Photodegradation of malachite green in the aqueous medium

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TiO₂ assisted photodegradation of malachite green (MG) has been examined in TiO₂ dispersions under both UV and visible light and found that degradation is faster in UV-light (λ 320 nm). Adsorption is prerequisite for the TiO₂ assisted photodegradation and the extent of degradation have been discussed in terms of the Langmuir-Hinshelwood model. Like most semiconductors the photocatalytic nature of TiO₂ is pH dependent because of its amphoteric nature. It has been found that pH ranging from 3-5 is suitable for the photodegradation of this system.

Much attention has been directed at investigating degradation of organic pollutants mediated by TiO₂ particles in aqueous dispersion under UV-light irradiation. Mechanistically, it is now commonly accepted that the photo catalyst TiO₂ is first excited by UV light and subsequently initiates the photo degradation process. However, artificial UV light and TiO₂ particles tend to be somewhat expensive and the UV component in sunlight reaching the earth surface and available to excite TiO₂ is relatively small (ca. 3-5%). Therefore, our efforts have been focused on exploring means to utilize the sunlight and artificial inexpensive UV or visible light sources and degrading agents for treating polluted water.

Organic pollutants like dyestuffs have the ability to absorb visible light. The electron transfer process from dye to semiconductor, especially TiO₂, have been found to be very effective. Kamat and co-workers reported the photo-degradation of Acid-Orange 7 and Naphthol Blue Black dyes pre-adsorbed on the surface of TiO₂ particles¹. The visible light mechanism suggests that the light excite the dyestuff.

\[ D + hv \rightarrow D^* \]  \hspace{1cm} (1)

\[ D^* + TiO₂ \rightarrow D^+ + TiO₂ (e) \]  \hspace{1cm} (2)

\[ TiO₂ (e) + O₂ \rightarrow TiO₂ + O₂^- \]  \hspace{1cm} (3)

\[ O₂^- + 2H₂O \rightarrow H₂O₂ + e \]  \hspace{1cm} (4)

\[ H₂O₂ + c \rightarrow \cdot OH + OH^- \]  \hspace{1cm} (5)

\[ D^*+O₂(=O₂^- or \cdot OH) \rightarrow \text{Degraded products} \]  \hspace{1cm} (6)

The excited dye (D*) injects an electron to the conduction band of TiO₂ where it is scavenged by O₂ to form active oxygen radicals. These active radicals drive the photodegradation or mineralization of organic compounds. However, only light of wavelengths below 400 nm can be absorbed by TiO₂ particles (Eg, 3.2 ev = 388 nm)². The photodegradation mechanism in the presence of light λ < 400 nm is somewhat different. In this process, TiO₂ absorbs light (λ < 400 nm) to generate e/h⁺ pair. The ejected photosensitized electron generates radicals (O₂-,OH) followed by degradation of dyestuff in the system. In this process degradation is faster than that of visible light.

In this report malachite green is degraded as an example of wastewater pollutants in different industries. Due to available light sources, it was possible to investigate the photodegradation of dyestuff by using both a visible and UV light in the aqueous medium. pH of the medium is one of the important factors for the degradation because of the amphoteric nature of most semiconductors. The effect of pH on degradation has also been discussed on the basis of the experimental results.

**Experimental**

TiO₂ photo catalyst (P25, 90% anatase, specific surface area 50 m² g⁻¹) used was supplied by Degussa. Malachite Green (MG) etc. were of laboratory reagent grade and were used without further purification. Doubly distilled and deionized water was used throughout the study.

**Photolysis of solution**

In order to prepare TiO₂ suspension, 100 mg TiO₂ was soaked overnight in 50 mL volumetric flask. The resulting mixture was then sonicated for 15 minutes and kept for an hour to settle down. A stock solution of MG \((1.00\times10^{-4} \text{ mol dm}^{-3})\) was prepared using distilled water. 10 mL of this solution was transferred into a 100 mL volumetric flask containing 50 mL TiO₂ suspension to prepare reaction mixture. This
reaction mixture was again kept overnight in dark. 50 mL of this solution was transferred in a cylindrical pyrex vessel (2.5 cm diameter) positioned at 10 cm apart from the light source. Temperature of the solution was monitored during photolysis setting a thermometer. A 500w high-pressure halogen lamp was used as visible light source whose UV portion was cut by using a UV filter. 320 nm mercury lamp was used for UV radiation source. The spectra of the solutions before and after photolysis were taken using an UV-visible spectrophotometer (Shimadzu- UV-Vis 160). All experiments were done in the open air.

Results and discussion

The change in absorption spectra takes place during the photodegradation of MG by TiO2 under visible and UV light. The absorption peaks corresponding to the dye molecule diminished and finally disappeared under photolysis indicating the degradation of MG. No new absorption band appeared both in visible and UV regions, especially bands for any aromatic moiety.

