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MINERALIZATION OF METHYENE VIOLET DYE USING TITANIUM DIOXIDE IN PRESENCE OF VISIBLE LIGHT

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ABSTRACT

Advanced oxidation processes are eco-friendly methods of destroying organic pollutants by using semiconductor and visible light. Photocatalytic degradation of methylene violet has been investigated in aqueous heterogeneous suspension. The results indicated that potocatalytic reaction was enhanced in alkaline medium. The degradation of dye depends on several parameters such as initial concentration of the dye, catalyst loading, pH, electron acceptors and light intensity. COD removal was measured at regular intervals to quantify the mineralization of methylene violet. Sunlight has also been effectively used to degrade methylene violet.

Key words: Semiconductor, Methylene violet, COD, Mineralization, Visible light, Wastewater.

INTRODUCTION

The textile industry consumes large amounts of water during the dyeing process. Dyes are extensively used and wastewater discharged in rivers is highly contaminated[1]. Dyes and organic pollutants produced toxic byproducts through oxidation, hydrolysis and other chemical reaction taking place in the wastewater[2]. Dyes used in textile industry are highly toxic, stable, soluble in water & non-biodegradable and have adverse impacts on the living organisms and humanbeings[3]. They are not removed by traditional methods such as biological, physical and chemical methods. Advanced oxidation processes (AOPs) have been found to be promising alternative for the detoxification of industrial effluents especially from the environmental point of view. Heterogeneous photocatalysis consists on the non-selective destruction of organic compound in presence of semiconductor materials as catalyst and visible light. This process allows the complete mineralization of organic pollutants to CO_2, H_2O and mineral acids. The photo reactor generally works at room

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temperature and pressure and does not require expensive oxidants[4-6].

TiO_2 has been in use since it is effective, insoluble, photostable, photoactive, inexpensive and nontoxic semiconductor photocatalyst for the degradation of a wide range of organic pollutants and synthetic dyes[7]. Most of the work done so far with TiO_2 is in presence of UV light, but artificial UV light is expensive and harmful. Moreover UV component in sunlight reaching the earth surface and available to excite TiO_2 is relatively small because it represents only 3-5% of the solar spectrum[1]. Therefore, our efforts have been focused on exploring means to utilize the artificial inexpensive visible light sources for degradation of organic pollutants in waste water. In some of the literature available, it is suggested that TiO_2 and visible light does not make an efficient system but at the same time dyes have the ability to absorb visible light and then transfer electron to semiconductor so as to result in photocatalytic degradation reaction. Further, the dye molecules are adsorbed onto the surface and thus, their translational mobility gets considerably reduced. It extends the range of excitation energies of the semiconductor into visible region[8].

Therefore, the present work deals with photocatalytic degradation of methylene violet dye using TiO_2 and visible light.

EXPERIMENTAL

Reagents

Titanium dioxide (Loba Chemie) and methylene violet 3 RX (Aldrich) (MV) were used. Titanium dioxide is mainly anatase (80%). All other chemicals used were of analytical grade. Double distilled water was used throughout the study to prepare the solution .The catalyst and dye were used without further purification.

Photoreactor and light source

A 500-W halogen lamp was used as the light source. The photocatalytic reaction was carried out in a batch reactor with dimension of 7.5 x 6.0 cm (height x diameter) provided with an external water flow jacket connected to a thermostatic bath and able to maintain the temperature in the range of 25-30^{o}C

Procedure

For irradiation experiment, 100 mL aqueous solution of the dye of desired concentration was taken in the photoreactor and the solution was stirred and bubbled with air for at least 10 min in the dark to establish the adsorption equilibrium. Aliquots were taken at 10 min time intervals and centrifuged to separate the catalyst from the solution. The solution was then analyzed spectrometrically. A visible spectrophotometer (Systronic model No. 116) was used for measuring the absorbance of the reaction mixture. The intensity of light was measured by Digital lux meter (Lutron LX-101). The pH of the solution was measured using a digital pH meter. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution. To quantify the extent of mineralization of mixture, COD was measured at regular time intervals using closed reflux titrimetric method.

