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ORIGINAL ARTICLE

Photodegradation of bromophenol blue in aqueous medium using graphene nanoplates-supported TiO_2

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Abstract

The bromophenol blue dye in aqueous medium was photodegraded (under UV irradiation) by graphene nanoplates-supported titanium oxide (TiO_2/GNP). The determination of various elements (percentage) and morphological study was performed using energy-dispersive X-rays and scanning electron microscopy, while the photodegradation study of dye was done by UV–visible spectrophotometer. The morphological study showed that the TiO_2 particles were dispersed well on the surface of GNP. The sizes of TiO_2 particles were below 500 nm. The photodegradation study was performed as function of time, and it was found that the photodegradation of dye in aqueous medium was increased as the time duration of UV irradiation increased. It was found that about 86% of dye was degraded within 8 h. The degradation of bromophenol blue is pH-dependent, and the photodegradation rate was increased as the pH of solution increased. The increase in dye degradation might be due to the formation of more hydroxyl radical at higher pH. The degradation of dye at pH 2, 4, 6 and 8 was about 70, 79, 90 and 95%, respectively.

Keywords Photodegradation · TiO_2 · Bromophenol blue · Graphene sheet

Introduction

The effluents were released from food processing, leather, paper, textile and dyes manufacturing industries containing various types of coloring materials, which generate non-aesthetic pollution and eutrophication. The majority of dyes is toxic and carcinogenic, non-biodegradable (large size and complex structures) and may contribute to the formation of dangerous by-products through the chemical reactions that take place in the wastewater bodies (oxidation, hydrolysis, etc.) (Ramírez et al. 2012). These coloring materials can be removed from the industrial effluents by using various chemical and physical techniques such as advance oxidation process, adsorption and coagulation, reverse osmosis and ultrafiltration (Ladakowicz et al. 2001; Lee et al. 2006; Nataraj et al. 2009; Zhao et al. 2012). Most of these techniques are nondestructive and transfer only pollutants from aqueous medium to another medium or convert them into products, which have low toxicity. Currently, semiconductor photocatalysis extensively used for the organic pollutants/organic dyes degradation. The photocatalytic degradation process is normally based on the production of hydroxyl radical and that radicals are responsible for the organic pollutants degradation (Moghaddam and Yangjeh 2011; Khan et al. 2016).

TiO_2 has attractive applications in cosmetics and in the production of electrochemistry electrodes, capacitors, solar cells and catalysis (Ghorai and Biswas 2013). Also, TiO_2 is widely used as a photocatalyst for the degradation of organic and inorganic substances because of low cost, high stability against corrosion and non-toxicity. When titanium oxide is irradiated by UV, the electrons on the surface of TiO_2 are excited from the valence band to the conduction band and that result a positive hole in the valence band. The excited electron may react with hydroxyl/water to generate hydroxyl radicals (strong oxidizing agent), which is responsible for the destroying of organic compounds. It was also reported that the organic compound is directly destroyed by positive hole (Tang et al. 1997).

In the present study, an attempt was made for the photodegradation of bromophenol blue using TiO_2/GNP. The

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bromophenol blue was selected because it is commonly used as a pH indicator and as a dye. It is also used for the determination of trace quantity of manganese(II), silver(I) and vanadium(V). The contact or inhalation of bromophenol blue may cause skin, eye and respiratory tract irritation. It may cause reproductive and fetal effects. It was also reported that the prolonged exposure may cause liver, kidney and heart damage (http://cdn2.lasecsa.co.za/pdf/sds/Bromophenol%20blue%20indicator.pdf. 2019). While the GNP exhibits large specific surface area, high mechanical and thermal conductivity and stable in air showed (Anastassia and Vagelis 2013). Due to these outstanding properties, the GNP showed wide potential applications in sensors, supercapacitors, filler in polymeric materials and photocatalysis (Xu and Zhang 2000; Fang et al. 2014). In our present work, the GNPs are used as support for the TiO_2 and then used as a photocatalyst for the degradation of dye. The TiO_2/GNP was characterized by SEM and EDX. The UV–Vis spectrophotometer was used for the determination of dye degradation. The photodegradation of dye was also performed at a different pH in order to study the effect of pH on degradation of dye.

