Original Article

Application of nanostructured graphene oxide/titanium dioxide composites for photocatalytic degradation of rhodamine B and acid green 25 dyes

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ABSTRACT

Graphene oxide/TiO₂ (X wt% GO/TiO₂, X = 3, 7, 10, 12 and 15) composites were synthesized by a hydrothermal method followed by calcination treatment at 300, 400 and 550 °C. These composites exhibit high efficiency for photocatalytic degradation of organic dyes such as rhodamine B (Rh B) and acid green 25 (AG-25) under UV-visible light irradiation. The photocatalytic degradation efficiency was influenced by the GO content, calcination temperature, dye concentration, photocatalyst dose, hydrogen peroxide concentration and initial pH. The samples were systematically evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-visible diffuse reflectance spectroscopy (DRS), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The results showed good distribution of TiO₂ nanoparticles on the GO surface. A significant enhancement in the photocatalytic degradation of dyes was achieved using 10 wt% GO/TiO₂ treated at 400 °C as a photocatalyst compared to pristine TiO₂ and/or other prepared samples, i.e., complete degradation of Rh B after 75 min and approximately 96% of acid green 25 after 180 min. This enhancement in photocatalytic degradation efficiency is attributed to the GO sheets, which are characterized by a high surface area that increases the adsorption capacity, a strong electron transfer ability and 2D, thin layers.

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1. Introduction

In the last few decades, interest in water and air purification using heterogeneous photocatalysis with semiconductor materials has notably increased [1]. These photocatalysts utilize different semiconductor photocatalysts, such as TiO₂, ZnO, Fe₂O₃, Bi₂WO₆, Bi₂O₃TiO₂, Ag₂CO₃, Nb₂O₅, BiTiO₃, SrTiO₃, Cu₂S/ZnS, ZnWO₄, WO₃, ZnS, and α-sulfur crystals, g-C₃N₄ and have established their effectiveness for pollutant degradation and complete mineralization [2-10]. TiO₂ is one of the most effective and attractive photocatalysts that has been investigated due to its low toxicity, low cost, high photocatalytic activity and high thermal and chemical stability [11,12].

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TiO₂ exists as three polymorphs: rutile, anatase and brookite phases. The rutile phase is considered the most stable form of TiO₂. Photocatalytic degradation remains a great challenge due to the large band gap of certain semiconductors that require UV radiation and have low absorption properties. The large band gaps limit the practical application of photocatalysis because only 4% of the sun’s energy that reaches Earth is UV radiation, while approximately 45% of the energy is visible light [13,14]. TiO₂ has a large band gap (3.2–3.0 eV) that is active under UV light [15]. To overcome this drawback, the band gap of TiO₂ particles should be reduced and absorption in the visible region enhanced. Different strategies have been employed to enhance the photocatalytic efficiency of TiO₂, including chemical modification by doping other components into TiO₂ crystals and morphological modification by increasing the porosity and surface area. Modification of TiO₂ for improved visible light photocactivity can be achieved by: (1) Metal doping that could introduce impurity energy levels near to valence band (VB) and conduction band (CB). In some cases, metal ions served as recombination centres due to formation of lattice defects. (2) Non-metal doping such as S, N, O, P and few others. After introducing non-metal to TiO₂ lattice, it makes red shift towards visible light to form new VB over the original one. An upward shift of VB and decrease of the forbidden band observed as a result of hybridization of p orbital of non-metals with O 2p. (3) Noble metal doping [16].

Separation of TiO₂ nanoparticles from aqueous media is difficult, so the nanoparticles are placed on supporting materials such as cellulose, zeolite, activated carbon, clay and ceramic, to allow easy separation and increase stability [17]. As a new carbonaceous material, graphene oxide (GO) has attracted significant attention in the past few decades for photocatalysis applications due to its unique properties, such as high surface area, flexible sheets, good thermal and electrical conductivity and excellent charge carrier mobility [18]. GO is an ideal material for use in optoelectronic devices, catalysis and energy conversion applications. This material is a novel catalyst promoter or carrier due to the abundance of reactive oxygen functional groups on the GO sheet surface [19]. Recently, attention has focused on the modification of TiO₂ using GO derivatives [13,17,20,21]. The VB and CB of graphene consist of two types of orbital bonding, i.e., π and antibonding π (π*) orbitals, which produce a single sheet of graphene with a zero band gap semiconductor [22]. Due to the close distance between carbon atoms, electrons and holes act as similar mass-free charge carriers, leading to electronic overlap. Introducing TiO₂ into nanostructured carbon materials, such as carbon nanotubes, fullerenes and GO sheets, can reduce charge recombination [23,24]. Here, we proposed a technique for preparing TiO₂ on GO sheets to achieve better photocatalytic degradation of some organic dyes.