RESULTS AND DISCUSSION

Effect of TiO_2 loading

The effect of different dosages of TiO_2 on the photocatalytic degradation of methylene violet was examined[9]. To avoid the use of excess amount of catalyst, it was necessary to find out the optimum catalyst loading for efficient removal of the dye[10]. The rate of degradation increased rapidly with increasing catalyst concentration form 50 mg/100 mL to 150 mg/100 mL (Fig. 1). Increase in the degradation rate was due to an increase in the number of active sites of TiO_2, available for the reaction which in turn increased the rate of hydroxyl radical formation. Further increase of TiO_2 concentration result in a decrease of rate constant. The decrease in the rate constant may be due to the reduction in the penetration of light with surplus amount of TiO_2, the surplus addition of the catalyst made the solution more turbid and light penetration got retarded[6]. 150 mg of TiO_2 in 100 mL was found to be the optimum for treatment, which showed maximum photodegradation efficiency.

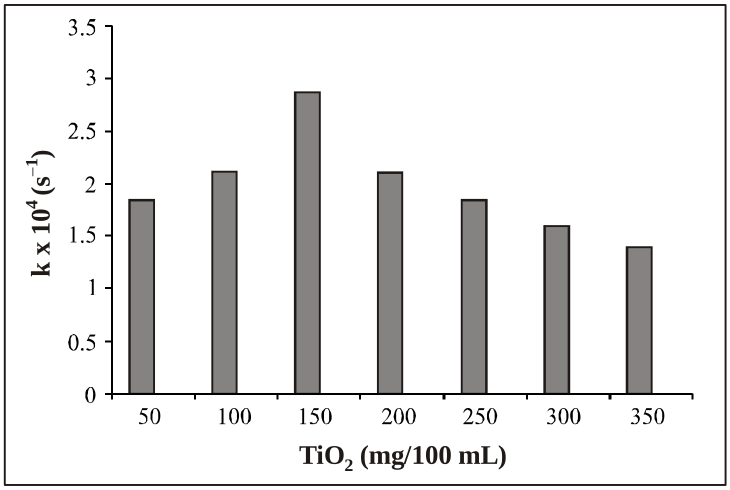

Fig. 1: Effect of TiO_2 loading: [MV] = 4.0×10^{-5} mol dm^{-3}; Irradiation intensity = 14×10^3 lux; pH = 9.5

Effect of initial dye concentration

The initial dye concentration is very important parameter in wastewater treatment. It is important from application point of view to study the dependence of photocatalytic degradation efficiency on the initial concentration[9]. The photocatalytic degradation of the methylene violet dye was studied by varying the initial concentration from 1.0 x 10^{-5} mol dm^{-3} to 7.0 x 10^{-5} mol dm^{-3} at pH 9.5 and with catalyst loading 150 mg/100 mL. Rate constant increases with increase in dye concentration from 1.0 x 10^{-5} mol dm^{-3} to 4.0 x 10^{-5} mol dm^{-3} (Fig. 2). Rate constant is maximum at 4.0 x 10^{-5} mol dm^{-3} of dye concentration. Thereafter, rate constant decreases with increase in concentration of dye above optimal value because at high dye concentration more dye molecules are adsorbed onto the surface of TiO_2 and the generation of $^{\bullet}OH$ radicals on the surface of catalyst is reduced since the active sites are covered by dye molecules. But the adsorbed dye molecules are not degraded immediately because the intensity of the light and the catalyst amount is constant. As the initial concentration of dye increases, the color of dye solution becomes deeper and deeper resulting in the reduction of the penetration of light to the surface of the catalyst[11].

