Nanocomposites of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO were prepared by in situ oxidation polymerization method. The prepared TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO Nanocomposites were characterized by the XRD, SEM, TEM, BET, UV-Vis, FTIR, Band gap energy and Photolumiscence. The XRD confirmed the presence of Anatase and rutile phase in the prepared photocatalysts. The average particle size was found 68, 15 and 12 nm for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO respectively. The SEM and TEM images also confirmed the formation of nanocomposites in the range of ~ 100 nm. The surface area 37.52, 76.68 and 96.24 m$^2$/g were observed for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO Nanocomposites respectively. The Band gap energy of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO were calculated by talc plot and obtained 3.0, 2.86 and 1.76 eV respectively. The Photocatalytic degradation of Rose Bengal dye was done at different condition viz concentration of dye, time of illumination, pH and dose of photocatalyst. The maximum photodegradation were found at neutral pH, 6.25 ppm concentration of dye solution, 800 mg/L amount of photocatalyst and 120 min irradiation of visible light. The Photocatalytic degradation of Thymol blue dye was done at the different conditions viz concentration of dye, time of illumination, pH, and the dose of the photocatalyst. The photodegradation of Thymol blue was found 98-99%, 72-93% and 12-17% presence of TiO$_2$/PAni/GO, TiO$_2$/PAni and TiO$_2$ respectively. Kinetics of photodegradation was investigated for Rose Bengal and Thymol blue dye and found first order kinetics The coating of PAni and GO were enhanced the photocatalytic activity of Titania. Hence TiO$_2$/PAni and TiO$_2$/PAni/GO are the efficient photocatalyst for the degradation of Rose Bengal B dye than pure TiO$_2$. 
5.1. Introduction

The major source of environmental pollution is the wastewater effluent of textile industries. The textile industries are using the very large amount of chemically stable dyes which causing water pollution. Several investigations reported that about 12% of dyes used in textile industries in each year. During the manufacturing and processing, 20% dyes are lost in environment such as Rose Bengal, Caramine, Rhodamine, Indigo Red, Thymol blue, Red 120, Eriochrome Black-T (EBT), Methylene Blue [2, 3]. Textile industries effluents contain coloured pigments which is causing carcinogenic effect on human being and also causing serious impact on aquatic life. There are lots of dyes used in the textile industries. The xanthene dyes are mostly used in textile industries. Xanthene dyes can be characterized by presence of xanthenes nucleus with aromatic groups as chromophore [4, 5]. Rose Bengal is a significant xanthene dye and widely used in textile and photochemical industries whose molecular structure as shown in Figure 1. Rose Bengal shows the severe toxic effects on the human health and also affects the corneal epithelium [6]. It is very hazardous for human being because it causes the irritation, itchiness, blistering and reddening. It is also affects on human eyes like eye redness, inflammation, itching etc. [8]. There are several, physical and chemical methods have been studied to remove the organic dyes such as Rose Bengal, Methylene blue etc. from the wastewater. Physical techniques like photo degradation, coagulation, flocculation, reverse osmosis, adsorption on the activated carbon, ion exchange method and ultra-filtration, have been used to reduce the toxic effects of dye effluents. Furthermore, various chemical methods like photosensitized oxidation, adsorption, photofenton’s reactions are also employed for removal of dyes. These techniques are not effective to remove the trace amount of dye from the waste water. Therefore we need green technology through which we can remove the dyes from the waste water. The photocatalytic degradation is the very advance oxidation process to remove the dye without any side product formation.

Titanium dioxide (TiO₂) is the mostly used photocatalyst due to its non-toxicity, high activity, photo stability, chemical stability, biological inertness, the good absorption, desorption rate of reactants and low cost [4]. TiO₂ photocatalyst has been applied to self-cleaning glasses, antibacterial tiles etc. as it has strong oxidizing power.
to decompose most organic compounds to CO$_2$ [5]. Organic compounds such as halogeno-aliphatic hydrocarbons, halogeno aromatic hydrocarbons, organic acids, colouring matters, nitro aromatic hydrocarbons, substituted anilines, multi-ring aromatic hydrocarbons, hydroxybenzenes, surface active agents, and pesticides can be changed into non-toxic, decoloured inorganic compounds and ultimately eliminated as pollutants [6].

It is very interesting fact that TiO$_2$ absorbs only 5% UV portion of the solar light spectrum. There are two issues namely, limitation of light absorption by TiO$_2$ in the UV portion of the solar light spectrum and recombination of electron (e-) - hole (h+) pairs. Several researches have been done to synthesized modified nanocomposites for the utilization of solar light [9]. Consequently, hundreds of TiO$_2$ variants and other oxide/non-oxides have been developed and tested in propose to conquer the recombination process [10]. It is believed that availability of visible light absorbing photocatalysts would largely solve the technological problems photo reactor considerations. Moreover, harnessing sunlight can be considered as a More recently, some groups have used conducting polymers to modify TiO$_2$ to improve visible light photoactivity and electron transfer performance; e.g., Polyaniline/TiO$_2$ [11], polypyrrole/TiO$_2$ [12] and polythiophene/TiO$_2$ [13]. Many published reports focussed on the preparation and photo catalytic studies on nanocomposites consisting of polyaniline and TiO$_2$ (PAni/TiO$_2$) [14-17]. Among these, PAni has several advantageous features over others because of its good environmental stability, ease of synthesis, controllable doping/dedoping chemistry, and reversible electrical properties by controlled charge transfer processes [18, 19].

The incorporation of inorganic nanomaterials into PAni, thereby forming nanocomposite materials, appears to be an effective approach for preparing photocatalytic materials [20]. Some study reported that by adding graphene to PAni, there is an increase in the electric double-layer capacitance as well as charge transfer and charge transport [21].

