INFLUENCE OF OPERATIONAL PARAMETERS ON DEGRADATION OF COMMERCIAL TEXTILE AZO DYE ACID BLUE 113 (CYANINE 5R) BY ADVANCED OXIDATION TECHNOLOGY

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ABSTRACT

In this research work, the effect of various parameters on the photocatalytic degradation of commercially available azo dye Acid blue 113 (AB 113) in aqueous heterogeneous suspension has been studied. Parameters such as pH, amount of photocatalyst, dye concentration and nature of photocatalyst as main operational parameters selected and their influence on degradation efficiency have been investigated. The progress of reaction was observed spectrophotometrically. The Kinetic analysis of photocatalytic degradation reveals that the degradation follows pseudo first order kinetics according to the Langmuir- Hinshelwood model. The effect of addition of transition metal ions (Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}) on photocatalytic degradation efficiency of TiO_2 have been investigated. It was observed that trace quantities of all the added metal ions increase 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 also been proposed.

Key words: Photocatalytic degradation, Heterogenous, Acid blue 113, TiO_2, Transition metal ions.

INTRODUCTION

Water pollution is a prominent environmental problem witnessed across the globe. A large number of organic substances like dyes, phenols, pesticides, fertilizers, detergents and other chemical products are disposed of directly into the water system from various sources such as industrial effluent, agricultural run off and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to society and regulation authorities around the world.

The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants[1-2]. Azo dyes, being the largest group of synthetic dyes, constitute upto 70% of all commercial dyes produced[3]. Highly substituted aromatic rings joined by one or more azo groups (-N=N-), characterize their chemical structures[4]. These dyes are extensively used in textile, paper, printing and dye- houses. Being released into the environment, the colored effluents damage the aesthetic quality of water and reduce the light penetration, photosynthesis, reoxygenation capacity of water and therefore disturbing the natural activity of aquatic life[5]. The improper handling of hazardous chemicals in textile water

also have some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcer etc. and even leads to respiratory problems. Some of the azo dyes are toxic or mutagenic, carcinogenic and allergenic due to photosensitization and photodynamic damage. Hence decolorization of the dye-bearing effluent is of great importance. Color removal, in particular, has recently become an area of major scientific interest as indicated by the multitude of related research reports. During the past two decades, several decolourization techniques have been reported to improve the recovery of water purification system. One of the best methods that are recently used is Advanced Oxidation Technology for the treatment of organic pollution[6-9]. This method appears to be effective in that it can convert organic pollutants into biodegradable molecules or mineralized into CO_2 and other inorganic. Among these processes, heterogeneous photocatalysis is an emerging technology leading to mineralization of most of organic pollutants. Photocatalytic process, which utilizes TiO_2 semiconductor photocatalyst, has received increasing attention because of its low coast, non-toxicity, relatively high chemical stability and the possibility of using sunlight as a source of irradiation[10]. The appropriate illumination of these particles produces excited state high energetic electron and hole pairs ($e-/h^+$). These pairs are able to initiate wide range of chemical reaction.

In this study, the influence of various parameters like dye concentration, amount of catalyst, pH and nature of photocatalyst for photocatalytic degradation of an azo dye (Acid Blue 113) have been investigated. Degradation efficiency of dye AB113 by TiO_2 in presence of dissolved transition metal ions has also been reported.
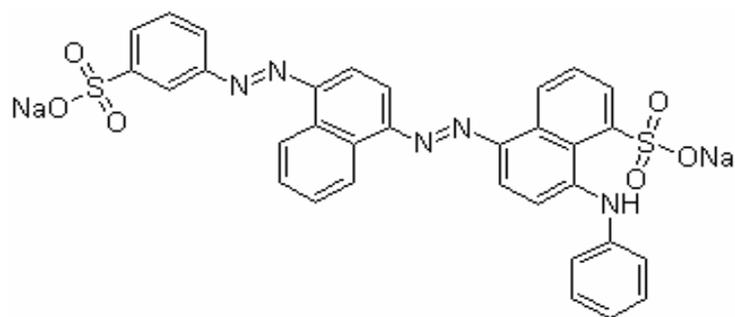
Molecular formula = $C_{32}H_{21}N_5Na_2O_6S_2$ Molecular weight = 681.65

Structure: Acid blue 113

Synonyms: Sodium 8-phenylamino-5-(4-(3-sulphonatophenylazo)-1-naphthyl azo) naphthalene sulphonate, Cyanine 5R

Acid blue 113 is diazo group containing acid dye. It is dark blue black powder, which is soluble in water. It is used for dyeing wool, nylon, silk and polyester fiber. It is toxic and carcinogenic in nature[11].