2. Experimental

2.1. Materials

Chemicals were purchased and used without further purification. Flake graphite powder (99.95%) was purchased from Alpha Aesar. Concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), 30% hydrogen peroxide (H₂O₂), absolute ethanol, titanium (IV) isopropoxide, sodium hydroxide (NaOH), rhodamine B and acid green 25 were purchased from Sigma–Aldrich.

2.2. Preparation of GO

GO was synthesized according to the improved Hummer’s and Offeman method from graphite powder [19,25–29]. First, 2 g NaNO₃ was completely dissolved in 25 mL of concentrated H₂SO₄, and 2 g graphite powder (99.95%) was added to the solution to exfoliate the graphite flakes. Then, the mixture was kept in an ice bath at 0 °C with vigorous stirring for approximately 2 h. After that, 4 g KMnO₄ was slowly added over approximately 1.5 h (maintaining the temperature below 20 °C), and after cooling for 2 h, the mixture was a green colour. Second, the mixture was allowed to stand overnight at room temperature with vigorous stirring. As the reaction occurred, the mixture gradually thickened. Then, 100 mL of deionized H₂O was slowly added to the paste, causing violent effervescence, brown vapour evolution, resulting from the oxidation of KMnO₄, and an increase in temperature. The temperature was maintained at 98 °C until the end of the effervescence, and the colour of the suspension changed to brown. After 15 min, 200 mL of hot deionized H₂O was added to the mixture. Next, 30 mL of H₂O₂ (30%) was added when the temperature had cooled to 60 °C to eliminate the residual KMnO₄, and the suspension became a golden yellow colour with bubbling. Finally, the solution was washed 3 times with HCl (10%) and then with deionized H₂O to completely remove residual H₂SO₄, which was tested by BaCl₂. Then, the samples were dried at 80 °C under vacuum overnight to obtain GO sheets.

2.3. Preparation of TiO₂

0.5 g of cetyltrimethylammonium bromide (CTAB) in an anhydrous system of 25 mL absolute ethanol was stirred until completely dissolved. Then 12.02 mmol (3.56 mL) of titanium (IV) isopropoxide was added to the reaction mixture and stirred for 2 h. Next, 10 mL of deionized H₂O was added dropwise to the solution until a white precipitate formed. The suspension was stirred for 6 h, transferred into a Teflon-lined stainless-steel autoclave, heated at 180 °C for 8 h and then dried under vacuum at 90 °C. The white precipitate was annealed in a muffle furnace at 300, 400 or 550 °C at a rate of 10 °C/minute and held at the required temperature for 2 h.

2.4. Preparation of GO/TiO₂

GO/TiO₂ composites were synthesized by a hydrothermal method. Different percentages (3, 7, 10, 12 and 15 wt%) of GO and 0.5 g of CTAB were added to an anhydrous system of 25 mL absolute ethanol and stirred until the GO sheets were completely suspended to give a brown suspension. A calculated amount of titanium (IV) isopropoxide was added to the reaction mixture and stirred for 2 h. Then, 10 mL of deionized H₂O was added dropwise to the mixture until a grey precipitate formed. The samples were stirred for 6 h, transferred into a Teflon-lined stainless-steel autoclave, heated at 180 °C for 8 h,
and then dried under vacuum at 90 °C. The precipitate was annealed in a muffle furnace at 300, 400 and 550 °C for 2 h [30].