In this study, the nanocomposites of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO were prepared by the co-deposition oxidation method. The prepared materials were characterized by the XRD, BET, TEM, SEM, UV-Vis, Band gap energy,
Photoluminescence spectra, and FTIR. The prepared materials were used as photocatalyst for the photodegradation of Rose Bengal dye in the visible light. The photodegradation of Rose Bengal has been done at different chemical parameters i.e. pH of solution, concentration of dye, amount of photocatalyst, photocatalyst, time of irradiation and recyclability of photocatalyst. The kinetic study of photodegradation has been performed and found the order of reaction.

![Molecular structure of Rose Bengal dye](image)

**Fig.5.1 Molecular structure of Rose Bengal dye**

### 5.2. Methods and materials

#### 5.2.1 Synthesis of Titanium dioxide

TiO$_2$ nanoparticles were prepared using H$_2$O$_2$ solution added to 10 ml of 1 mol/L ethanol solution of titanium tetra isopropoxide (TTIP). Ethanol was added to the brown coloured solution obtained, and the total volume of the solution was adjusted to 100 ml. The solution was then heated at 120°C for 1 hr in a closed vessel. The solution was filtered and obtained the solid material, further it was washed with double distilled water 2 to 3 time and dry in oven at 60 °C for 24 h. The obtained solid was calcined at 600°C for 3 hr to get white titanium oxide powder [22-23].

#### 5.2.2 Synthesis of TiO$_2$/PAni nanocomposite

The synthesis of the TiO$_2$/PAni nanocomposite was done by using aniline, TTIP as the TiO$_2$ precursor and Ammonium per sulphate as the oxidizing agent. In a typical process, 10 mL of CCl$_4$ and 4.0 mL of TTIP were placed in a beaker to which 1 mL of aniline were added. The entire system was stirred constantly on an ice bath. To the
above dispersion of aniline, the solution of oxidant (0.5 M APS in 500 mL of 1M HCl) was added drop-wise, which simultaneous initiated the polymerization of aniline and the synthesis of TiO\(_2\). The reaction mixture soon turned into greenish black slurry, which was filtered after 2 hours, and washed sequentially with an excess of water and acetone to remove the excess APS and PAni oligomers. The synthesized TiO\(_2\)/Pani nanocomposite was then de-doped with a 1M ammonia solution to neutralize the remaining acid, which converted the TiO\(_2\)/PAni nanocomposite to its emeraldine base (EB) form. To render it conductive, the EB of TiO\(_2\)/PAni nanocomposite was doped with 100 mL of 1M HCl solution for 12 hours, later filtered and dried in an air oven at 80 °C for 24 hours. Pure PAni was prepared in a similar manner but in the absence of TTIP. [24-25].

### 5.2.3 Synthesis of TiO\(_2\)/PAni/GO nanocomposite

The synthesis of the TiO\(_2\)/PAni nanocomposite was done by using aniline, TTIP as the TiO\(_2\) precursor and Ammonium per sulphate as the oxidizing agent. In a typical process, 10 mL of CCl\(_4\), 4.0 mL of TTIP and 60 mg of prepared Graphene oxide were placed in a beaker to which 1 mL of aniline were added. The entire system was stirred constantly on an ice bath. To the above dispersion of aniline, the solution of oxidant (0.5 M APS in 500 mL of 1M HCl) was added drop-wise, which simultaneous initiated the polymerization of aniline and the synthesis of TiO\(_2\). The reaction mixture soon turned into greenish black slurry, which was filtered after 2 hours, and washed sequentially with an excess of water and acetone to remove the excess APS and PAni oligomers. The synthesized Pani-TiO\(_2\) nanocomposite was then de-doped with a 1M ammonia solution to neutralize the remaining acid, which converted the TiO\(_2\)/PAni nanocomposite to its emeraldine base (EB) form. To render it conductive, the EB of TiO\(_2\)/PAni nanocomposite was doped with 100 mL of 1M HCl solution for 12 hours, later filtered and dried in an air oven at 80 °C for 24 hours.

### 5.2.4 Characterizations

The prepared TiO\(_2\)/PAni, TiO\(_2\)/PAni and TiO\(_2\)/PAni/GO nanocomposites were characterized by x-ray diffraction (XRD) patterns in the range of 2θ = 20–80°. The size of TiO\(_2\) particles was investigated with transmission electron microscope (TEM). The
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morphology of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO nanocomposites were investigated by scanning electron microscopy. Fourier-transform infrared (FTIR) was used for the bonding determination, UV-visible DRS was used for band gap energy determination and Photoluminescence was used for the hydroxyl radical mechanism determination and e$^-$-h$^+$ recombination determination.

5.2.5 Irradiation procedure
The dye and photocatalyst suspension were stirred in the dark for 30 min to reach adsorption equilibrium with the nanocomposites (TiO$_2$, PAni, TiO$_2$/PAni and TiO$_2$/PAni/GO) surface. Irradiation experiments of dyes were carried out on stirred aqueous solutions contained in a 100 mL beaker. Degradations were performed on 20 mL of aqueous solutions containing the desired concentration of Rose Bengal. The amount of nanocomposites material varies from 100 mg/L to 800 mg/L. Irradiations were carried out using one UV-365 nm, Hanovia lamp (450 W). At any given irradiation time interval, the dispersion was sampled (5 mL), centrifuged, and subsequently filtered through a Millipore filter to separate the TiO$_2$ particles and take UV-Vis spectra to determine the residual concentration [26].

