Graphite Oxide modified TiO\textsubscript{2} Composite: An Efficient Photocatalyst for Degradation of Methylene Blue

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ARTICLE INFORMATION
ABSTRACT

The graphite oxide (GO)-modified TiO\textsubscript{2} is prepared to enhance the photocatalytic property of TiO\textsubscript{2} for the degradation of organic dye. The structural modification of TiO\textsubscript{2}-GO has been characterized by XRD and FTIR technique. The interfacial electron transfer between the dye (MB) and the photocatalyst has been confirmed by measuring the electrical conductivity during the photocatalytic reaction. The effect of GO-doped TiO\textsubscript{2} photocatalyst, its interaction with the dye (MB) and thereby photo degradation of MB which is exposed to the sunlight irradiation has been studied by UV-visible spectroscopy and the electrical conductivity. The rapid disappearance of the blue color of MB has been observed when it is exposed to the sunlight in presence TiO\textsubscript{2}-GO nano composites. The rapid decrease in absorbance at \( \lambda_{\text{max}} = 663 \) nm upon adding graphite oxide (GO) to the MB-TiO\textsubscript{2} system is being observed. The degradation efficiency in presence of TiO\textsubscript{2} and TiO\textsubscript{2}-GO was found to be 78.2 and 97.7 percent respectively after 3 h. The reaction rates of Photo degradation of MB by TiO\textsubscript{2} and TiO\textsubscript{2}-GO are found to be 3.54 x 10\textsuperscript{-3} min\textsuperscript{-1} and 4.70 x 10\textsuperscript{-3} min\textsuperscript{-1} respectively.

1. Introduction
The TiO\textsubscript{2}-based Photocatalytic oxidation of organic and dyes stuff has been extensively studied in aqueous dispersion under UV light irradiation by Sabin \textit{et al.}(1992) and Prashant \textit{et al.}(1995). TiO\textsubscript{2}-mediated photocatalytic degradation of methylene blue has been reported by Lakshmi \textit{et al.}(1995) and Ioannis \textit{et al.}(2004). Taixing \textit{et al.}(1999) studied the TiO\textsubscript{2}-assisted photodegradation of Dyes. The photocatalytic activities of pure rutile particles isolated from TiO\textsubscript{2} powder by dissolving the anatase component in HF Solution reported by Ohno \textit{et al.}(2001). Three-
dimensionally ordered macro-porous Titania were used for photodegradation methylene blue by Madhavi and Tim (2007). The nature of carbon doped TiO₂ photo-catalyst by grinding TiO₂ with ethanol and heating treatment has been studied by Kang et al. (2008). In-Cheol Kang et al. (2008) studied the improvement in photocatalytic activity of TiO₂ under visible light through addition of N-TiO₂. Recently the studies on graphene attracted the interest of the scientist recently. Graphene was prepared by Novosolev et al. (2004). Graphene is one-atom thin sheet of carbon with atoms typically arranged in two-dimensional honey comb like structure. The other very interesting properties observed in graphene viz electronic quantum Hall Effect and Berry’s phase in graphene (Novoselov et al 2004, 2007, Yuanbo et al. 2005). Mykola et al. (2010) has reported the adsorption of ammonia on the surface of graphite oxide (GO). Brodie and Hummers (1958) reported the methods of synthesis of GO at ambient temperature. The aim of this work is to sensitized TiO₂ with GO to increase its quantum efficiency and thereby to improve the light utilization property of TiO₂ photo-catalyst. We report here the graphene based composite material used as a photocatalyst for photodegradation of methylene Blue (MB).