2.5. Characterization

X-ray diffraction (XRD) patterns of all the prepared samples were obtained at a high angle using a PW 150 instrument (Philips) with a Cu Kα radiation source with a Ni filter. The instrument was operated at a current of 45 mA and a voltage of 40 kV. The IR spectra were measured using a Nicolet 550 FTIR spectrometer in the range of 400–4000 cm⁻¹. Scanning electron microscopy (SEM) images were used for surface morphological evaluation and were obtained using a JEOL-JSM-6510LV scanning electron microscope, Japan. Transmission electron microscope (TEM) images and particle size were obtained using a JEOL-JEM-2100 transition electron microscope, Japan that operated at 200 kV. The TEM samples were prepared by dropping an alcohol suspension of the fine sample powders onto a copper grid coated with holey carbon foil and then drying the grid at ambient temperature. UV-visible diffuse reflectance spectroscopy (UV-visible DRS) measurements of the samples were recorded on a UV/visible/NIR spectrophotometer (V-570, JASCO, Japan). The samples were analysed by a PHI 5800 ESCA system, Physical Electronics, USA, instrument at 45° in FAT mode with an X-ray gun and Mg target (1486.6 eV) at a power of 12 kV, an analytical background vacuum of 2 × 10⁻⁷ Pa, a channel energy of 93.90 eV and a step length of 0.1 eV/s. The surface of the samples was sputtered with Ar⁺ ions to eliminate interferences from contaminants and subsequently preserved under high vacuum. To determine the concentrations of the dye solutions, we used a Unicam 5625 UV/visible spectrophotometer (Perkin Elmer, USA).

2.6. Photocatalytic activity

The photocatalytic activities of the samples were evaluated by monitoring the degradation of Rh B and AG-25 dyes under UV/visible-light irradiation. A Hg lamp was purchased from Westinghouse, UAE, and the reaction temperature was kept at 35 °C. The degradation of dyes was performed in a system consisting of 50 mL of dye with a concentration of 10 mg/L for Rh B and 40 mg/L for AG-25 using a 1.0 g/L photocatalyst concentration. The suspension was magnetically stirred in the dark for 1 h to reach adsorption/desorption equilibrium. At given time intervals, 1.0 mL of sample was diluted 10 times with deionized H₂O and then centrifuged until complete separation was achieved. The samples were analysed by UV-visible spectrophotometry at the wavelengths (λmax) 554 and 642 nm for the Rh B and AG-25 dyes, respectively.

3. Results and discussion

3.1. Characterization of GO/TiO₂ photocatalysts

TiO₂ particles were prepared by a hydrothermal method in the presence of the CTAB capping agent. The intense peak at 2θ = 26.4° in the graphite flake XRD pattern is shown in Fig. 1a. During oxidation of the graphite powder, oxygen atoms were introduced as different functional groups, such as —OH, —COOH and epoxy groups, which attached to the graphite planner surface [27]. Fig. 1b shows a broad band at 2θ = 10.7°, which corresponds to the [200] crystal plane of the GO sheets. The XRD patterns of the graphite flakes and GO showed that the inner spacing (d) increased from 0.34 Å (graphite flakes) to 0.82 Å (GO) due to the presence of a large number of oxygenated functional groups on the surface of the GO sheets and due to the increasing oxidation degree, the peak shifted to a lower angle (2θ) [18]. The characteristic peak of the graphite flakes was not observed in the pattern of GO, which can be explained by the small lateral size of the GO sheets, as shown in the SEM images. Although the GO sheets are stacked due to self-assembly through van der Waals forces and hydrogen bond and the GO sheets have enough disorder that they do not produce the signature π–π stacking diffraction peak [31], Fig. 2 shows the XRD patterns of TiO₂ at different calcination temperatures. As the calcination temperature increased from 300...
to 400 and 550 °C, the signals for anatase (tetragonal), polymorphous TiO₂ increased. At 550 °C, the XRD pattern shows a pure anatase structure with peaks at 2θ = 25.28, 37, 37.8, 38.6, 48.1, 53.9, 55.1, 62.1, 62.7, 68.8, 71.3 and 75°, which can be indexed to the [101], [103], [004], [112], [200], [105], [211], [213], [204], [116], [220] and [215] crystal faces of TiO₂, respectively [32]. The average crystal size of the TiO₂ nanoparticles treated at 300, 400 and 550 °C was estimated by Scherrer’s equation for the [101] crystal face. The crystallite size was 5.9, 10 and 18.1 nm for TiO₂ at 300, 400 and 550 °C, respectively. When the composites were calcined above 400 °C, the anatase crystals within the agglomerates were sintered, and the crystals grew through coalescence, which transformed the original agglomerate into a single anatase grain; thus, the crystal size of the prepared TiO₂ samples increased [18]. This result indicated that a good distribution of TiO₂ nanoparticles as shown in Figs. 3 and 4. No other peaks shown in the XRD patterns of prepared titania, which indicates that no other metal ions have entered into TiO₂ lattice [33]. The lack of the characteristic peak for GO at 2θ = 10.7° may be attributed to the low concentration of GO or the excellent distribution of TiO₂ nanoparticles coating the surface leading to good exfoliation of the GO sheets in the nanocomposites [26,27,34,35].

