and Pigments*, **2005**, 66(3) 189-196.
[29] 28. E Bardos; S H Czili; A Horvath. *J. Photochem. Photobiol. A: Chem.,* **2003,**154, 195-201