2. Materials and Method
Titanium IV oxide, TiO₂ (CDH, New Delhi) powder having particle size 200-250 nm was used without further purification. TiO₂ powder was dispersed in double distilled water at the concentration of 0.25 g/L. The same molar solution of TiO₂ was used for the degradation of MB for the initial concentration of 20µM. A conical flask of capacity ca.100 mL was used as the photo reactor. The absorption maximum for methylene blue was obtained at 663 nm for calculation of initial degradation rates. The pH of the suspension was maintained within the range of 3-4 with HClO₄ standard solution. The suspension of TiO₂-MB was stirred magnetically for 5 minutes to allow the equilibrium adsorption of dye on TiO₂ under natural sunlight illumination. Graphite oxide was prepared by modified Hummer’s method. Graphite Oxide (GO) as-prepared was used to sensitize TiO₂. The TiO₂-GO were mechanically mixed in different ratios (1:1, 1:2 and 1:3) by weight (w/w) in ethanol and then grinding was operated in mortar-pestle for 15 minutes. The powdered samples were subsequently applied for photocatalysis of dye. The experiments were repeated under identical conditions to reproduce the results. The TiO₂ was used as the reference to compare the photocatalytic activity under the similar experimental conditions. Under the natural sunlight, the photodegradation of MB was monitored in the temperature range of 25-30 °C during the month of October. The solution was stirred continuously for some time to obtain a good dispersion of the catalyst to establish the adsorption and desorption equilibrium between MB and the TiO₂-GO composite. The two different photo reactors containing TiO₂ and TiO₂-GO for the photocatalytic degradation (PCD) of MB were carefully exposed to the natural sunlight for one hour. To settle down the composite at the bottom, it was left un stirred for some time. Samples of aliquots were withdrawn from the reactor intermittently during the irradiation and filtered through Whatman filter paper (125 nm Toyo Roshi Kaisha, Japan) to remove TiO₂-GO suspended particles and subsequently absorbance and conductivity were measured. Aliquots of (2-3 mL) using syringe were collected at regular time of intervals for the recording of change in the concentration under UV-irradiations. The gradual decrease in absorbance was observed for the degradation of MB dyes with TiO₂ and TiO₂ sensitized with GO at λmax=663 nm. The rates of photocatalytic oxidative degradation were evaluated by monitoring their optical density as a function of time.

Powder X-ray diffraction (XRD) was conducted using Bruker D8-advance diffractometer with CuKα radiation (λ=1.54060 Å) and step scanned over the 2θ range of 5°-80° with scan step time 15-5 sec at temperature of 25 °C to study the interaction between TiO₂-MB and TiO₂-GO-MB composites particles. The change in electrical conductivity during the photo degradation was measured by Fisher conductivity meter. The absorption spectra of aliquots of sample containing MB for the PCD were recorded by UV-Vis spectrophotometer (1240 Shimadzu, Japan). FTIR spectra are taken to explore the binding interaction between the MB and TiO₂-GO composite using Interspec 2020 (UK) spectrophotometer at resolution of 4 cm⁻¹ in absorption mode. Fluorescence emission spectra are taken by using F-2500 Fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was performed by using DTH 60H analyzer of Shimadzu, Singapore. The measurement was recorded under air atmosphere in the range 30-800 °C, with heating rate of 20 °C/min.
2. Results and Discussion

2.1 Crystallinity of TiO$_2$-GO Composite

The XRD patterns of the TiO$_2$-GO composite were studied for the samples collected before and after the photodegradation of MB which indicates that TiO$_2$-GO photocatalyst without MB adsorption has higher degree of crystallinity as shown in Figure 1. When MB is adsorbed on the surface of TiO$_2$-GO, the crystalline nature of composite decreases and the intensity of diffraction peaks also decreases, suggesting thereby an interaction between TiO$_2$-GO composite and methylene blue dye.

![Figure 1. XRD pattern of TiO$_2$-GO and TiO$_2$-GO-MB after MB adsorption](image)

2.2 TiO$_2$-GO Composite: An efficient photocatalyst

The titanium oxide has been most widely and extensively used semiconductor as a photocatalyst. The composite of TiO$_2$ with GO has been prepared with the aim to enhance the photocatalytic performance and electron transfer rates. The photocatalytic activity of TiO$_2$-GO composite has been observed under natural sunlight for the photodegradation of dyes viz: methylene blue. A comparative study of TiO$_2$ and TiO$_2$-GO composite for the PCD of MB has been performed. There was slow decline in the absorbance for the system containing TiO$_2$-MB where the rapid decrease in absorbance was observed for TiO$_2$-MB-GO system at $\lambda_{max}$ = 663 nm during exposure to sunlight with equal intervals of time, as shown in the Figure 2.