Experimental work

Materials

HNO_3 and bromophenol blue were purchased from Sigma-Aldrich and used as received. The GNPs are purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. The thickness and diameter of graphene nanoplates are 4–20 nm and 5–10 µm, respectively.

Purification of GNP

The GNP was purified by an acid treatment using the same method as discussed somewhere else (Saeed and Khan 2014). Three grams of GNP was sonicated in 160 mL of 10 M HNO_3 and then refluxed at 125 °C for 6 h. The acid-treated GNPs were separated from HNO_3 solution by filtration and then washed with distilled water until they were free from acid. The GNPs were dried at 105 °C and stored for further use. The acid treatment not only purifies the GNP but also introduces the carboxyl groups.

Preparation of catalyst

A known amount of GNP (1 g) and TiO_2 (1.5 g) were taken in 50 mL distill water and were sonicated for 30 min. When both GNP and TiO_2 are fully mixed and dispersed, then the solution was filtered and dried in oven at 100 ^{o} C for 2 h. The dried graphene nanoplates-supported titanium oxide (TiO_2/GNP) sample was stored for further use.

Photodegradation of bromophenol blue

0.02 g of GNP/TiO_2 was added to 10 mL of 100 ppm bromophenol blue solution. The dye solution was then irradiated under UV light (254 nm, 15 W) for various time durations with constant stirring. After the specific irradiation time, the TiO_2/GNP was separated by centrifugation and then the UV–Vis absorption measurements were taken using UV–visible spectrophotometer. The degradation rate of bromophenol blue dye was calculated by using the following equation (Ameen et al. 2010):

$$\text{Degradation rate}\,(\%) = \frac{(C_o - C)}{C_o} \times 100$$

$$\text{Degradation rate}\,(\%) = \frac{(A_o - A)}{A_o} \times 100$$

where C_o is the initial concentration of dye, C is the dye concentration after UV irradiation, A_o shows the initial absorbance, and A is the dye absorbance after UV irradiation.

Instrumentation

The morphological study of gold-coated GNP and TiO_2/GNP was analyzed using JEOL, JSM-5910 scanning electron microscope. The energy-dispersive X-rays (EDX) spectrometric study analysis of TiO_2/GNP was performed on EDX (Model INCA 200/Oxford Instruments, UK, company oxford), in order to investigate the elemental composition of the samples. The FT-IR study was performed by FT-IR spectrometer (PerkinElmer, serial number 95120), where IR beam was pass through solid-dried TiO_2/GNP sample. The photodegradation study of bromophenol blue was performed using UV–visible spectrophotometer (UV-1800, Shimadzu, Japan).

Result and discussion

SEM study

The morphological study of untreated GNP and TiO_2/GNP was performed in order to confirm the presence/dispersion of TiO_2 onto the GNP. Figure 1 shows the SEM images of untreated GNP and GNP-supported TiO_2. The SEM micrographs showed the TiO_2 particles (sized below 500 nm) on the surface of GNP, while these particles are not present on