EXPERIMENTAL

Materials

For the present studies the commercially available azo dye Acid blue 113 and the photocatalyst titanium dioxide (Merck, 99% purity) were used. For the preparation of stock solution, 0.0716 g of dye Acid blue (95%) was dissolved in 100 mL of double distilled water so that the concentration of dye solution was 1.0×10^{-3} M. 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 (2×10^{-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 2×200 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 561 nm after filtration through a centrifugal machine. 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 degradation of Acid blue 113 is graphically presented Fig. 1.
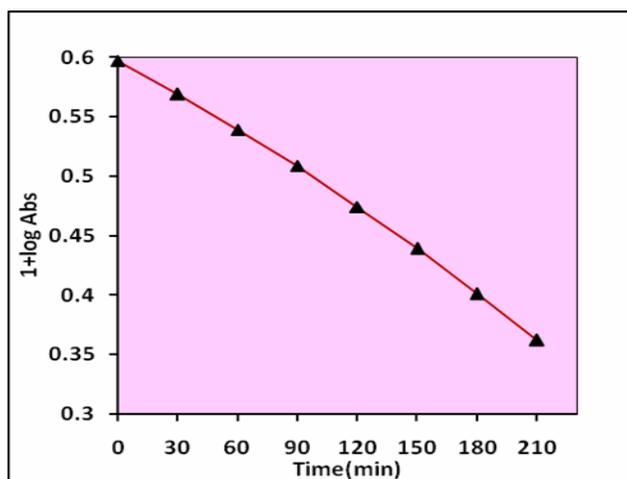
Fig. 1: Typical run of photochemical degradation of Acid Blue 113

[Acid Blue 113] = 3.0×10^{-5} M, TiO_2 = 0.30 g, pH = 8.5, λ_{max} = 561 nm

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 photocatalytic degradation of dye.

The photocatalytic degradation of Acid blue 113 was studied at 561 nm. The optimum conditions for the removal of dye is [Dye] = 3.0×10^{-5} M, pH = 8.5, TiO_2 = 0.30 g. The rate of reaction (k) was determined using the expression:

Rate constant k = 2.303 x Δ [log Abs/ time] = 4.29×10^{-5} sec^{-1}

The plot of 1+log O.D. was found to be straight line suggesting that degradation 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 degradation of Acid blue 113 with TiO_2 was investigated in the pH range of 6.0 to 10.0 under visible light source, shown in Fig. 2.

It was observed that the rate of photocatalytic degradation of Acid blue 113 increases with an increase in pH up to 8.5. 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 positive holes of the semiconductor. These hydroxyl radicals are responsible for degradation of dye[12]. After a certain pH value i.e. above pH 8.5 the rate of photobleaching of Acid blue 113 decreases due to coulombic repulsion between the negatively charged surface of photocatalyst and hydroxide anions. This fact could prevent the formation of hydroxyl radicals. This results into a decrease in rate of photocatalytic degradation of dye[13,14].
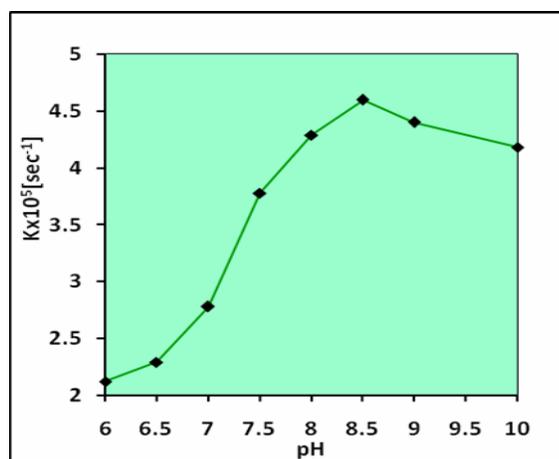
Fig. 2: Effect of variation in pH on the photocatalytic degradation of Acid blue 113 by TiO_2