![Figure 2. The relationship between time and absorbance at 663 nm of TiO$_2$ and TiO$_2$-GO Composite](image)

On the basis of the difference in the absorbance recorded before and after photocatalytic degradation of dye, the concentration of the reduced dye has been estimated under equilibrium conditions in each experiment.

![Figure 3. Comparison of first-order degradation rates for MB solution containing TiO$_2$ and TiO$_2$-GO composite (1:1,w:w)](image)

Considering that the photo degradation of dye under sunlight irradiation is initiated by the interfacial electron transfer from excited dye molecules to the GO-modified TiO$_2$ catalyst. For this the interaction between dye molecules and photocatalyst is a prerequisite as reported by Kongk and Prashant (2007). The study of reaction kinetics of photocatalytic degradation of MB depends greatly on the electron transfer efficiency as reported by Dan Zhao and Chuncheng Chen (2008). The interaction between MB and modified TiO$_2$-GO, as studied by IR spectra and fluorescence emission spectra is stronger than that between MB and TiO$_2$, indicating higher adsorption of MB on GO-TiO$_2$ catalyst. The degradation efficiency in presence of photocatalyst (TiO$_2$) was evaluated by using first order integrated kinetics equation and found to be...
The addition of TiO$_2$-GO has significantly accelerated photodegradation with higher rate constant value and it is calculated to be approx. 97.7 percent for the solution of same concentration. The PCD reaction follow pseudo first order kinetics with rate constant $k$ is given by:

$$k = \frac{2.303}{t} \log\left(\frac{C}{C_o}\right)$$

where $C_o$ and $C$ are initial and final concentration of MB respectively. The rate constant ($k$, min$^{-1}$) evaluated from the plot of ln($C/C_o$) vs irradiation time from Figure 3. The reaction rates observed for photodegradation of MB using two different catalysts (i.e. TiO$_2$ and TiO$_2$-GO) under similar experimental conditions are evaluated as $k_{TiO2}=3.54 \times 10^{-3}$ min$^{-1}$ and $k_{TiO2-GO}=4.70 \times 10^{-3}$ min$^{-1}$, respectively. The enhanced rate of degradation using TiO$_2$-GO may be attributed to the larger surface area and more electron donating capability of TiO$_2$-GO composite. It has increased the rate of degradation of MB about 10-15%. The titania powder was deposited on graphite oxide (GO) surface, thereby improving the quantum efficiency of GO doped-TiO$_2$. The photo-catalyst TiO$_2$-GO can be recovered at 45$^\circ$C in the powder form and re-used for PCD.

2.3 UV-visible spectroscopy

The UV-Vis spectra of the supernatant were taken using Uni 1240 UV-Vis spectrophotometer (Shimadzu). All observations were made under the Beer’s-Lambert law range, $A=\varepsilon \cdot \lambda \cdot B$, for determining the concentration of MB, where $A$ is the absorption at $\lambda_{max}$, $\varepsilon$ is the molar absorptivity of MB, and $B$ is the sample cell length (1 cm). Under sunlight irradiation, the characteristic peak of MB at 663 nm almost disappeared in 60 minutes (Figure 4).

The color of the dispersion was changed from light blue color to transparent solution. It might be interpreted in terms of entrapment of the electrons trapped by the GO-TiO$_2$ composite particles and these particles did not possess any characteristic absorption property in visible region. The blue color of MB is primarily due to the chromophore group attached and it could be de-linked as reported by Prashant and Vinod (1995).

The disappearance of blue color of MB was observed by measuring the absorbance at 663 nm. The $\lambda_{max}$ of MB declined with UV-illumination time and slight blue shift (hypsochromic effect) in the wavelength were also seen in Figure 5, for complete degradation of MB in almost 60 minutes.