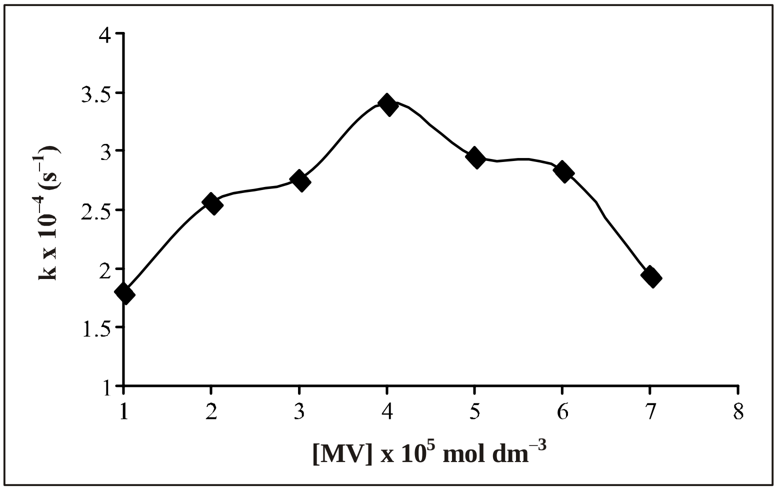

Fig. 2: Effect of initial dye concentration: TiO_2 = 150 mg/100 mL; Irradiation intensity = 14 x 10^3 lux; pH = 9.5

Effect of pH

pH is an important parameter in photocatalytic reactions. The surface charge of TiO_2 is also affected by the pH of the solution. This is because TiO_2 is amphoteric in nature. When TiO_2 is in contact with water, its surface becomes hydroxylated. The point of zero charge (pzc) of TiO_2 is 6.8. Upon changing the pH, the surface hydroxyl group could undergo protonation and deprotonation according to the following reactions: [12]

$$TiOH + H^+ \rightleftharpoons TiOH_2^+ \quad ...(1)$$

$$TiOH + OH^- \rightleftharpoons TiO^- + H_2O \quad ...(2)$$

TiO_2 surface will remain positively charged in acidic medium and negatively charged in alkaline medium. Methylene violet dye is a cationic dye. In the acidic pH there was a poor adsorption, because the TiO_2 surface and cationic dye both are positively charged in the acidic medium. Therefore, decrease in pH causes a decrease in degradation rate. High pH favors adsorption on the catalyst surface, which results in high decolorization efficiency because at higher pH, electrostatic interactions between the negative TiO_2 surface and cationic dye lead to strong absorption and enhancing degradation rate.

The photocatalytic reactions are conducted at different pH values ranging from 4.0 to 11.0 and dye concentration 4.0 x 10^{-5} mol dm^{-3} at catalyst loading of 150 mg/100 mL (Fig. 3). The results indicated that the photodegradation of methylene violet was most efficient in alkaline medium and that the optimal pH was observed at about 9.5. At optimized conditions, better photocatalytic degradation has been reported.

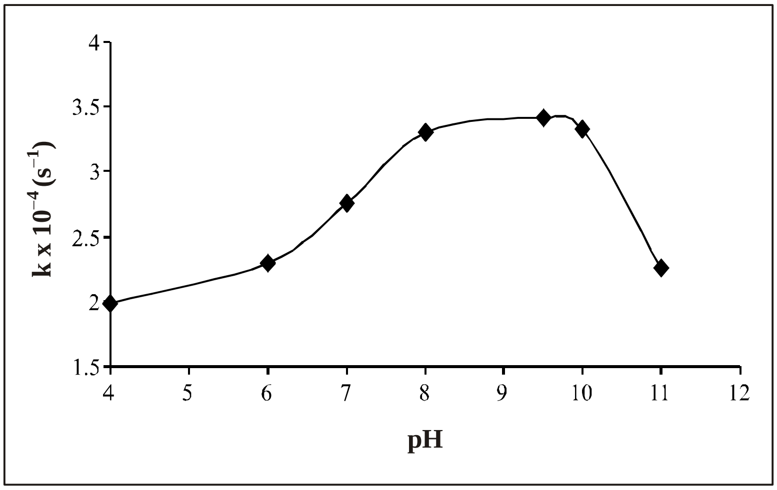

Fig. 3: Effect of pH: [MV] = 4.0 x 10^{-5} mol dm^{-3}; TiO_2 = 150 mg/100 mL; Irradiation intensity = 14 x 10^3 lux

In the present case, it can be presumed that the main reaction is presented by the hydroxyl radical attack, which can be favored by the high concentration of the hydroxyl radical at pH 9.5. After optimal pH value, when pH was further increased, the rate of degradation was found to decrease. This might be due to the fact that at high pH values, the hydroxyl radicals are rapidly scavenged and they do not have the opportunity to react with dyes.