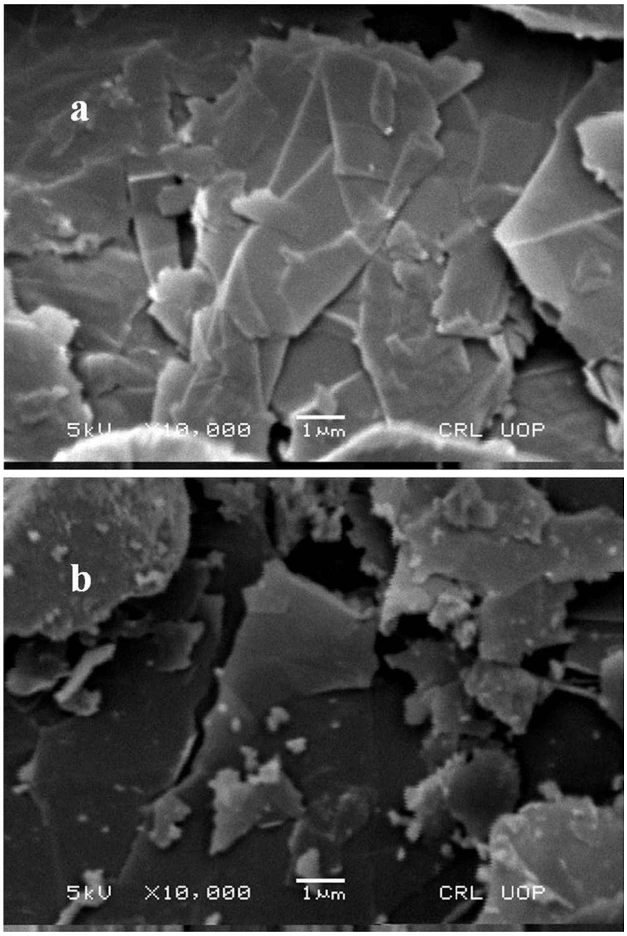


Fig. 1 SEM micrographs of **a** GNP and **b** TiO_2/GNP

the untreated GNP (Fig. 1a). Figure 1b shows that the TiO_2 particles were dispersed well on the surface of GNP. The better dispersion of TiO_2 particles on GNP enables larger number of active catalytic centers available for the photocatalytic reaction. It is also clear from Fig. 1 that the acid treatment did not affect the surface morphology of the GNP.

EDX study

EDX is an important tool for the determination of various elements (percentage) in any types of materials. Figure 2 shows the EDX spectra of untreated GNP and GNP-supported TiO_2, which showed the percentage of various elements. The result showed that the carbon and Ti are present as major elements, while oxygen is present in less quantity. The untreated GNP showed only carbon and oxygen contents while in the case of GNP-supported TiO_2 contain carbon, oxygen and titanium. The presence of oxygen in GNP presented that the acid treatment not only purified the GNP but also introduced the carboxylic acid onto the GNP. The EDX spectrum (Fig. 2b) also showed that the height of oxygen peak was increased in the case of GNP-supported TiO_2, which is due to the presence of oxygen in TiO_2.

Figure 3 shows the FT-IR spectra of TiO_2/GNPs, which presented peaks in the range of 400–900 cm^{-1}. The peaks might due to the mixture of polymorphic phases of anatase and rutile (Chellappa et al. 2015). The peaks which appeared in the region 1670–1695 cm^{-1} might be due to the stretching vibration of COOH group. The appearance of COOH group indicated that the carboxylic functional groups are formed onto the GNPs during the acid treatment.

Photodegradation study

The photocatalytic properties of TiO_2-based materials are depend on a variety of parameters such as particle size, large surface area and active functional groups available on the surface. The GNPs are excellent support for TiO_2, as they provide large surface area for TiO_2 and enhance their photodegradation properties. Figure 4a shows the degradation of bromophenol blue in the presence of GNP-supported TiO_2 in UV light irradiation as a function of time. The extent of dye degradation was calculated from the relative intensity of UV–visible spectra (Fig. 4). The results illustrated that bromophenol blue solution shows maximum absorbance at 592 nm, which was found to continuously decrease as the UV irradiation time was increased. This suggests that the degradation of dye was enhanced by GNP-supported TiO_2 with increase in the UV irradiation time. Figure 4b shows percent degradation of bromophenol blue, where the percent degradation was found to gradually increase, and about 86% of dye was found to degrade within 8 h.

The proposed mechanism for the photodegradation of organic dye by TiO_2 is that the TiO_2 was initially photoexcited to generate conduction band electrons (e^-) and valence band holes (h^+). The promoted electron is creating hole (+ ve charged hole), which might react with water and result in the generation of hydroxyl radicals or it would directly oxidize organic dye molecules at the semiconductor surface. The hydroxyl radicals (Eq. 3) are strong oxidizing agent, which are responsible for the degradation of organic dye (Dlamini et al. 2011; Giwa et al. 2012).

$$TiO_2 + h\nu \rightarrow TiO_2\left(e^- + h^+\right) \tag{1}$$

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + H^+ + OH^{\cdot} \tag{2}$$

$$\text{Dye} + OH^{\cdot} \rightarrow \text{Degradation} \tag{3}$$

It was also suggested that the photogenerated electron reduces dissolved oxygen to produce superoxide anion radical. The superoxide anion radical is also a strong oxidizing agent (Eq. 4), which can easily attack any organic molecules adsorbed on, or located close to the surface of the catalyst,