5.2.6 Determination of Hydroxyl radicals
To determine whether reactive oxygen species involved in the photocatalytic degradation of dyes is hydroxyl radical or not, terephthalic acid photoluminescence probing technique was used. In this, alkaline solution of terephthalic acid, having TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposites was irradiated with visible light. After 30 min of irradiation, sample was withdrawn from the reaction mixture and was centrifuged to separate photocatalyst particles. The photoluminescence spectrum of sample was recorded between 335 and 600 nm at an excitation wavelength of 325 nm and variation in intensity of peak at 425 nm was monitored using Perkin Elmer LS 55 Fluorescence Spectrometer [27].

5.3. Results and discussion

5.3.1 Characterisation
5.3.1.1 X-Ray Diffraction

The XRD patterns of TiO₂, PANi, TiO₂/PANi, TiO₂/PANi/GO nanocomposite are showing in Fig 5.2. The XRD pattern of TiO₂ showing in Fig. 5.2(a) a series of characteristic peaks: \(2\theta = 25.32^\circ\) (101), 37.86° (103), 48.06° (200), 55.09° (211) and 62.75° (204) are observed due to the tetragonal anatase phase of TiO₂ (JCPDS file No: 86-1157). Fig.5.2 (b) showing the XRD pattern of PANi, a broad peak corresponding to the periodicity parallel to the polymer chain to (200) plane was observed at 19.26° 2\(\theta\) [28]. The peak at 2\(\theta\) ~25° due to the periodicity perpendicular to the polymer chain and other crystal planes at 2\(\theta\) ~15° was absent, which shows that the as-synthesized PANi is highly amorphous in nature. In the XRD pattern of the TiO₂/PANi nanocomposites (Fig.5.2c) the usual broad peak corresponding to the periodicity parallel to the polymer chain encompassing a slight crystalline small peak at 20° 2\(\theta\) was not observed. All the peaks corresponding to anatase TiO₂ were also present. In the XRD pattern of the TiO₂/PANi/GO nanocomposites (Fig. 5.2d), all the peaks corresponding to anatase TiO₂ were also present suggesting that the state of TiO₂ did not change during the polymerization process. On the other hand, a slight reduction in the peak intensity and red shift was observed for TiO₂ peaks in the TiO₂/PANi nanocomposite [29]. This might be due to the surface coating of PANi on TiO₂ during the polymerization process and the interactions between the TiO₂ nanoparticles and the PANi chain [30].

![Fig.5.2 XRD Pattern](image)

Fig.5.2 XRD Pattern of (a) TiO₂ (b) PANi (c) TiO₂/PANi (d) TiO₂/PANi/GO
5.3.1.2 FTIR

FT-IR spectra of TiO$_2$, PAni, TiO$_2$/PAni and TiO$_2$/PAni/GO are shown in Figure 5.3. In Figure 5.3(a), five peaks are observed due to O-Ti-O bond stretching (3418, 1628, 1502, 1302 and 1231 cm$^{-1}$) the main characteristic bands of polyaniline were seen in Figure 5.3b. The band at 3439 cm$^{-1}$ is attributable to N-H stretching. Also the band at 1663 cm$^{-1}$ assigned to N-H bend of a primary aromatic amine. The peaks at 1484 and 1419 cm$^{-1}$ belong to C-C stretch in ring and N-O asymmetric and 1219 cm$^{-1}$ C-O stretching and this confirms the presence of PAni and GO in the TiO$_2$/PAni/GO nanocomposite. Because titanium is a transition metal, it has intense tendency to form coordination compound with nitrogen atom in PAni Macromolecule. This interaction may weaken the bond strengths of N-H, C=C, and C-O in PAni Macromolecule. These results confirm to the presence of PAni and GO in nanocomposite [31].

![Fig.5.3. FTIR Spectra of (a) TiO$_2$ (b) PAni (c) TiO$_2$/PAni (d) TiO$_2$/PAni/GO](image)

5.3.1.3 Scanning Electron Microscopy (SEM)

The morphology of the prepared nanocomposites was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Fig.5.4 (a, b, c and d) clearly show that all the prepared nanocomposites are obtained in nanodimension which is agglomerate form. The TiO$_2$, PAni, TiO$_2$/PAni and TiO$_2$/PAni/GO are indicating that the particle morphology is in spherical shape and disc shape. The TiO$_2$ molecule is agglomerate with PAni to form chips like structures which are partially
spherical and disc shape. The nanocomposites were found to be in nanometer range. Fig. 5.4 showing the TiO$_2$/PAni morphology which is in nanodimension with little change in surface morphology. Fig. 5.4 d showing the SEM image of TiO$_2$/PAni/GO which is in nanodimension and the surface morphology of TiO$_2$/PAni/GO has been changed slightly, due to the coating of PAni and GO layer on the TiO$_2$ lattice. The surface of TiO$_2$/PAni/GO was observed like disk shape and spherical [32, 33].

![SEM images of (a) TiO$_2$ (b) PAni (c) TiO$_2$/PAni (d) PAni/TiO$_2$/GO](image)

5.3.14 TEM analysis

The TEM images of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO are shown in Fig 5. In the TEM of TiO$_2$ hexagonal crystal lattice structure has been observed (Fig. 5.5a). Fig. 5.5b showed the TEM image of pure polyaniline. In the TEM images, the spiral chain structure of PAni has been observed. From the TEM images, we find that PAni-modified TiO$_2$ does not change the size of TiO$_2$ significantly (Fig. 5.5c). The sizes of both modified and TiO$_2$ are monodisperse about 10–20 nm. Moreover, the crystal lattice line can be clearly found in the TEM images. The aggregations of both kinds of
particles are caused by high surface energy; however, the agglomeration of the modified one is alleviated obviously compared with that of the neat TiO$_2$ [34, 35]. Generally, PAni synthesized by a chemical oxidative method in hydrochloric acid solution is the emeraldine salt (ES) form (Fig. 5.5), only which is electrically conducting. Anatase TiO$_2$ nanoparticles were deposited by PAni (ES) so as to avoid TiO$_2$ particles agglomeration because the positive charges exclude each other.