Influence of hydrogen peroxide

Hydrogen peroxide is a well known electron acceptor and a green oxidant. It played a vital role in photcatalytic degradation. Hydrogen peroxide has different effects on dye degradation depending on its concentration. Addition of small amount of H_2O_2 increases the photodegradation efficiency significantly. Hydrogen peroxide is expected to promote degradation since it may react with conduction band electrons and the superoxide radical anion to yield hydroxyl radicals and anions as follows[13].

$$H_2O_2 + e^- \longrightarrow OH^- + {}^\bullet OH \qquad ...(3)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow OH^- + {}^\bullet OH + O_2 \qquad ...(4)$$

The effect of amount of hydrogen peroxide on the rate of degradation of methylene violet was investigated. The addition of H_2O_2 into a semiconductor suspension enhances the photodegradation. In order to examine the rate of hydrogen peroxide, experiments of the photocatalytic degradation of methylene violet employing different initial concentrations of the H_2O_2 was conducted. The degradation of the dye was increased with increasing H_2O_2 concentration. This is due to trapping of electrons by hydrogen peroxide; thereby, reducing the recombination of e^- and h^+ pairs and thus, increasing formation of $O_2^{\bullet -}$ and ${}^\bullet OH$ on TiO_2 surface[14]. The degradation of dye increased rapidly up to H_2O_2 concentration of 9.0×10^{-6} mol dm^{-3} (Fig. 4). The further increase of H_2O_2 concentration considerably decreased the rate of the degradation of dye because at higher concentrations, H_2O_2 can also become a scavenger of valence band holes and ${}^\bullet OH$ and perhydroxide radical is formed, which is less reactive then hydroxyl radical[15].

$$H_2O_2 + {}^\bullet OH \longrightarrow HO_2^\bullet + H_2O \qquad ...(5)$$

$$H_2O_2 + e^-_{CB} \longrightarrow {}^\bullet OH + OH^- \qquad ...(6)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow {}^\bullet OH + OH^- + O_2 \qquad ...(7)$$

$$H_2O_2 + h\nu \longrightarrow 2\,{}^\bullet OH \qquad ...(8)$$

$$H_2O_2 + h^+_{VB} \longrightarrow O_2 + 2\,H^+ \qquad ...(9)$$

$$HO_2^\bullet + {}^\bullet OH \longrightarrow H_2O + O_2 \qquad ...(10)$$

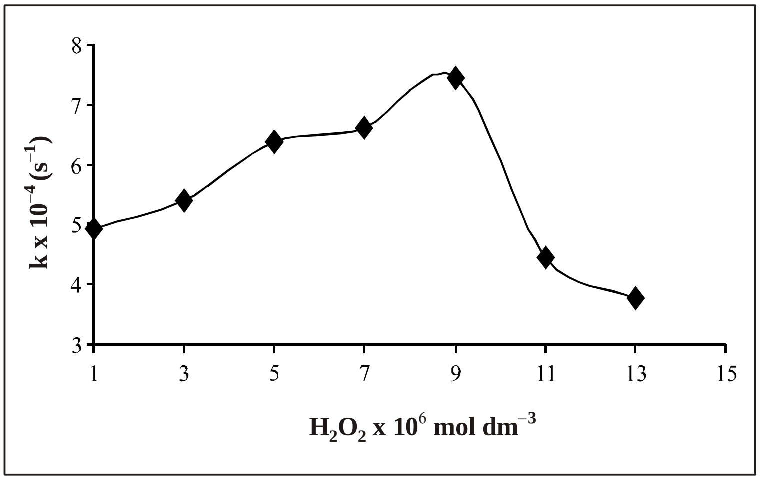

Fig. 4: Influence of hydrogen peroxide: [MV] = 4.0 x 10^{-5} mol dm^{-3}, TiO_2 = 150 mg/100 mL; Irradiation intensity = 14 x 10^3 lux; pH = 9.5

Estimation of chemical oxygen demand (COD)