[Acid Blue 113] = 3 x 10^{-5} M, TiO_2 = 0.30g, λ_{max} = 561 nm, Irradiation time = 180 min

Effect of amount of photocatalyst

The amount of semiconductor powder may also affect the process of dye degradation. Keeping all the factors identical, different amounts of photocatalyst varing fron 0.10-0.40 g/100 mL were used. It was observed that the rate of dye decolourization increases with increasing catalyst level up to 0.30 g 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 TiO_2 active sites on the surface that in turn increases the number of $^{\bullet}OH$ and $O_2^{\bullet-}$ radicals. As a result the rate of degradation is increased. Above a certain level (saturation point) the number of substrate molecules is not sufficient to fill the active sites of TiO_2 and increase in turbidity of solution reduces the light transmission through the solution. Hence, further addition of catalyst does not lead to the enhancement of the degradation rate and it remains constant[15,16].

Effect of concentration of dye

The effect of substrate concentration on the degradation of Acid blue 113 was studied at different concentrations varying from 1.0×10^{-5} M to 7.0×10^{-5} M at fixed concentration of TiO_2 = 0.30 g, pH = 8.5. The highest efficiency was observed at lower concentration[17,18] which decreases with the increase in substrate concentration from 1.0×10^{-5} M to 7.0×10^{-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 $^•OH$ and $O_2^{•-}$ free radicals attacking the dye molecules and photodegradation efficiency.
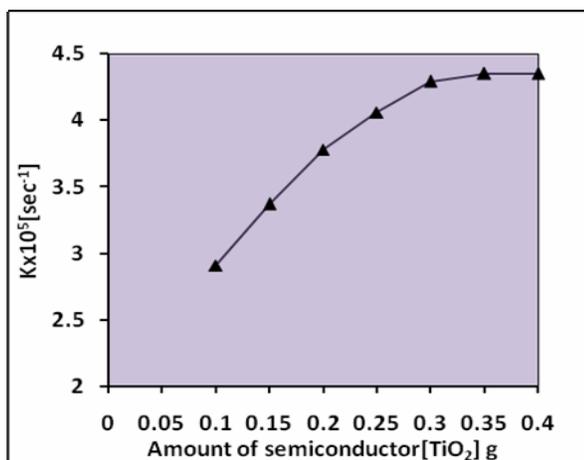
Fig. 3: Effect of amount of photocatalyst on the photocatalytic degradation of AB 113

[Acid Blue 113] = 3 x 10^{-5} M, pH= 8.5, λ_{max} = 561 nm, Irradiation time = 180 min]
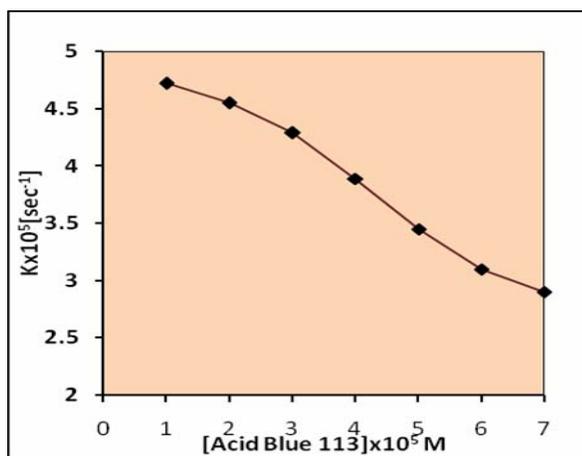
Fig. 4: Effect of dye concentrations on photocatalytic degradation of Acid blue 113

TiO_2 = 0.30g, pH = 8.5, λ_{max} = 561 nm, Irradiation time = 180 min

Effect of amount of semiconductor

        Keeping all the factors identical the effect of the nature of the photocatalyst on photocatalytic degradation of Acid blue 113 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 photocatalytic degradation of AB 113 decreases with the increase in the band gap of semiconductor Fig. 6. The rate of photocatalytic degradation of AB 113 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 $\lambda_{max} > 400$ nm absorb more efficiently in visible region[19].