Fig. 5a shows the FT-IR spectra for the graphite flakes and GO, which display a band at 3433 cm⁻¹ that is characteristic of the stretching vibration of the OH functional group that forms during the oxidation of graphite flakes. The bands at 1726 cm⁻¹ appeared due to the C=O stretching vibration. Those at 1635 cm⁻¹ indicate the C=C stretching vibration and 1600 cm⁻¹ represent unoxidized graphite domains. We also noted the characteristic bands for the C=OH and C=O stretching vibrations at 1222 and 1051 cm⁻¹, respectively [36]. As shown in Fig. 6, the bands in the GO/TiO₂ composites are the same as those of GO, as previously illustrated. Fig. 7 shows that the intensity of the bands decreased with increasing calcination temperature of 10 wt% GO/TiO₂.

SEM and TEM images for GO are displayed in Fig. 8a and b, and the images reveal thin, randomly aggregated and crum-
pled sheets close to each other, forming a disordered solid [37]. The aggregated and crumpled surfaces formed because of the high surface area of the GO sheets. Fig. 8c–k show the TEM images of pure TiO₂, 3, 10 and 15 wt% GO/TiO₂ calcined at 400 and 550 °C. The GO loaded with TiO₂ presents a good distribution of TiO₂ nanoparticles on the surface of the GO sheets at low temperature, and the TiO₂ nanoparticles may self-assemble on the surface of GO during the preparation process [17]. The TiO₂ nanoparticles were highly distributed upon increasing the GO concentration. In the case of increasing the calcination temperature to 550 °C, the TiO₂ nanoparticles tended to aggregate as large particles due to crystal growth, as shown in Fig. 8g, i and k, which matches the XRD results. Fig. 8l–n show pure TiO₂ (300 °C), pure TiO₂ (400 °C) and 10 wt% GO/TiO₂ (400 °C). The anatase structure was confirmed by selected area electron diffraction (SAED), which proves polycrystalline nature of the polymorphs [38]. The bright diffraction rings of SAED, associated with anatase structure, was consistent with the results obtained from XRD [39,40]. The SAED pattern shows clear ring diffraction patterns and does not indicate dislocations in the lattice planes, which confirmed that the prepared TiO₂ nanoparticles have a high crystallinity. A comparison study of the crystal sizes of the composites obtained from the XRD patterns and TEM images. As the calcination temperature increased, a larger crystal size was obtained because above 400 °C the anatase crystals within the agglomerates are sintered, and the crystals grow through coalescence, transforming the original agglomerate into a single anatase grain and increasing the crystal size of the prepared TiO₂ samples [18].

Fig. 7 – FTIR spectrums of 10 wt% GO/TiO₂ calcined at (a) 300 °C, (b) 400 °C and (c) 550 °C.

The aggregated and crumpled surfaces of the GO sheets, which are present in the TEM images of pure GO and GO/TiO₂, are due to the formation of Ti-O bonds between GO and TiO₂ during the calcination process [17,37]. The TiO₂ nanoparticles are highly distributed upon increasing the GO concentration in the GO/TiO₂ mixture [37]. The GO/TiO₂ nanoparticles tend to aggregate as large particles due to crystal growth, as shown in Fig. 8g, i and k, which matches the XRD results. Fig. 8l–n show pure TiO₂ (300 °C), pure TiO₂ (400 °C) and 10 wt% GO/TiO₂ (400 °C). The anatase structure was confirmed by selected area electron diffraction (SAED), which proves polycrystalline nature of the polymorphs [38]. The bright diffraction rings of SAED, associated with anatase structure, was consistent with the results obtained from XRD [39,40]. The SAED pattern shows clear ring diffraction patterns and does not indicate dislocations in the lattice planes, which confirmed that the prepared TiO₂ nanoparticles have a high crystallinity. A comparison study of the crystal sizes of the composites obtained from the XRD patterns and TEM images. As the calcination temperature increased, a larger crystal size was obtained because above 400 °C the anatase crystals within the agglomerates are sintered, and the crystals grow through coalescence, transforming the original agglomerate into a single anatase grain and increasing the crystal size of the prepared TiO₂ samples [18].