The measurement of the chemical oxygen demand of the irradiated solution was used for monitoring the mineralization of the dye. This is an effective technique to measure the organic strength of polluted wastewater[12]. The COD of the remaining dye in the solution was measured at regular intervals to examine whether the dye was mineralized on photodegradation. The aqueous solution of a mixture of methylene violet (4 x 10^{-5} mol dm^{-3}) was exposed separately to visible light in the presence of TiO_2 at a dose of 150 mg/L. Aliquots were taken at regular intervals and COD was measured using closed reflux titrimetric method[16]. As the irradiation time increased more dye molecule got degraded to mineral products such as CO_2 and H_2O and COD values decreased from 300 mg/L to 4 mg/L. Further, increase in CO_2 value from 22 mg/L to 110 mg/L with 8 h of illumination also indicated photodegradation of treated dye solution (Table 1). The reduction in pH and increased conductivity of solution is observed with increase in the extent of mineralization. This effective technique allows measurement of waste in terms of the total quantity of oxygen required for oxidation of organic to CO_2 and water.

Influence of anions

Wastewater contains not only organic contaminants but also considerable amount of inorganic anions such as nitrate, sulfate, chloride, carbonate, phosphate, etc. Hence, it is useful to study the influence of these ions on this photocatalytic process because inorganic ions may influence the photocatalytic degradation either by changing the ionic strength of reaction medium or by inhibiting the catalytic activity of the photocatalyst[17]. However, these species always inhibit the photocatalytic oxidation reaction of organic pollutants since they can compete for oxidizing radicals or the active sites of the TiO_2 catalyst.

Table 1: COD and CO_2 measurements for degradation of methylene violet dye. Methylene violet concentration = 4.0 x 10^{-5} mol dm^{-3}; Amount of TiO_2 = 150 mg/100 mL; Irradiation intensity = 14 x 10^3 lux; pH = 9.5.

Irradiation time (h)	COD (mg/L)	CO_2 (mg/L)	Efficiency (%)	pH
0	300	22	0	8.7
2	176	33	41	8.5
4	64	55	78	8.2
6	32	77	89	7.9
8	4	110	98	7.7

Effect of sodium carbonate

Sodium carbonate is mainly used in the dyeing bath in order to adjust the pH as it plays an important role in the fixing of dye on the fabrics and in the fastness of the color. Therefore, carbonate ions are frequently present in industrial wastewater. The anion may have an effect on the rate of degradation. The decoloration of the methylene violet dye declined significantly with increasing concentration of sodium carbonate from 1 x 10^{-6} mol dm^{-3} to 13 x 10^{-6} mol dm^{-3} (Fig. 5). The decrease in the rate of degradation in the presence of carbonate ion may be due to the hydroxyl scavenging property of carbonate ion[17].

$$^{\bullet}OH + CO_3^{2-} \longrightarrow OH^- + CO_3^{\bullet-} \quad ...(11)$$

$$^{\bullet}OH + HCO_3^- \longrightarrow H_2O + CO_3^{\bullet-} \quad ...(12)$$

Effect of sodium chloride

The rate of photocatalytic degradation is considerably decreased upon the addition of inert salts like sodium chloride, sodium sulfate and sodium phosphate.

Sodium chloride usually comes out in the effluent along with sectional wastes of textile mills[18]. Experiments were performed with increasing concentration of sodium chloride from 1 x 10^{-6} mol dm^{-3} to 13 x 10^{-6} mol dm^{-3}.

$$^{\bullet}OH + Cl^- \longrightarrow Cl^{\bullet} + OH^- \quad ...(13)$$

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{\bullet-} \quad ...(14)$$

The decrease in the photocatlytic degradation of the dye in the presence of chloride ions is due to the hydroxyl radical scavenging effect.