Semiconductor	BandGap (eV)	Rate constant k x $10^5(sec^{-1})$
Fe_2O_3	2.2	5.58
TiO_2	3.2	4.29
ZnO	3.4	3.22
SnO_2	3.8	0.71
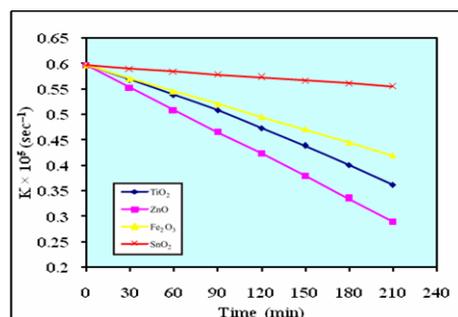
Fig. 5: Effect of nature of semiconductor on photocatalytic degradation of Acid blue 113

[Acid Blue 113] = 3.0 x 10^{-5} M, pH = 8.5, Amount of semiconductors = 0.30 g, Irradiation time = 180 min

Effect of various transition metal ions

Effect of addition various transition metal ions on photocatalytic degradation of Acid blue 113 by TiO_2 was studied by taking different transition metal ions like Cu^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+} and results are shown in Fig. 6. The results show that the trace quantities of all the added metal ions enhance the rate of photocatalytic degradation of Acid blue 113 to some extent.
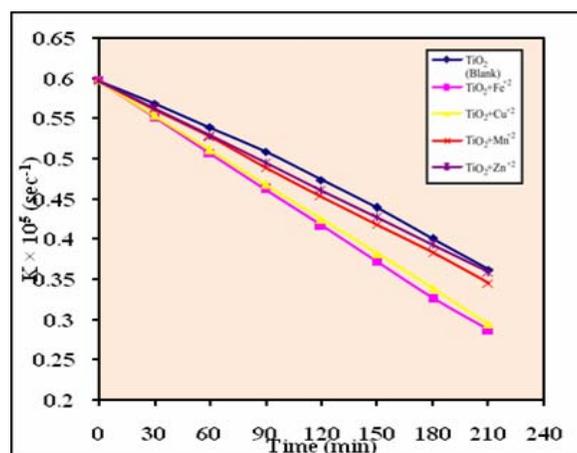
Fig. 6: Effect of transition metal ions on photocatalytic degradation of Acid blue 113

[Acid blue 113] = 3.0 x 10^{-5} M, pH = 8.5, TiO_2 = 0.30 g, M^{n+} = 1.0 x 10^{-5} M

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), producing electron–hole (e^-/h^+) pairs.

$$TiO_2 + h\nu \longrightarrow TiO_2{}^* + h^+ (VB) + e^-(CB) \qquad ...(1)$$
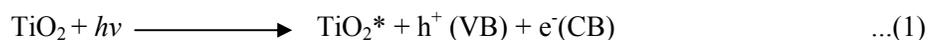
Where **CB** is conduction band and **VB** is valence band.

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

$$h^+ + OH^- \longrightarrow {}^\bullet OH \qquad\qquad ...(2)$$

$$h^+ + H_2O \longrightarrow {}^\bullet OH + H^+ \qquad\qquad ...(3)$$

The presence of oxygen prevents recombination by trapping electrons through the formation of superoxide ions, maintaining electrical neutrality within TiO_2 particles[20]. The final product of the reduction is hydroxyl radicals ($^\bullet OH$) and hydroperoxy radicals ($HO_2^\bullet$).