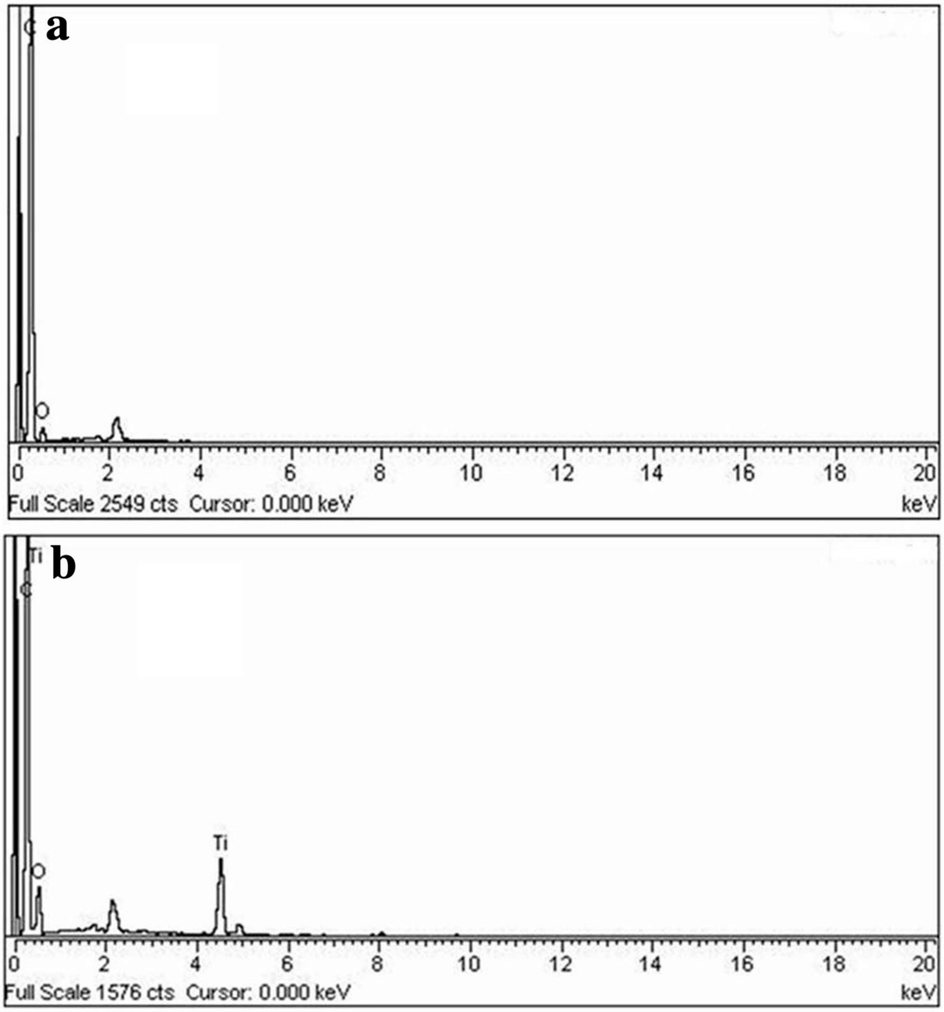


Fig. 2 EDX study of **a** GNP and **b** TiO_2/GNP

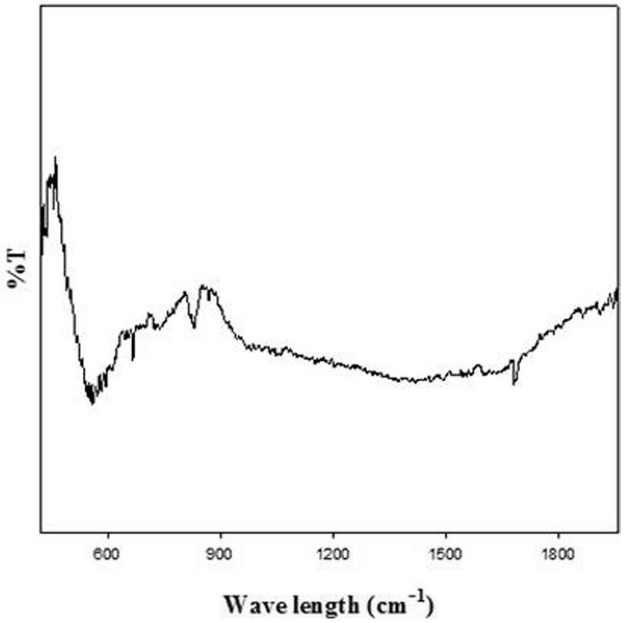


Fig. 3 FT-IR spectrum of TiO_2/GNP

and as a result, degradation of organic dyes molecules occurs (Muneer et al. 1997).