Fig. 8a shows DRS UV–visible spectra for modulation the band gap energy (Eg) of the prepared composites calculated from Kubelka–Munk transformation Eq = 1240/λ, where λ is the cut off wavelength [41]. The term of the band gap is the energy from the top of the VB to the bottom of the CB. For the pure titania, the absorption threshold energy is about 393.5 nm, which is corresponding to band gap about 3.16 eV. The band gap energy for 3, 10 and 15 wt% GO/TiO₂ are 3.06, 2.98 and 2.3 eV, respectively. The red shift of λ value to visible light is due to incorporation of graphene oxide into titania lattice [42]. The results obtained in case of composites calcined at 550 °C but the band gap energy decreased by lower extent than in case of 400 °C as shown in Fig. 8b.

The GO was examined by XPS, and the obtained spectrum provides an elemental analysis of the GO surface. The XPS spectrum of the GO sheets includes C(1s) and O(1s) signals (Fig. 10a). The symmetrical broad peaks of C(1s) suggest the existence of distinguishable species. By analysing the peak in the spectrum, three bands at 284, 285.6 and 288.6 eV were deconvoluted. The sharp peak at 284 eV can be attributed to sp² hybridized carbons (C–C). The peaks at 285.6 and 288.6 eV are due to the existence of C–OH and C–OOH bonds (Fig. 10b) [19,27,43–46]. The band at a high energy of 532 eV may be attributed to the C–O bond originating from residual oxygen-containing groups and/or residual water (Fig. 10c) [18].

3.2. Photocatalytic degradation of Rh B and AG-25 using GO/TiO₂ composites

3.2.1. Photocatalytic degradation of Rh B and AG-25

Photocatalytic degradation of Rh B and AG-25 dyes under UV-visible light in the presence of pure TiO₂ particles resulted in nearly 75% degradation of the dyes after 60 and 90 min, respectively. This percentage increased when GO was used as a dopant. GO allows the incident UV and/or visible radiation to penetrate the TiO₂ nanoparticles and proceed with the photocatalytic degradation. As shown in Fig. 11a and b, increasing the GO content to 10 wt% GO/TiO₂ increased the photocatalytic degradation efficiency of Rh B and AG-25. With a high concentration of GO, the photocatalytic activity decreased, which can be explained by the increasing light absorption into the GO sheets and the lower relative content of TiO₂ for the generation of radicals [47]. GO acts as an adsorbent for organic contaminants that diffuse to the phase boundary or the interphase to undergo effective degradation. A higher GO content results in more oxygen-containing groups, such as hydroxyl,
epoxy and carboxyl groups, leading to high ionic-electronic interactions with contaminants. The GO sheets also act as an electron scavenger to increase the electron transfer rate of TiO$_2$ particles, which enhances the photocatalytic properties and inhibits charge carrier recombination. Additionally, during the photocatalytic degradation process, the GO sheets may be reduced to graphene under UV radiation and regenerate electrons. This action can lead to an increase in the possibility of $\pi$-$\pi$ interactions with organic contaminants to enhance charge separation [21].
Fig. 9 – Band gap modulation for pure (a) TiO₂, 3, 10 and 15 wt% GO/TiO₂ calcined at 400 °C. (b) TiO₂, 3 and 10 wt% GO/TiO₂ calcined at 550 °C.

Fig. 10 – XPS analysis (a) Graphene oxide sheets, (b) Peak analysis of C (1 s). (c) Peak analysis of O (1 s).

Fig. 11 – Photocatalytic reaction using different contents of GO loaded on TiO₂ nanoparticles used in degradation of (a) Rh B and (b) AG-25.

In the present work, the kinetics of photocatalytic degradation of Rh B is fitted using Langmuir–Hinshelwood model as expressed in Eq. (1).

\[
r = \frac{dC}{dt} = \frac{kKC}{1 + KC}
\]  

where \( r \) is the photocatalytic degradation rate (mg/(L minute)), \( t \) is the illumination time (minute), \( C \) is the dye concentration, \( k \) is the reaction rate constant (mg/(L minute)) and \( K \) is the adsorption coefficient of the dye (L/mg). Fig. 12a shows the photocatalytic degradation of Rh B under UV/visible light, which can be described as a first-order reaction with a rate constant of 0.051 min\(^{-1}\) (\( R^2 = 0.984 \)). Fig. 12b shows the first-order reaction for the degradation of AG-25 with 10 wt% GO/TiO₂, which has a rate constant of \( 1.577 \times 10^{-6} \) min\(^{-1}\) (\( R^2 = 0.984 \)), as illustrated in Table 1. Table 2 shows a comparison studies of present and pervious works on degradation of Rh B and AG-25.