2.4 Conductivity measurement

To probe the electron transfer phenomenon between the dye and the photocatalyst, a continuous change in conductivity during the photo degradation reaction indicates the occurrence of electron transfer phenomenon. The rapid increase in the conductivity has been observed when GO was added (5-20 mg) to the suspension of TiO$_2$-MB (Figure 6). A decreasing trend in conductivity was also observed during the
PCD of MB upon addition of 1 mL of MB (50 ppm) solution in each step to the TiO$_2$-GO system (Figure 7). Thus, the electron transfer property of semiconductor catalyst TiO$_2$ and TiO$_2$-GO system has been probed by adding MB that was accomplished by accepting electrons from the conduction bands of TiO$_2$ and TiO$_2$-GO. It indicates phenomenon of transfer of electron. Thus higher adsorption of MB on the surface of GO modified TiO$_2$ catalyst causes more electrons transfer between the photocatalyst and the MB molecules which results in faster photo degradation of the dye.

2.4 FT-IR spectroscopy
The chemical interaction between the molecules of the photocatalyst and MB and subsequently the process of interfacial electron transfer from the excited MB dye to photocatalyst TiO$_2$-GO is a prerequisite for photocatalysis. IR study helps to identify the binding modes. For the pure dye, IR spectrum is shown in Figure 8. The stretching vibration band of N=N observed at 1587 and the broad peak at 3436 cm$^{-1}$ ascribes the stretching vibrations of N-H. The characteristic strong C-N band located at 1319 cm$^{-1}$. The stretching vibration assigned to the C-S linkage occurred at 616 cm$^{-1}$. For the dye (MB) adsorbed on GO modified TiO$_2$ photocatalyst composite(TiO$_2$-GO) surfaces, the splitting vibrations are being observed and shown in Figure 9, at 1705 and 1538 cm$^{-1}$. The spectrum of TiO$_2$-GO also illustrates the presence of C=O vibration at 1700-1705 cm$^{-1}$ reported by Yongchao and Edward (2008).

2.5 Fluorescence emission spectroscopy
At low concentration, the fluorescence intensity will generally be proportion to the concentration of the fluorophore. The fluorescence emission
spectrum of MB after it has been partially and completely photodegraded by the photo-catalyst shows emission peak around 660 nm. The decrease in fluorescence intensity over a time period results mainly due to photodecomposition of dye in the suspension and finally emission peak disappeared indicating the complete excitation of electron has occurred between the donor and acceptor molecules.

The phenomenon of photosensitization occurs through donor-acceptor system, the donor (TiO$_2$-GO) D, acts as sensitizer, absorbs the energy from incident photon and since the triplet state of the donor is higher than the triplet state of the acceptor (MB) A, the absorption of the photon produces the singlet excited state of the donor, $^1$D which, via intersystem crossing, gives rise the triplet excited state of the donor, $^3$D. The triplet excited state of donor then interacts with the acceptor molecule and the resulting in the formation of triplet excited state of the acceptor, $^3$A and the ground state of the donor. The decomposition of MB occurs in the triplet excited state $^3$A of the acceptor molecules.

2.6 Thermogravimetric Analysis

The thermogravimetry/derivative thermogravimetry (TG/DTG) studies of GO modified TiO$_2$ photocatalyst towards high-temperature has been performed to explore the thermal behavior. The TG/DTG curve of TiO$_2$-GO after the adsorption of MB dried at 30 °C is shown in Figure 11. Three distinct weight loss steps are seen in the TiO$_2$-GO composite. The first region up to 149-200 °C is ascribed to the loss of water molecule and organic content of the dye. There is very slow decomposition between 200-499 °C whereas TiO$_2$-GO decomposition speed up around 499-576 °C, which is attributed to the removal of oxygen-containing groups and carbon oxidation.

![Figure 11 Thermogravimetric and differential scanning curve of the TiO$_2$-GO (1:1/w:w) composite](image)

3. Conclusions

The complete decolonization of MB was achieved due to fast oxidation using TiO$_2$-GO composite semiconductor under natural sunlight. The rate of PCD of the MB in aqueous solution could be raised by treating a coupled TiO$_2$-GO semiconductor system. The enhance photocatalysis (PCD) of MB observed by TiO$_2$-GO composite was attributed to it the higher electron accepting tendency, thus, favor the oxidative degradation of the substrate molecule resulting in decrease in the absorbance and absorbance maxima. The results are also encouraging for other dyes Rhodamine B and Azodyes. Therefore, it is confirmed that the TiO$_2$-GO could be used as an efficient, environmentally benign and also cost effective material for water treatment contaminated with dyes stuff.

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References