$$O_2 + e^- \rightarrow O_2^{-\cdot} \tag{4}$$

$$\text{Dye} + O_2^{-\cdot} \rightarrow \text{Degradation} \tag{5}$$

pH effect on dye degradation

Wastewater from textile industries contains dyes, which are discharge at a different pH, so it is an important to study the role of pH on the degradation of organic dyes. The pH not only plays an important role both in characteristics of textile wastes and formation of hydroxyl radicals but also affects the catalyst particles charge, size of catalyst aggregates and the positions of conductance and valence bands (Giwa et al. 2012; Neppolian et al. 2002). The pH study was performed at pH 2, 4, 6 and 8 at constant dye concentration (100 ppm), TiO_2/GNP and irradiation time was 6 h. The pH of the dye solution was adjusted by adding HNO_3 and NaOH. Figure 5 shows the effect of pH on the degradation of bromophenol blue,

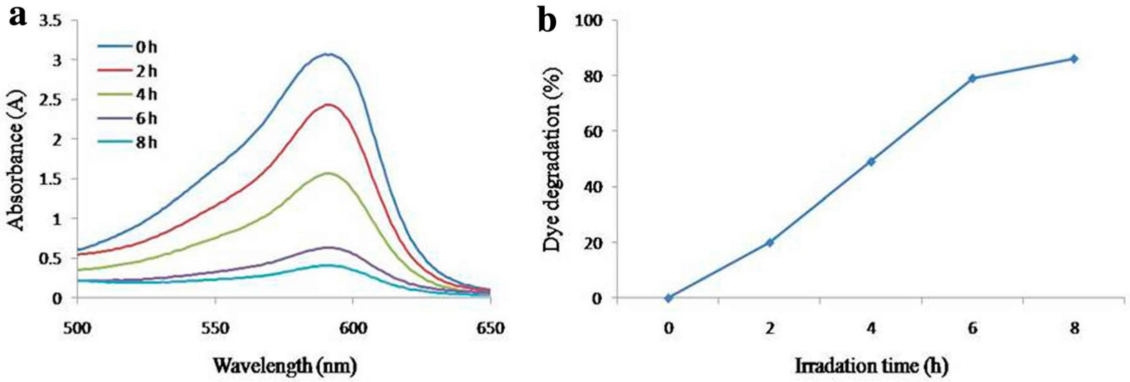


Fig. 4 **a** UV–Vis absorbance spectra of bromophenol blue photodegraded by TiO_2/GNP. **b** % Degradation of BPB by TiO_2/GNP at various time intervals

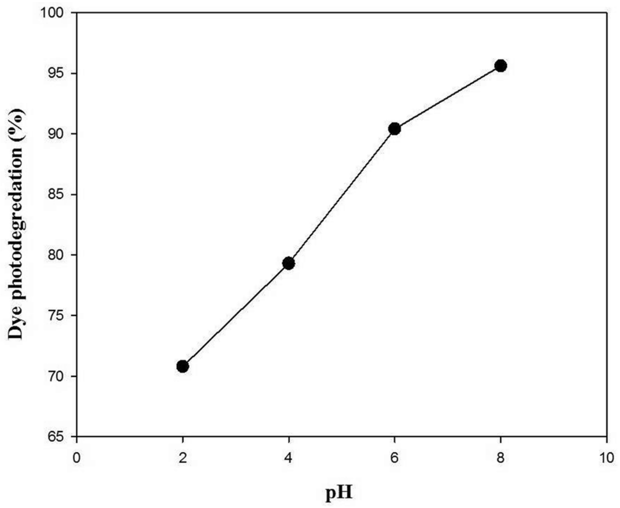


Fig. 5 Effect of pH on the photodegradation of bromophenol blue (%)

which presented that the degradation of dye increased as the pH of solution increased. The result (Fig. 5) showed that about 70% of the dye degraded at pH 2, which was gradually increased and about 79, 90 and 95% of bromophenol blue was degraded at pH 4, 6 and 8, respectively. The high degradation of bromophenol blue dye in basic medium might be due to the enhanced formation of hydroxyl radicals. These hydroxyl radicals are widely accepted as principal oxidizing species, which are responsible for degradation of organic dye high pH levels. Similarly, Kansal et al. (2009) also reported that the decolorization/degradation of Reactive Black 5 and Reactive Orange 4 dyes was increased as the pH increased, where they used TiO_2 and ZnO as a photocatalyst.