$$e^- + O_2 \text{ (ads.)} \longrightarrow O_2^{\bullet -} \text{ (ads.)} \qquad\qquad ...(5)$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^\bullet \qquad\qquad ...(6)$$

$$2\,O_2^{\bullet -} + 2\,H^+ \longrightarrow 2\,{}^\bullet OH + O_2^\bullet \qquad\qquad ...(7)$$
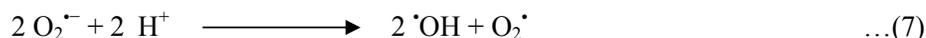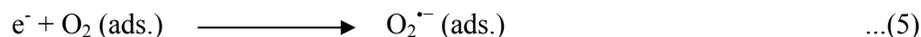
$HO_2^\bullet$, $^\bullet OH$ and $O_2^\bullet$ are strong oxidizing species and they react with dye molecules to oxidize them. In the second pathway where a dye molecule absorbs radiation of suitable wavelength and excited to its first singlet state followed by intersystem crossing to triplet state.

$$^1Dye_0 \xrightarrow{\quad hv \quad} {}^1Dye_1 \text{ (singlet excited state)} \qquad\qquad ...(8)$$

$$^1Dye_1 \longrightarrow {}^3Dye_1 \text{ (triplet excited state)} \qquad\qquad ...(9)$$
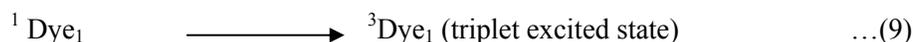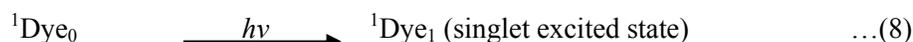
The excited dye may oxidize to product by highly reactive hydroxyl radical ($^\bullet OH$). The participation of $^\bullet OH$ radical as an active oxidizing species was confirmed using its scavenger, i.e. 2-propanol, where the rate of degradation was drastically reduced[21]. Initially the $^\bullet OH$ radicals attack on the azo linkage of the dye molecule and abstract a hydrogen atom or add itself to double bond. After continuous irradiation, the complete mineralization of dye occurred via. into end products. The end products are simple molecules or ions and less harmful to environment.

$$^3Dye_1 + {}^\bullet OH \,/\, HO_2^\bullet \,/\, O_2^{\bullet -} \longrightarrow \text{End Products} \qquad\qquad ...(10)$$

$$[CO_2 + H^+, NO_3^-, SO_4^{2-}]$$
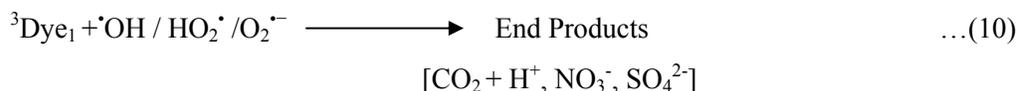
The end products were detected and their presence in the reaction mixture were ascertained either by chemical test or by ion selective electrode method.

Nitrate ions were detected and confirmed by using nitrate ion selective electrode which is having a solid-state PVC polymer membrane. Sulphate ions were detected and confirmed by gravimetric analysis in which excess of barium chloride solution was used and sulphate ions are precipitated as $BaSO_4$. CO_2 was confirmed by introducing the gas to freshly prepared lime water. The lime water turns milky which indicates its presence.
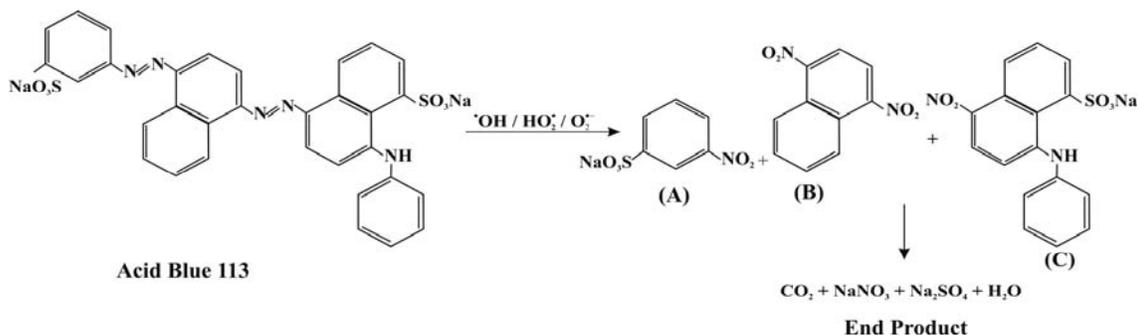
A = Sodium 3-nitrobenzene sulphonate; B = 1,4-dinitronapthylene; napthlene-1-sulphonate; C = Sodium 5-nitro-8-(phenylamino)