3.2.2. Effect of the dye concentration
An experiment was conducted with different concentrations of the dyes, i.e., 10, 20, 30 and 50 mg/L for Rh B and 20, 40, 70...
Table 1 – Rate constants and $R^2$ on photocatalytic degradation reaction using GO/TiO$_2$ composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>[Rh B]</th>
<th>[Acid green 25]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Pure TiO$_2$ (400 °C)</td>
<td>0.033</td>
<td>0.942</td>
</tr>
<tr>
<td>3 wt% GO/TiO$_2$ (400 °C)</td>
<td>0.037</td>
<td>0.978</td>
</tr>
<tr>
<td>7 wt% GO/TiO$_2$ (400 °C)</td>
<td>0.034</td>
<td>0.981</td>
</tr>
<tr>
<td>10 wt% GO/TiO$_2$ (400 °C)</td>
<td>0.051</td>
<td>0.984</td>
</tr>
<tr>
<td>12 wt% GO/TiO$_2$ (400 °C)</td>
<td>0.041</td>
<td>0.948</td>
</tr>
<tr>
<td>15 wt% GO/TiO$_2$ (400 °C)</td>
<td>0.036</td>
<td>0.985</td>
</tr>
</tbody>
</table>

and 100 mg/L for AG-25, with 1.0 g/L of 10 wt% GO/TiO$_2$ photocatalyst. Fig. 13a and b show that as the initial concentration of the dye increased, the photocatalytic degradation efficiency decreased because the amount of light absorbed by the photocatalyst decreased. Light radiation has difficulty penetrating a solution with a high concentration of dye. The concentration of organic pollutants such as dyes may affect the photocatalytic degradation mechanism. At low concentrations, both the photoinduced electron and hole participate in degradation by the typical mechanism. However, at high concentrations, the degradation mechanism depends on the contact angle of the photocatalyst, and the radical concentration is not as high as that in the previous mechanism due to pollutant or dye molecules blocking the active centres on the catalyst surface, resulting in a large amount of dye remaining [51].

3.2.3. Effect of the photocatalyst concentration

One of the most important factors influencing the kinetics of photocatalytic degradation is the catalyst concentration. An experiment was carried out using four different concentrations, 0.5, 1.0, 1.5 and 2.0 g/L, of the photocatalyst. As shown in Fig. 14a and b upon increasing the concentration of photocatalyst from 0.5 g/L to 2.0 g/L, the photocatalytic degradation of dyes increased. Additionally, by increasing the photocata-

Table 2 – Comparison of the previous studies of photocatalysts for degradation of Rh B and AG-25.

<table>
<thead>
<tr>
<th>Photocatalyst materials</th>
<th>Dye concentration (mg/L)</th>
<th>Dose (g/L)</th>
<th>Duration (min.)</th>
<th>Degradation %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$PO$_4$@GO</td>
<td>6</td>
<td>1.0</td>
<td>40</td>
<td>100</td>
<td>[48]</td>
</tr>
<tr>
<td>Bi$_2$S$_3$/3DOM-TiO$_2$</td>
<td>10</td>
<td>9.0</td>
<td>360</td>
<td>95</td>
<td>[49]</td>
</tr>
<tr>
<td>TiO$_2$@GO</td>
<td>20</td>
<td>0.6</td>
<td>210</td>
<td>100</td>
<td>[50]</td>
</tr>
<tr>
<td>TiO$_2$@GO (Rh B)</td>
<td>20</td>
<td>1.0</td>
<td>120</td>
<td>100</td>
<td>Our work</td>
</tr>
<tr>
<td>TiO$_2$@GO (AG-25)</td>
<td>40</td>
<td>1.0</td>
<td>180</td>
<td>97</td>
<td>Our work</td>
</tr>
</tbody>
</table>
3.2.3.4. Photocatalyst dependence of the photocatalyst performance on the initial pH for the photocatalytic degradation of Rh B dye. The optimum pH for Rh B was 4, and the optimum pH was 2 for AG-25 using 10 wt% GO/TiO₂, which proves that dyes tend to degrade in acidic media. Any change in the initial degradation rate with the varying initial pH can be attributed to the acidic/basic characteristics of the TiO₂ nanoparticles on the surface [52]. The initial pH of the solution affects the photocatalytic degradation of dyes, but it is very difficult to isolate the pH effect because of its multiple roles. First, an ionized species forms on the surface of the photocatalyst, according to Eqs. (9) and (10).

\[
\begin{align*}
\mathrm{TiOH} + \mathrm{H}^+ & \rightarrow \mathrm{TiOH}_2^+ \quad (9) \\
\mathrm{TiOH} + \mathrm{HO}^- & \rightarrow \mathrm{TiO}^- + \mathrm{H}_2\mathrm{O} \quad (10)
\end{align*}
\]

Second, hydroxide ions and positive holes interact with each other, producing hydroxyl radicals (HO•). At low pH, positive holes are the major oxidant species, whereas HO• is the predominate species at neutral and high pH values. It is easy to generate hydroxyl radicals by oxidizing hydroxide ions on the surface of TiO₂ in alkaline media. At a high pH, there is repulsion between the negative charges on the photocatalyst surface and the hydroxyl radicals that inhibits photodegradation.