Fig.5.5 TEM images of (a) TiO$_2$ (b) Pure PAni (c) TiO$_2$/PAni (d) TiO$_2$/PAni/GO

**5.3.1.5 Brunauer-Emmett-Teller (BET) Surface Area Analysis**

Nitrogen adsorption–desorption isotherms were used to determine the structural characteristics and surface area of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO nanocomposite. The N$_2$ adsorption desorption isotherms of the TiO$_2$, TiO$_2$/PAni, and TiO2/PAni/GO nanocomposite were measured at 77 K, as shown in Figure 5.6. The specific surface areas (from BET and Surface area, pore volume and pore radius of the TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite are showing in Table 5.1. The surface area was found 37.52, 76.68 and 96.24 m$^2$/g for TiO$_2$, TiO$_2$/PAni, and
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TiO$_2$/PAni/GO respectively. There is an increase in pore volume ($V_p$) of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite and pore radius is decreased [36-38].

Table 5.1. The specific surface area, pore volume and pore radius of the TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area ($m^2/g$)</th>
<th>Pore volume ($cm^3/g$)</th>
<th>Pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>37.52</td>
<td>3.132</td>
<td>1.84</td>
</tr>
<tr>
<td>TiO$_2$/PAni</td>
<td>76.68</td>
<td>6.5124</td>
<td>1.64</td>
</tr>
<tr>
<td>TiO$_2$/PAni/GO</td>
<td>96.24</td>
<td>9.5124</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Fig.5.6. BET and Adsorption-desorption plot for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO
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From these results, it may be concluded that the high surface area of the TiO$_2$/PAni/GO nanocomposite may favour rapid electron transport and high ion diffusion, allowing improved photochemical performance. Moreover, the BET surface areas increased remarkably in the TiO$_2$/PAni/GO nanocomposite, which suggests that TiO$_2$ is well intercalated in PAni matrix and may also provide direct conduction pathway for electrons. The formation of TiO$_2$ with PAni by co-deposition oxidation synthesis resulted in the generation of well dispersed TiO$_2$ in PAni Matrix giving one TiO$_2$/PAni system with unique set of properties [39].

5.3.1.6. UV- Vis spectrophotometer

The absorption spectrum of TiO$_2$ consists of a single broad intense absorption around 263 nm (shown in Fig.5.7) in the region of hypsochromic shift. The PAni (Fig.5.7b) showed absorbance in the shorter wavelength region about 225 nm while TiO$_2$/PAni results showed a red shift in the absorption onset value and the broad peak observed at 287 nm.

![UV-Vis spectra of TiO$_2$, PAni, TiO$_2$/PAni, TiO$_2$/PAni/GO](image)

Fig.5.7. UV-Vis spectra of TiO$_2$, PAni, TiO$_2$/PAni, TiO$_2$/PAni/GO

This due to the coating of PAni layer on the surface of Titania [40]. The red shift that is observed at 298 nm in the absorption spectra with the decrease in particle size has been reported in TiO$_2$/PAni/GO nano hybrid composite. This is due to the coating of PAni and Graphene oxide in the Titania and the Titania completely interacted with PAni and GO.
5.3.1.7 Determination of Optical Band Gap energy of composites

The band gap of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO were determined from absorption spectra and Tauc relation (Eq. (1))

$$\alpha h\nu = B(h\nu - E_{gap})^m$$  \hspace{1cm} (1)

The band gap energy of prepared materials was calculated by extrapolation of the $(\alpha h\nu)^2$ versus $h\nu$ plots, where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy, $h\nu = (1239/\lambda)$ eV. The value of $h\nu$ extrapolated to $\alpha = 0$ gives an absorption energy, which corresponds to a band gap ($E_g$) (showing in Fig.5.8).

Fig. 5.8. Band gap energy of (a) TiO$_2$ (b) pure Pani (c) TiO$_2$/PAni (d) TiO$_2$/PAni/GO

The Band gap energy of TiO$_2$, pure polyaniline, TiO$_2$/PAni and TiO$_2$/PAni/GO were observed 3.2, 2.98, 2.85 and 1.67 eV [41]. The slight decrease in band gap energy in case of TiO$_2$/PAni is due to formation heterostructures. In case of TiO$_2$/PAni/GO the band gap energy 1.67 eV was observed due to the coating of PAni and GO on the surface of Titania. In the other word, the PAni and GO form a heterostructures on surface of Titania [42].
5.3.1.8 EDX (Energy Dispersive X-ray Spectrometer)

Low energy secondary electrons, backscattered electrons, and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays (EDX or EDS analysis) emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron. It is confirmed the presence of Titania, oxygen, Nitrogen carbon in the prepared sample.

![Fig.5.9 EDX Analysis of materials](image)

**5.3.2 Photodegradation of Rose Bengal dye**

The photo-catalytic degradation of Rose Bengal in the presence of TiO₂, TiO₂/PAni and TiO₂/PAni/GO nanocomposites has been studied. The solutions of dye were prepared in 10:1 (V/V) ratio of water and alcohol. The known amount of photocatalyst 100 mg/L to 1600 mg/L was dispersed in the dye solution. The reaction mixture was illuminated under visible light, while kept continuously under agitation,
for the different time intervals and different concentration. The residual concentration of dye in the reaction mixture was measured spectrophotometrically. The results obtained for the degradation of Rose Bengal is shown in Fig.5.10-5.15.

Photocatalytic degradation efficiencies ($\eta$) are obtained by using the following equation.

$$\eta = \frac{R_{B_0} - R_{B_F}}{R_{B_0}} \times 100$$

where $R_{B_0}$ is the initial absorbance and $R_{B_F}$ is the final sampled absorbance.