Effect of catalyst amount

The effect of catalyst dosage was also studied by using different amounts of catalyst (0.010 g, 0.020 g, 0.025 g and 0.030 g). Figure 6 shows the UV–Vis spectra of bromophenol blue in aqueous solution before and after degradation using different amounts of TiO_2/GNP photocatalyst. The spectra illustrated that the photodegradation of bromophenol blue increased as the quantity of catalyst increased. The increase in photodegradation of dye with increase in catalyst amount might be due to the increase in active sites, which results to increase the number of hydroxyl and superoxide radicals as a result, dye degrades significantly. Figure 6b shows the % degradation of bromophenol blue dye using different amounts of photocatalyst which declares that 0.01 g of TiO_2/GNP degraded 24% dye, which increased gradually up to 86% by using 0.03 g catalyst in 4 h.

Effect of the initial dye concentration

The effect of dye concentration on photodegradation rate of bromophenol blue was also carried out by studying photodegradation at various concentrations (25, 50,100,150 and 200 ppm) of dye. The results show that the rate of photodegradation of dye decreased as the dye concentration increased. The promising reason is that as increases in the initial dye concentration, the dye molecules get adsorb on surface of catalyst, which significantly absorb UV light rather than TiO_2 particles. It also decreases hydroxyl radical's formation because the active sites of photocatalyst are blocked by dye molecules (Saeed et al. 2017). Figure 7 shows % degradation of dye at different dye concentrations degraded by TiO_2/GNP, which illustrates that about 20 and 80% dye was decomposed at concentration of 200 and 25 ppm, respectively, in 4 h with constant catalyst dosage (0.02 g).

Effects of H_2O_2 on photodegradation

The effect of H_2O_2 on dye degradation rate was carried out by adding a small amount of H_2O_2 (0.01, 0.015, 0.02, 0.025 and 0.03 mL) to the dye solution by using catalyst amount (0.02 g) and constant time (30 min) under UV light irradiation. The result shows that the degradation of dye was significantly increased by addition of H_2O_2. Figure 8a shows

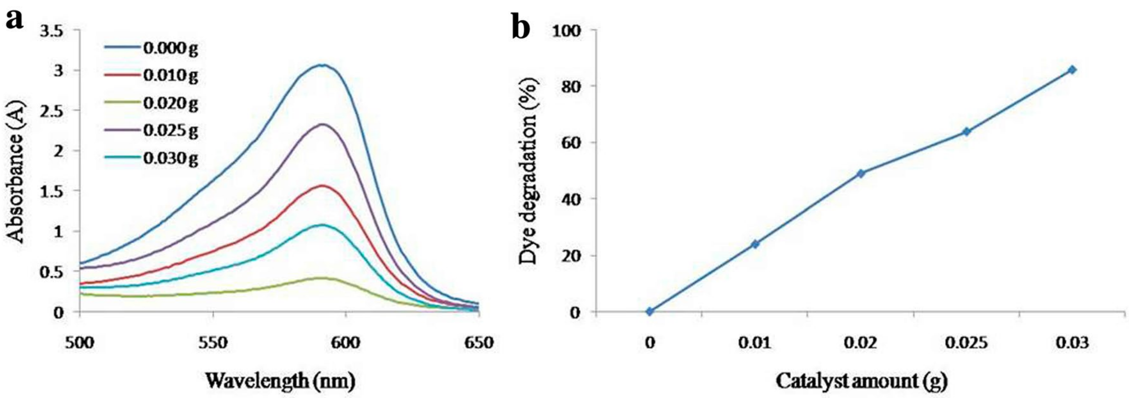
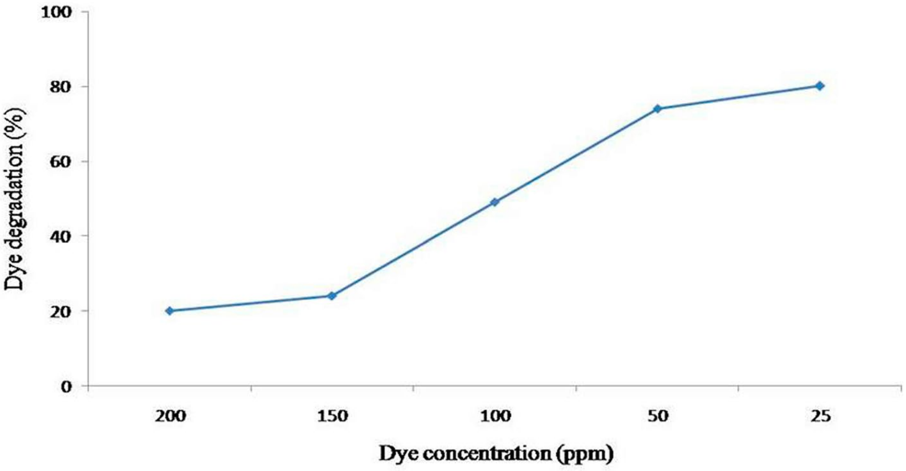