Third, in acidic media, TiO₂ particles tend to agglomerate, which decreases the adsorption of dye molecules and photons. TiO₂ particles tend to adsorb cationic dyes better than anionic dyes, where the pH depends on the charge [59].

3.2.3.3. Reusability of photocatalysts. The catalyst with high performance in photocatalytic degradation of Rh B and AG-25 selected to measure the recyclability and stability. From the general trend of the curve, photocatalytic activity decreases from 100% to 91% and from 96.2% to 88% after the fourth run in case of Rh B and AG-25, respectively (Fig. 17a and b). These tests conducted after an hour of adsorption for each run. The loss of activity is small and can be neglected that may attributed to the diminution of adsorption property of composites. It can be concluded that, the prepared photocatalysts can reused many times with high stability and performance during degradation of different organic dyes.

Photocatalyst concentration, the number of photons adsorbed on active sites increased, and the number of adsorbed dye molecules increased with the amount of photocatalyst [52–56].

3.2.3.1. Effect of hydrogen peroxide (H₂O₂). Fig. 15a shows the effect of 0.5, 1.0 and 2.0 mL of H₂O₂ on the photocatalytic degradation of Rh B dye. Approximately 95.5% of the dye photodegraded after 20 min using 2.0 mL H₂O₂. Upon increasing the H₂O₂ concentration, the degradation and number of adsorbed dye molecules both increased. The addition of H₂O₂ has two important functions. First, it increases the amount of the hydroxyl radical (HO•), which inhibits recombination of photoinduced holes and electrons, Eq. (2).

\[
e^- (\text{TiO}_2) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2 + \cdot \text{OH} + \cdot \text{OH} \quad (2)
\]

The second function of H₂O₂ is promoting charge separation by accepting the electron in the conduction band to form \(\cdot\text{OH}\), as expressed in Eqs. (3) and (4) [46,57,58].

\[
\begin{align*}
\text{H}_2\text{O}_2 + e^- & \rightarrow \cdot \text{OH} + \cdot \text{OH} \quad (3) \\
\text{H}_2\text{O}_2 + \text{O}_2^- & \rightarrow \cdot \text{OH} + \cdot \text{OH} + \text{O}_2 \quad (4)
\end{align*}
\]

In the case of AG-25, increasing the concentration of H₂O₂ resulted in a decrease in the photocatalytic degradation, as shown in Fig. 15b. A high concentration of H₂O₂ may inhibit the oxidation rate because of very reactive hydroxyl radicals, and H₂O₂ may consume the valance band holes (Eqs. 5–7). Additionally, a competitive reaction due to radical-radical recombination must be considered (Eq. 8) [59].

\[
\begin{align*}
\cdot \text{OH} + \text{H}_2\text{O}_2 & \rightarrow \cdot \text{OH}_2^- + \text{H}_2\text{O} \quad (5) \\
\cdot \text{OH} + \cdot \text{OH}_2^- & \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (6) \\
\text{TiO}_2 (\text{h}^+_\text{VB}) + \text{H}_2\text{O}_2 & \rightarrow \text{TiO}_2 + 2\text{H}^+ + \text{O}_2 \quad (7) \\
\cdot \text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad (8)
\end{align*}
\]

3.2.3.2. Effect of the initial pH of the dye solution. The effect of the solution pH on the degradation of Rh B was studied at pH values of 2, 4, 6, 8 and 10. Fig. 16a and b show the strong
Photocatalysis depends on the semiconductor materials which interact with certain wavelength (or sufficient energy) to generate reactive oxidizing species (ROS) which play the main role in degradation of organic pollutants. There are two simultaneous processes take place in order to produce a highly reactive oxidizing species. The first is oxidation of adsorbed H$_2$O molecules by hole and the second involves the reduction of dissolved oxygen by exited electrons, these two processes generate hydroxyl and superoxide anion radical. In photocatalysis, the photons energy must equal or greater than the band gap energy ($E_g$) of the semiconductor. Certain energy required to shoot each photon of the outer occupied orbital of the valance band (VB) and excited to the unoccupied orbital of the conduction band (CB) in the semiconductor materials.