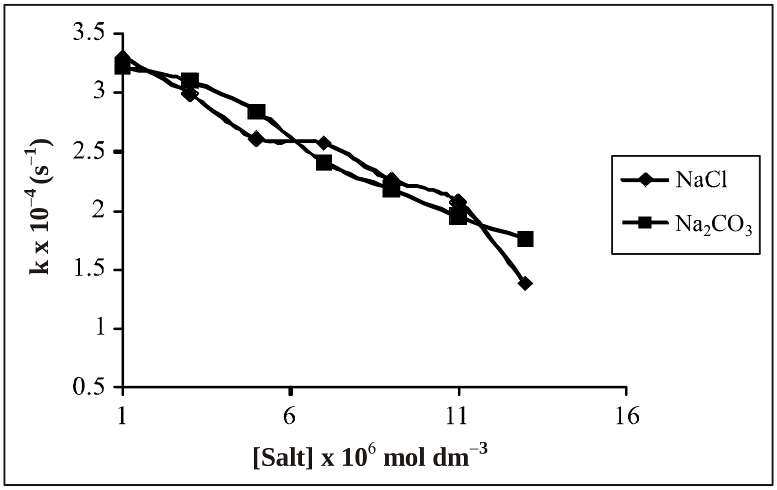

Fig. 5: Influence of anions: [MV] = 4.0 x 10^{-5} mol dm^{-3}; TiO_2 = 150 mg/100 mL; Irradiation intensity = 14 x 10^3 lux; pH = 9.5

Comparison of photocatalytic activity of commercial catalysts

The influence of various photocatalysts such as ZnO, BiOCl, CdS and $BaCrO_4$ on the degradation kinetics of methylene violet was investigated. Though ZnO is the most efficient catalyst, it has disadvantage of undergoing photocorrosion under illumination in acidic conditions. It is unstable with respect to incongruous dissolution to yield $Zn(OH)_2$ on the ZnO particle surfaces and thus, leading to catalyst inactivation[18]. The conduction and valence band of both; ZnO and TiO_2 are larger than the corresponding redox potential of H^+/H_2 and H_2O/O_2 and the photogenerated electron and hole can be separated efficiently. CdS with smaller band gaps show less activity since their conduction bands are much lower than those of ZnO and TiO_2. The electron (CB) in these semiconductors rapidly falls into the hole; thus, showing reduced activity[19]. The occasional release of metal ions (Cd^{2+}) into aqueous medium may cause heavy metal ion pollution. In addition, CdS is unsuitable as it readily undergoes photoanionic corrosion. Thus, the use of CdS, though able to degrade organic contaminants in wastewater, will lead to heavy metal pollution of water. CdS and $BaCrO_4$ are less reactive compared to TiO_2. The observed results revealed that under the chosen reaction conditions in presence of visible light ZnO and BiOCl have shown better photocatalytic activity. TiO_2 is well known for its efficiency under UV system. But the present study suggested that TiO_2 could also be efficiently used with visible light as well.

Effect of light intensity

The effect of the light intensity on the photocatalytic degradation of methylene violet was investigated. The degradation experiments were carried out with varying light intensity. The rate of degradation increased with increasing light intensity from 10×10^3 lux to 20×10^3 lux. This may be due to an increase in the number of photons striking per unit area [20.]

Mechanism of photocatalytic degradation

The photocatalyst, TiO_2, is a wide bandgap (3.2 eV) semiconductor, corresponding to radiation in the near UV range. The use of high energy UV light is not only costly, but can be hazardous also. Therefore, the possible use of visible light has recently drawn attention[21]. Organic pollutants like dyestuffs have the ability to absorb visible light. When dye molecules are adsorbed onto the surfaces of TiO_2, their translational mobility is considerably reduced and it extends the range of excitation energy of the semiconductor TiO_2 into visible region[22]. The visible light excites the dye molecules adsorbed on TiO_2 and subsequently inject electrons to conduction band (CB) of TiO_2. While the CB acts as a mediator for transferring electrons from the dye molecule to substrate electron acceptors on TiO_2 surface, the valence band (VB) remains unaffected in a typical photosensitization[23]. The conduction band electron of TiO_2 is scavenged by O_2 molecule to form $O_2^{\bullet -}$ or more active radicals such as $^{\bullet}OH$. These active oxygen species attack the cationic dye radical or dye molecule, leading to degradation (mineralization) of organic pollutant. Photosensitized degradation of organic dyes has been carried out on TiO_2 where the organic dye serves as both; sensitizer and substrate to be degraded[24]. Such type of electron transfer mechanism has been called a "photosensitizing oxidation". The mechanism of dye degradation under visible light irradiation may be[25] -

$$\text{Dye} + h\nu\ (\text{visible}) \longrightarrow \text{Dye}^* \qquad \ldots(15)$$