5.3.2.1 Effect of Irradiation time

The effect of the irradiation time on photodegradation of VB dye has been studied in presence of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO nanocomposite. The UV spectrum has been taken for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite at different irradiation time (30, 60, 90, 120 and 180 min) (Fig. 4.10). It is interesting to remark that the absorbance decreases with increase of time with photocatalyst. At 120 minutes the photodegradation efficiency observed was 14, 93 and 97 % for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite respectively. The Titania was showed very low photodegradation efficiency in visible light. This is due to high band gap energy (3.2 eV) which is not active in visible light region. Whereas TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite show very high photodegradation efficiency 93 and 97 %, this is due to the formation of sub band in Titania. The coating of PAni and GO decrease the band gap energy of Titania and Titania becomes active in visible light [43].

5.3.2.2 Effect of photocatalyst

The effect of photocatalyst was investigated. It is clear from the results shown in Fig.5.11 that TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO nanocomposites are proving as an effective photo-catalyst for the degradation of Rose Bengal (RB) dye. However, TiO$_2$/PAni/GO seems to be more effective as photo-catalyst for the degradation of Rose Bengal (RB). The prominent degradation of Rose Bengal was found in 120 min study in the presence of TiO$_2$/PAni/GO in comparison to the prepared TiO$_2$ and TiO$_2$/PAni. This is due to the coating of polyaniline of Titania surface which provide the electron
from the HOMO to LUMO. The electrons of HOMO get excited into LUMO which is further jump into the conduction band of Titania [44].

Fig. 5.10 UV-Vis spectrum showing the effect of irradiation time on photodegradation with TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite

Fig. 5.11. Effect of irradiation time on photo-degradation of RB with (a) TiO$_2$, (b) TiO$_2$/PAni and (c) TiO$_2$/PAni/GO nanocomposite

5.3.2.3 Effect of concentration of dye

The effect of dye concentration Keeping the catalyst loading concentration constant at 800 mg/L of the dye solution, the effect of varying concentration of the dye was studied on its rate of degradation (25, 50, 75, 100 and 125 ppm) as given in Fig. 5.12. The rate of photodegradation was decrease with increasing concentration of RB. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating into the dye solution to reach the catalyst surface is reduced owing to the hindrance in the path of light. Thereby the formation of the
reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved [45, 46].

Fig. 5.12. Effect of concentration on photo-degradation of RB with (a) TiO$_2$, (b) TiO$_2$/PAni and (c) TiO$_2$/PAni/GO nanocomposite

5.3.2.4 Effect of pH

The photodegradation was carried out under varying pH conditions from (3 to 11), by adjusting with H$_2$SO$_4$ and NaOH, with TiO$_2$ kept at constant amounts of photocatalyst of 800 mg/L and 25 ppm concentration of dye solutions (Fig.5.13). The photodegradation was found to have highest rates at neutral ranges of pH. While at lower pH it was found to decrease. In the basic condition, the photodegradation rate was found slow and very poor degradation. Hence highly acidic and basic condition is not favourable for the degradation of VB. This implies that neutral conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in basic and acidic conditions, the formation of reactive intermediates is relatively less favourable and hence less spontaneous [47-48].
5.3.2.5 Effect of photocatalyst amount

It is clear from the results shown in Fig.5.14 that TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO nanocomposites are proving as an effective photo-catalyst for the
degradation of Rose Bengal dyes. The photodegradation of Rose Bengal was increasing with increases the amount of photocatalyst. It is observed that TiO$_2$/PAni/GO is the more effective photocatalyst than TiO$_2$ and TiO$_2$/PAni [44]. When the photocatalyst amount increases, the number of active site increase for the reaction of dyes. The amount of photocatalyst increases two times the rate of photodegradation increase about 30% and 60 %, in presence of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO respectively [49].

5.3.3 Recyclability of Photocatalyst

The recyclability of photocatalyst has been studied. The photocatalyst and Rose Bengal mixture was agitated, illuminated with visible light and after desired time, the mixture was centrifuge to remove the photocatalyst. The obtained photocatalyst washed three times with distilled water and finally kept in oven for 24 h at 60 °C temperature and further it is reuse for the degradation of Rose Bengal. The photodegradation of Rose Bengal by the recyclized Photocatalyst are showing in Fig. 5.15. The result shows that the recyclized photocatalyst efficiency is decreasing due to the loss of some active sites and decrease of collection efficiency of photon [50, 51].

![Fig.5.15. Photodegradation of Rose Bengal by Photocatalyst and recyclable Photocatalyst TiO$_2$, TiO$_2$/PAni, TiO$_2$/PAni/GO](image)

5.3.4 Lowering of electron-hole recombination

Photoluminescence spectra have been used to examine the mobility of the charge carriers to the surface as well as the recombination process involved by the electron-hole pairs in semiconductor particles. PL emission results from the radiative
recombination of excited electrons and holes. In other words, it is a critical necessity of a good photocatalyst to have minimum electron-hole recombination. To study the recombination of charge carriers, PL studies of synthesized materials have been undertaken. PL emission intensity is directly related to recombination of excited electrons and holes. Fig. 5.16 shows the photoluminescence spectra of synthesized photocatalysts. It means TiO$_2$ and TiO$_2$/PAni with strong PL intensity has high recombination of charge carriers where as TiO$_2$/PAni/GO has weak intensity.

![Photoluminescence Spectra of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO](image.png)

Fig.5.16. Photoluminescence Spectra of TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO

The weak PL intensity of TiO$_2$/PAni/GO may arise due to the coating of polyaniline on Titania lattice. The photo excited electrons were trapped into the graphene oxide. This delays the electrons- holes recombination process and hence is utilized in the redox reaction leading to improved photocatalytic activity [52, 53].