In case of anatase structure, the energy of light ($\lambda \leq 387$ nm) is required due to the band gap is 3.2 eV. The absorption of energy excites an electron from the valance band forming positively charged hole ($h^+_\text{VB}$) to conduction band generating an electron ($e^-_{\text{CB}}$) Eq. (11).

$$\text{TiO}_2 + h\nu \rightarrow h^+_\text{VB} + e^-_{\text{CB}}$$  \hspace{1cm} (11)

$\text{Ti}^{3+}$ and $O^{-}$ defect sites trapped as charge carriers in the TiO$_2$ lattice or they disperse the energy by recombination process. Positive holes oxidize H$_2$O and HO$^-$ at the surface producing hydroxyl radical (HO$^*$) Eq. (12) which is the strongest oxidants with oxidation potential equal 2.8V. The organic
species can be oxidized by the HO* producing CO₂, H₂O and mineral acids Eq. (15).

\[ h_{\text{VB}}^+ + e_{\text{CB}}^- \rightarrow \text{Energy} \]  
(12)

\[ \text{H}_2\text{O} + h_{\text{VB}}^+ \rightarrow \text{HO}^* + \text{H}^+ \]  
(13)

\[ \text{O}_2 + e_{\text{CB}}^- \rightarrow \text{O}_2^{**} \]  
(14)

Titania particles adsorbed molecular oxygen on its surface which trap electrons in the conduction band producing superoxide radical anion by reduction reaction Eq. (14) that may react with H⁺ to produce hydroperoxyl radical followed by reduction reaction producing H₂O₂ Eqs. (16) and (17). The reactive oxygen species may pass another way for degradation of organic pollutants in the aqueous solution Eqs. (18) and (19) [60].

\[ \text{HO}^* + \text{Pollutant} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]  
(15)

\[ \text{O}_2^{**} + \text{H}^+ \rightarrow \text{HO}_2 \]  
(16)

\[ \text{HO}_2^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
(17)

\[ \text{O}_2^{**} + \text{Pollutant} \rightarrow \text{H}_2\text{O}_2 + \text{CO}_2 \]  
(18)

\[ \text{HO}_2^* + \text{Pollutant} \rightarrow \text{H}_2\text{O}_2 + \text{CO}_2 \]  
(19)

GO sheets may act as electron conductor that accelerate the electron-hole separation and prompt the rate of electron migration. Strong oxidizers like O₂** and HO* produced from migration of electron to CB of TiO₂ that reacted to oxygen species distributed along the GO surface. Photocatalytic activity enhanced as a result of GO sheets prolong the charge carrier separation, which generate more active oxidizing species [61].

To determine the photodegradation mechanism, different quenchers like EDTA, benzoquinone and methanol were used to trap holes, superoxide anion and hydroxyl radicals, respectively [62]. This experiment carried out at constant concentrations of inhibitors with fixed amount of catalyst that added to dye solutions. As shown in Fig. 18, additives inhibit the photocatalytic degradation of dyes. EDTA and methanol show the lowest degradation of dyes that proved that holes and hydroxyl radicals, respectively. The rate decreased in case of benzoquinone, which indicates superoxide anion radicals also necessary for photodegradation process [63].

4. Conclusion

A facile technique was used for the synthesis of GO/TiO₂ composites by hydrothermal methods. Different contents of GO were incorporated into TiO₂ nanoparticles to enhance the photocatalytic degradation activity. The most effective sample was 10 wt% GO/TiO₂, which enhanced the degradation of Rh B and AG-25 dyes. Samples were calcined at 300, 400 and 550 °C, and the optimal calcination temperature was 400 °C. Many experiments were conducted to study the effect of the dye concentration, photocatalyst dosage, concentration of H₂O₂ and initial pH of the solution. By increasing the dye concentration, the photocatalytic degradation efficiency decreased, but the degradation efficiency was enhanced by increasing both the concentration of the photocatalyst and/or the H₂O₂ concentration for Rh B. The optimum pH for the degradation of the dye was 4 for Rh B and 6 for AG-25. The prepared samples were examined by X-ray diffraction, TEM, FT-IR, UV/visible DRS and XPS.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