In absence of light (UV visible) no photodegradation occurs. The oxidation potential of excited dye (MG) is more negative than the potential of the conduction band of TiO2 (refs 3,5). When dye molecule is absorbed on the surface of TiO2 and excited by visible light, it can eject electron to the conduction band of colloidal TiO2 and these electrons are responsible for radical generation 7,8. On the other hand, after adsorption of dye molecules on TiO2 surface followed by self-excitation of TiO2 by 320 nm light, TiO2 produces e·/h+ pairs. These photoelectrons are responsible in this case for radical generation followed by photodegradation of the dye molecules 5,6. So in both cases adsorption is the prime condition of photodegradation.

Since the photodegradation of dye occurs predominantly on TiO2 surface, the adsorption of dye molecules from aqueous solution particularly on to TiO2 surface is very important. The extent of adsorption of dye at various concentrations was measured by monitoring its concentration in blank solution after the adsorption/desorption equilibrium had been reached. The photodegradation kinetics of many organic compounds often modeled using simple Langmuir-Hinshelwood equation which expresses the relation between rate (v) as function of concentration 5,6.

\[
\frac{1}{v} = \frac{1}{kK} [\text{MG}] + \frac{1}{k} \\
\]  \hspace{1cm} \ldots (7)

where \( k \) is the apparent rate constant for the process and \( K \) is adsorption co-efficient under irradiation conditions. Examining degradation rate of MG at different initial concentrations, photodegradation kinetics under UV light irradiation was assessed. A good linear relationship between \( v^{-1} \) and \([\text{MG}]^{-1}\) indicates that degradation kinetics of MG also follows L-H model. The adsorption constant \( K \) determined from Eq. (7) for the process is \( 2.44 \times 10^5 \) Lmol\(^{-1}\). While adsorption co-efficient \( K' \) is \( 3.2744 \times 10^5 \) Lmol\(^{-1}\) from Langmuir equation (8) in the dark.

\[
[\text{MG}]e \left( \frac{x}{m} \right) = [\text{MG}]eK' + 1/ kK' \]  \hspace{1cm} \ldots (8)

where \([\text{MG}]e\) is equilibrium concentration and \( x/m \) is the amount of MG adsorbed per gram of TiO2, \( k \) is adsorption constant and \( K' \) is adsorption coefficient. The difference between \( K \) and \( K' \) was caused by photo desorption and/or photo adsorption of substrate molecules on the TiO2 surface.

Figure (1) shows the photodegradation of MG at different conditions. No change in concentration was found in 120 min upon irradiation of MG solution even by 320 nm light (curve a). When TiO2 suspension is added to the MG solution, during visible light irradiation, concentration of dye initially increases and upon further irradiation, concentration decreases. This complicated change of MG concentration may be due to aggregation of MG molecules leading to poor solubility of MG molecules in water. As the irradiation time increases, some molecules redissolve in the solution to cause the increase in concentration of MG followed by photo degradation. The visible light irradiation causes only 25% of degradation of MG (curve b) in 125 minutes.

![Fig.1—Dependence of TiO2 and irradiation on degradation of MG. (a) MG irradiated with 320nm light in absence of TiO2 suspension; (b) MG irradiated with visible light in presence of TiO2 suspension; (c) MG irradiated with 320nm light in presence of TiO2 suspension.](image-url)
Almost 100% degradation is obtained in 80 min by using 320 nm light source. UV radiation causes quicker redissolution followed by degradation of MG molecules (curve c). The quicker degradation is obtained in presence of UV radiation because in this case TiO$_2$ particles produce e/h$^+$ pairs which are responsible to produce more OH radicals as described early.

pH of the medium is one of the important factors for the degradation kinetics because of amphoteric behaviour of most semiconductors. pH of the medium influences surface charge properties of TiO$_2$ photo catalyst. The point of zero charge (pzc) for TiO$_2$ particles is at pH $\sim$6.8$^{56}$. The surface of TiO$_2$ is positively charged in the acidic pH. On the other hand the spectrum of MG is pH dependent, $\lambda_{\text{em}}$ (absorption maxima) at 617 nm remains constant in the pH range of 3-5. Thus a fixed pH of 3.5 was chosen throughout the whole experiment.

The study confirms that MG undergoes total degradation because no new peaks of any aromatic moiety in the UV visible spectrum was observed after almost complete degradation. In the present study we were not concerned about the reaction intermediates even though we tried to analyze the end products but we could not identify the intermediate species. During the experiment qualitatively the generation of CO$_2$ was identified. By analyzing the end product, qualitatively, NO$_3^-$ was found. And the decrease in pH indicates the formation of some mineral acids. We assumed that there should have some other end products, which could not be identified.

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**References**