### 5.3.5 Hydroxyl radical formation

As hydroxyl radical performs the key role for the decomposition of the organic pollutants, it is necessary to investigate the amount of hydroxyl radicals produced by each photocatalyst. Thus, there is a technique to establish the formation of hydroxyl radicals using terephthalic acid (TA) as a probe molecule. In this method, TA was directly attacked by OH radical forming 2- hydroxyl terephthalic acid (TAOH) which gives a fluorescence signal at 426 nm. Fig.5.17 depicts the fluorescent signal of all the photocatalysts after reacting with TA solution. The fluorescent intensity is linearly related to the number of hydroxyl radicals formed by the photocatalysts. It means
higher is the generation of hydroxyl radical, yield of TAOH will be more and hence more intense will be the fluorescence peak. Thus, TiO$_2$/PAni/GO with highest intensity confirms the generation more number of hydroxyl radicals compared to other photocatalysts. The fluorescence intensity follows the trend (i.e. TiO$_2$, < TiO$_2$/PAni < TiO$_2$/PAni/GO) of photocatalytic performance of all the photocatalyst [54, 55].

![PL spectra of photocatalyst with terephthalic acid (0.001M) TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO](image)

Fig.5.17. PL spectra of photocatalyst with terephthalic acid (0.001M) TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO

### 5.3.6 Mechanism of photo-oxidation process

The acceleration of a chemical transformation by the presence of a catalyst with light is called photocatalysis. The catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction and itself remaining unaltered at the end of each catalytic cycle. Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor. The molecular orbital of semiconductors has a band structure. The bands of interest in photocatalysis are the populated valence band (VB) and it’s largely vacant conduction band (CB), which is commonly characterized by band gap energy (E$_{bg}$). The semiconductors may be photo-excited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidising sites), providing great scope for redox reaction. When the semiconductor is illuminated with light (h$\nu$) of greater energy than that of the band gap, an electron is promoted from the VB to the CB leaving a
positive hole in the valence band and an electron in the conduction band as illustrated in Fig. 5.18.

Fig. 5.18 Mechanism of photodegradation of Rose Bengal in visible light

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with absorbed species. Specially, $h^+_{\text{VB}}$ may react with surface-bound $\text{H}_2\text{O}$ or $\text{OH}^-$ to produce the hydroxyl radical and $e^-_{\text{cb}}$ is picked up by oxygen to generate superoxide radical anion ($\text{O}_2^-$), as indicated in the following equations 3-5; absorption of efficient photons by Titania ($h\nu \geq E_{bg} = 3.2 \text{ eV}$)

$$\text{TiO}_2 + h\nu \rightarrow e^-_{\text{cb}} + h^+_{\text{dye}} \quad (3)$$

Formation of superoxide radical anion

$$\text{O}_2 + e^-_{\text{cb}} \rightarrow \text{O}_2^- \quad (4)$$

Neutralization of $\text{OH}^-$ group into $\text{OH}$ by the hole

$$(\text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH})_{\text{ads}} + h^+_{\text{dye}} \rightarrow \text{OH} + \text{H}^+ \quad (5)$$

It has been suggested that the hydroxyl radical ($\cdot\text{OH}$) and superoxide radical anions ($\text{O}_2^-$) are the primary oxidizing species in the photocatalytic oxidation processes [56]. These oxidative reactions would results in the degradation of the pollutants as shown in the following equations 6-7; Oxidation of the organic pollutants via successive attack by $\text{OH}$ radicals,
for oxidation reactions to occur, the VB must have a higher oxidation potential than the material under consideration. The redox potential of the VB and the CB for different semiconductors varies between +4.0 and -1.5 volts versus Normal Hydrogen Electrode (NHE) respectively. The VB and CB energies of the TiO$_2$ are estimated to be +3.1 and -0.1 volts, respectively, which means that its band gap energy is 3.2 eV and therefore absorbs in the near UV light ($\lambda$<387 nm) [61]. Many organic compounds have a potential above that of the TiO$_2$ valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the TiO$_2$ conduction band.

Photodegradation of Rose Bengal can be expressed by the following reaction mechanism:

\[
\text{TiO}_2 \xrightarrow{hv} h^+_{\text{VB}} + e^-_{\text{CB}}
\]

\[
h^+_{\text{VB}} + \text{H}_2\text{O} \rightarrow \text{OH}^*
\]

\[
\text{RB} + \text{OH}^* \rightarrow \text{RB}^*
\]

\[
\text{RB}^* \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{NH}_3 + \text{other product}
\]

The TiO$_2$/PAni nanocomposite absorbs radiation of energy corresponding to its band gap and generates electron-hole pair. The electron and hole may recombine non-radiatively to release the energy absorbed in the form of heat. The cationic dye RB$^+$ combines with two electrons and a proton to give its reduced form (RBH$^-$). This step is the rate determining step for the photocatalytic degradation of Rose Bengal. The leuco form of the dye ultimately degrades to final products containing CO$_2$ and NH$_4$.