$$\text{Dye}^* + TiO_2 \longrightarrow \text{Dye}^{\bullet +} + TiO_2\,(e_{CB}^-) \qquad \ldots(16)$$

$$TiO_2\,(e_{CB}^-) + O_2 \longrightarrow TiO_2 + O_2^{\bullet -} \qquad \ldots(17)$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \qquad \ldots(18)$$

$$HO_2^{\bullet} + H^+ + TiO_2\,(e_{CB}^-) \longrightarrow H_2O_2 + TiO_2 \qquad \ldots(19)$$

$$O_2^{\bullet -} + 2\,H_2O \longrightarrow H_2O_2 + e^- \qquad \ldots(20)$$

$$H_2O_2 + TiO_2(e_{CB}^-) \longrightarrow {}^{\bullet}OH + OH^- + TiO_2 \qquad \ldots(21)$$

$$\text{Dye}^{\bullet +} + OH^- \longrightarrow \text{Dye} + {}^{\bullet}OH \qquad \ldots(22)$$

$$\text{Dye}^{\bullet+} + O_2^{\bullet-} \longrightarrow \text{Degradation products} \quad ...(23)$$

$$\text{Dye}^{\bullet+} + {}^{\bullet}OH \longrightarrow \text{Degradation products} \quad ...(24)$$

This process of dye sensitization (Fig. 6) has an advantage in degradation of organic pollutants with visible light.

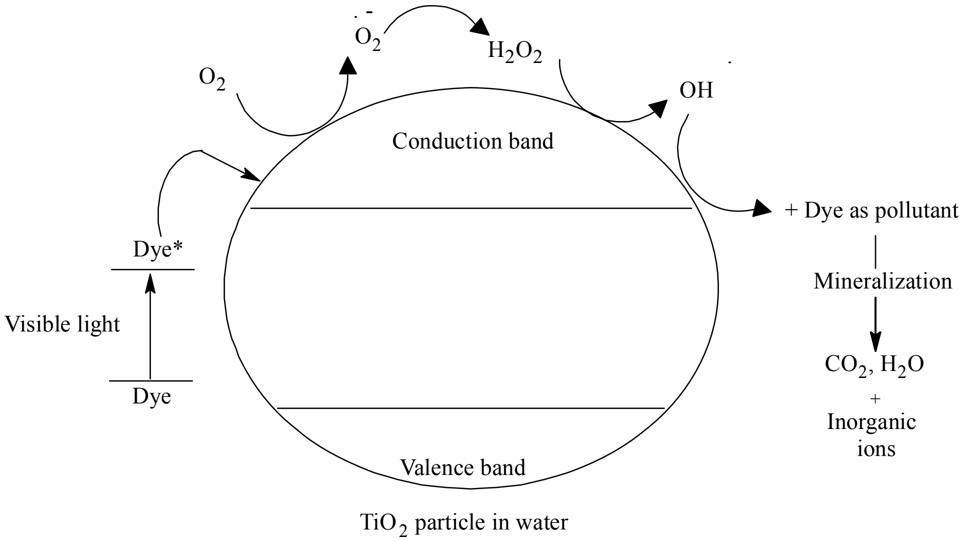

Fig. 6: Dye sensitization degradation on a TiO_2 semiconductor surface

CONCLUSION

The detailed observations revealed that the photoassisted mineralization of methylene violet could be effectively carried out utilizing TiO_2 with visible light. TiO_2 has been found to be an efficiently photocatalyst for the photomineralization of methylene violet dye. The dye concentration, catalyst loading, pH of the medium and light intensity play important role in the degradation efficiency. pH 9.5 was found to be the optimal pH under the given experimental conditions. The addition of electron acceptors such as hydrogen peroxide can enhance the degradation. The presence of inorganic salts such as sodium carbonate and sodium chloride hinders the photocatalytic degradation of textile dyes. The reduction in COD of the effluent suggested that the dye molecules were completely mineralized. This study confirms that photo catalysis is suitable not only for decolorizing colored aqueous effluents but also degrading the dyes to innocuous mineral products such as CO_2, H_2O and mineral acids.

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