Fig. 6 **a** UV–Vis spectra of bromophenol blue dye by TiO_2/GNP. **b** % Degradation of bromophenol blue by TiO_2/GNP by various catalyst amounts

Fig. 7 % Degradation by TiO_2/GNP at various dye concentrations



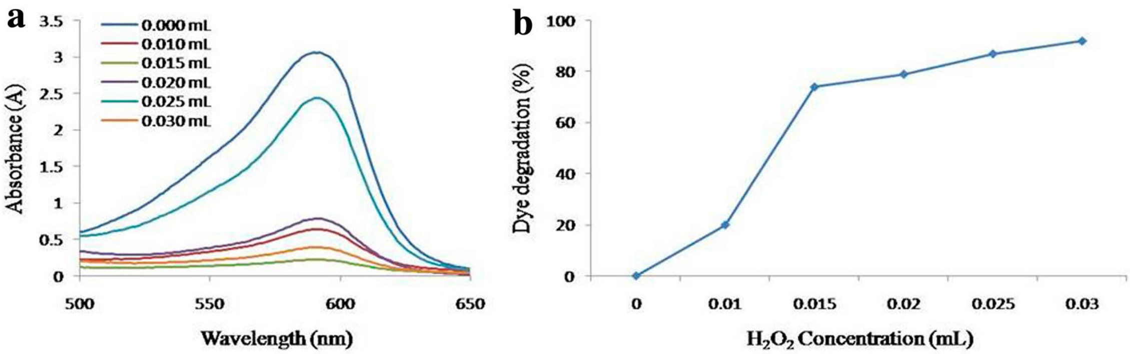


Fig. 8 **a** UV–Vis spectra of bromophenol blue photodegraded via TiO_2/GNP using different concentrations of H_2O_2. **b** % Degradation of MB by various concentrations of H_2O_2

the UV–Vis spectra of bromophenol blue using H_2O_2. The results presented that about 92% of bromophenol blue was photodegraded in 30 min of irradiation using minute amount of H_2O_2. Figure 8b shows that photocatalysts degraded about 20 and 92% MB dye using 0.01 and 0.03 mL of H_2O_2, respectively.

Conclusion

It is concluded that the morphological study showed that the TiO_2 particles were dispersed well on the surface of GNP. The GNP is not so effective for the photodegradation, but it provides large surface for the TiO_2 because TiO_2 is effective for the photodegradation. The results showed that about 86% of dye was degraded within 8 h. The dye degradation at pH 2, 4, 6 and 8 was about 70, 79, 90 and 95%, respectively. It means that the high pH is favorable for high photodegradation of bromophenol blue. The catalyst dosage study presented that 0.01 g of TiO_2/GNP degraded 24% dye, which increased gradually up to 86% by using 0.03 g catalyst. The increase in dye photodegradation with increase in catalyst quantity might be due to the enhanced active sites, which results to increase the number of hydroxyl and superoxide radicals, and as a result, significant photodegradation of dye occurs.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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