It is observed that rate constant in the presence of TiO$_2$/PAni nanocomposite photocatalyst is larger than that in the presence of pure TiO$_2$ photocatalyst. The electron from the conduction band of TiO$_2$ may be transferred to the empty PAni states, making the valence band hole of TiO$_2$ stable, thus enhancing the oxidative efficiency of the
TiO₂ nanoparticles. The same may be the case when an electron is transferred from the trapped states of the nanoparticles. On the other hand, PAni may also absorb light and then energy transfer is possible to the nanoparticles followed by creation of the valence band hole and the conduction band electron adding to the process of creating a strong oxidative -reductive state of the oxide nanoparticles. Other way, by attaching PAni Particles on the surface of TiO₂, it is possible to drive the photogenerated electrons farther away from the TiO₂, thereby achieving more charge separation in these semiconductor particles. As a result, more efficient photocatalyst is obtained. It is already reported that coupled semiconductors exhibit enhanced spatial separation of the photogenerated electrons and holes as a consequence of charge transfer between the two semiconductors [57]. The conduction band of PAni is lower than that of TiO₂ so that the former can act as a sink for the photogenerated electrons. Since the photogenerated holes move in the opposite direction from the electrons, the photogenerated holes in PAni are trapped within the TiO₂ particles. Thus likelihood of charge carrier recombination is reduced and more charge carriers will be available for production for free radicals through interfacial charge transfer. In all the photodegradation experiments, it is observed that the characteristic absorption band of RB dye decreases but no hypsochromatic shift appears, which indicates that the photodegradation mechanism is favourable to cleavage of the whole conjugated chromophore structure of the RB dye.

5.3.7 Kinetics of photodegradation

For the kinetic study of photocatalytic degradation, a control experiment was first carried out under two conditions, vis (i) dye + Visible light (no catalyst) (ii) catalyst+ dye in dark without any irradiation (Fig.5.19). It can be seen that under dark conditions, the amount of dye adsorbed on the surface of photocatalyst becomes constant after 20 min, where the adsorption equilibrium is achieved with all the nanocomposites [58].
The Langmuir-Hinshelwood kinetic model [59, 60] is widely used to describe the kinetics of photodegradation of many organic compounds. According to this model, the degradation rate $r$ of the dye is described as:

$$ r = -\frac{d[RB]}{dt} = -\frac{kK[RB]}{1+K[RB]} $$

(8)

Where $r$ is the rate of degradation of RB, $k$ is the rate constant, $[RB]$ is the dye concentration, and $K$ is the adsorption coefficient. The implicit solution is given in Eq.(9):

$$ \ln \frac{[RB]}{[RB]_0} + k ([RB] - [RB]_0) = -kKt $$

(9)

This can be solved explicitly for $t$ by using discrete changes in $[RB]$ from the initial concentration to a zero reference point. The model presented in Eq. (9) yields an exact solution for the degradation of RB. However, when the concentration of RB is very small in the ppm range, a pseudo-first-order model can be assumed, ignoring $K[RB]$ in the denominator of eq. (9) leads to Eq. (10),

$$ r = -\frac{d[RB]}{[RB]_0} = kK[RB] = K'[RB] $$

(10)

Integration of eq. (9) yields eq. (10)

$$ [RB] = [RB]_0 e^{-K't} $$

(11)
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\[ \ln \left( \frac{[RB]}{[RB]_0} \right) = kKt = K't \]  \hspace{1cm} (12)

Where \( k' \) is the pseudo rate constant and is in units of time\(^{-1}\).

Figure 5.20 shows the \( \ln [RB_o-RB] \) vs. time plots for TiO\(_2\), TiO\(_2\)/PAni and TiO\(_2\)/PAni/GO nanocomposite. Samples were dispersed in the same concentration of dye solutions. Pseudo-first-order degradation rate constants \( k' \) calculated from the slopes of Fig.5.20 [61, 62].

![Fig.5.20. kinetics of photodegradation of RB with (a) TiO\(_2\) (b) TiO\(_2\)/PAni (c) TiO\(_2\)/PAni/GO](image)

### 5.3.8. Photodegradation of Thymol blue dye

The photo-catalytic degradation of Thymol Blue in the presence of TiO\(_2\), TiO\(_2\)/PAni, and TiO\(_2\)/PAni/GO has been studied. The solution of dye was prepared in 5:1 (V/V) ratio of water and alcohol. The known amount of photocatalyst was dispersed in the dye solution. The reaction mixture was illuminated under visible light, while kept continuously under agitation, for the different time intervals. The residual concentration of dye in the reaction mixture was measured spectrophotometrically. The results obtained for the degradation of Thymol Blue is shown in Fig 5.21. Photocatalytic degradation efficiencies (\( \eta \)) are obtained by using following equation [43-44].
where \( \eta = \frac{TB_0 - TB_F}{TB_0} \) 

(13)

5.3.8.1. Effect of concentration of dye

Effect of dye concentration Keeping the catalyst loading concentration constant at 800 mg/litre of the dye solution, the effect of varying concentration of the dye was studied on its rate of degradation (25, 50, 75, 100 and 125 ppm) as given in Fig.5.21. The rate of photodegradation was decrease with increasing concentration of TB. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating into the dye solution to reach the catalyst surface is reduced owing to the hindrance in the path of light [45].

5.3.8.2. Effect of photocatalyst amount

The effect of photocatalyst amount is showing in Fig.5.21. The photodegradation of Thymol blue was increased with increase the amount of photocatalyst. It is observed that TiO\(_2\)/PAni/GO is the more effective photocatalyst than TiO\(_2\) and TiO\(_2\)/PAni. When the photocatalyst amount increases, the number of active site increase for the reaction of dyes. The amount of photocatalyst increases two times the rate of photodegradation increase about 30% and 60 %, in presence of TiO\(_2\), TiO\(_2\)/PAni and TiO\(_2\)/PAni/GO respectively [46].