The effect of addition of transition metal ions (M^{n+} = Fe^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}) on photodegradation efficiency of TiO_2 has been investigated. The results show that the trace quantities of all the added metal ions enhance the rate of photocatalytic degradation of Acid blue 113. The increase in the photocatalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions[22,23]. As the surface of catalyst particles is negatively charged in alkaline medium and hence, it permits more metal ions to get adsorbed on the TiO_2 particles surface. As consequence, the surface of semiconductor will become positively charged. As Acid blue 113 is anionic dye, so it will face more electrostatic attraction with metal ions (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.

$$TiO_2 + h\nu \longrightarrow TiO_2^* (h^+VB + e^-CB) \qquad ...(12)$$

$$M^{n+} + TiO_2^* (e^-CB) \longrightarrow M^{(n-1)+} \text{ (electron trapping)} \qquad ...(13)$$

$$M^{(n-1)+} + O_2 \longrightarrow M^{n+} + O_2^{\bullet-} \qquad ...(14)$$

$$TiO_2^* (h^+VB) + OH^- \longrightarrow TiO_2 + {}^{\bullet}OH \qquad ...(15)$$

$$^3Dye_1 + {}^{\bullet}OH \longrightarrow \text{Degradation of the dye} \qquad ...(16)$$
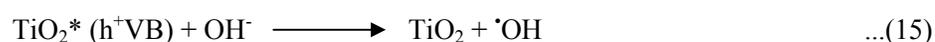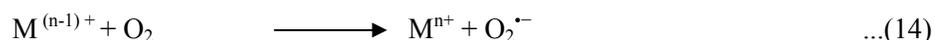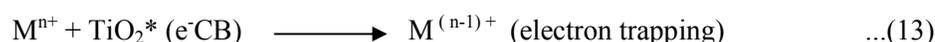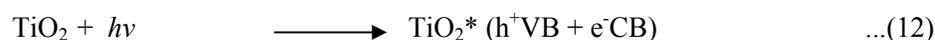
The concentration of transition metal ions is very small and large concentrations are adverse.

The whole TiO_2-semiconductor photocatalytic processes can be summarized as
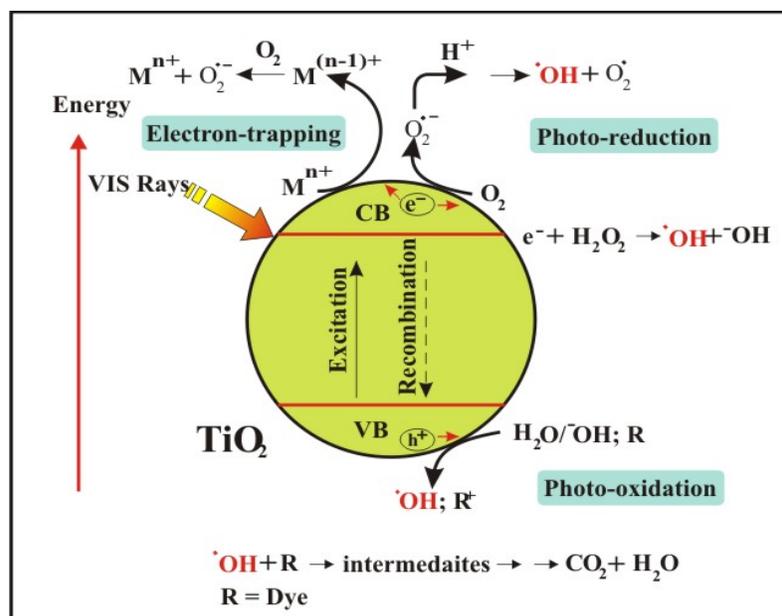
R= Acid Blue 113

ACKNOWLEDGEMENT

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