5.3.8.3. Effect of Irradiation Time

The effect of irradiation time of visible light was investigated. TiO\(_2\)/PAni/GO seems to be more effective as photo-catalyst for the degradation of Thymol Blue (TB). The prominent degradation of Thymol Blue was found in 180 min (Fig.5.21) study in the presence of TiO\(_2\)/PAni/GO in comparison to the prepared TiO\(_2\) and TiO\(_2\)/PAni. This is due to the coating of polyaniline of Titania surface which provide the electron from the HOMO to LUMO. The electrons of HOMO get excited into LUMO which is further jump into the conduction band of Titania [47].
5.3.8.4. Effect of pH

The photodegradation was carried out under varying pH conditions from (3 to 11), by adjusting with H₂SO₄ and NaOH, with TiO₂, kept at constant amounts of photocatalyst of 800 mg/L and 25 ppm concentration of dye solutions (Fig. 5.21). The photodegradation was found highest rates at neutral ranges of pH. While at lower pH it was found to decrease. In the basic condition, the photodegradation rate was found slow and very poor degradation. Hence highly acidic and basic condition is not favourable for the degradation of TB. This implies that neutral conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in basic
and acidic conditions, the formation of reactive intermediates is relatively less favourable and hence less spontaneous [48-49].

5.3.8.5. Recyclability of Photocatalyst

The photocatalyst recyclability has been studied. The photocatalyst and Thymol blue mixture was agitated, illuminated with visible light and after desired time, the mixture was centrifuge to remove the photocatalyst. The removed photocatalyst washed three times with distilled water and finally kept in the oven for 24 h at 60°C temperature and further it is reuse for the degradation of Thymol Blue. The photodegradation of Thymol blue by the recyclized Photocatalyst showed in Fig. 5.22. The result shows that the recyclized photo-catalyst efficiency is decreased [51]. The decrease in the efficiency of dye removal for the recyclized catalyst can be attributed to the reduction in the active sites on the surface of the catalyst after one use as well as sticking species that may remain adsorbed on the pores of the catalyst. These observations can lead to reduce the ability of adsorption and consequently reduce its catalytic activity.

![Fig.5.22. Recyclability of Photocatalyst for the degradation of Thymol Blue.](image)

Table 5.2 showing the comparative data of different catalyst used for the degradation of dyes.
### Table 5.1: Nanomaterials and their Degradation Efficiencies for Rose Bengal and Thymol Blue Dyes

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>time</th>
<th>Name of Dye</th>
<th>% Degradation of Dye</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titania</td>
<td></td>
<td>RB</td>
<td>20</td>
<td>38</td>
</tr>
<tr>
<td>Polyaniline</td>
<td>3</td>
<td>RB</td>
<td>18</td>
<td>39</td>
</tr>
<tr>
<td>Graphene Oxide</td>
<td>1h</td>
<td>MO</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>TiO2/PAni</td>
<td>3</td>
<td>MG</td>
<td>94.4</td>
<td>41</td>
</tr>
<tr>
<td>TiO2/PAni/GO</td>
<td>3h</td>
<td>TB</td>
<td>96</td>
<td>42</td>
</tr>
<tr>
<td>ZnO/PAni</td>
<td>4h</td>
<td>MB</td>
<td>99</td>
<td>43</td>
</tr>
<tr>
<td>PAni/G</td>
<td>3</td>
<td>RB</td>
<td>56</td>
<td>39</td>
</tr>
</tbody>
</table>

#### 5.3.9. Kinetic study of Photocatalytic degradation of Thymol Blue

For kinetic study of photocatalytic degradation, a control experiment was first carried out under two conditions, viz (i) dye + Visible light (no catalyst) (ii) catalyst+dye in dark without any irradiation (Fig. 5.23). It can be seen that in under dark conditions, the amount of catalyst adsorbed becomes constant after 20 min, where adsorption equilibrium is achieved. For the kinetic study of bleaching of Victoria Blue and Rose Bengal, the initial concentration of the dyes was varied and the experiments were first conducted in dark for 20 min and then immediately followed by irradiation (Fig. 5.23). The amount of catalyst was kept constant (0.2 g) throughout the experiment. Applying the Langmuir Hinshelwood model for determining the oxidation rate of the photocatalysis of dye:

$$\text{Rate} \ (r) = -\frac{dC}{dt} = k\theta = \theta = \frac{kK_A C}{1 + K_A C}$$  \ (14)

Where \(k\) is the rate constant (mg/L min\(^{-1}\)), \(C\) is the concentration of dye, \(K_A\) is the adsorption constant of the dye (L/mg), and \(t\) is the illumination time (min).

During the course of reaction, the initial pH, amount of catalyst, and photointensity were kept same. In addition to it, the formation of intermediates may interfere in the rate determination; hence the calculation was done at the beginning of irradiation. The rate expression can be written as:

$$r_o = \frac{kK_A C_o}{1 + K_A C_o}$$  \ (15)

Where \(r_o\) is the initial rate of degradation of Thymol Blue and \(C_o\) is the initial concentration (almost equal to \(C_{eq}\)). When the initial concentration \(C_{initial}\) is very small, \(C_o\) will also be small and Eq. (15) can be simplified as an first-order equation [56-61]:

---

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\[
-\frac{dc}{dt} = kK_A C_o = \frac{ln C_o}{C} = kK_A t
\]  \hspace{1cm} (16)

\[
C = C_o e^{-k_{photo} t}
\]  \hspace{1cm} (17)

Where \(k_{f,\text{photo}} = k A\). The value of \(k_{f,\text{photo}}\) can be determined from the plot of \(ln \frac{C}{C_o}\) vs. \(t\) (Fig.5.24).

---

Fig.5.23. % Adsorption of Thymol Blue dye under dark condition in presence of (a) TiO\(_2\), (b) TiO\(_2\)/PAni and (c) TiO\(_2\)/PAni/GO

The slope of the straight line obtained will be the value of first order rate constant [61]. The Value of apparent rate constant were determine at definite concentrations of dye solution for photocatalysis reaction in presence of TiO\(_2\), TiO\(_2\)/PAni and TiO\(_2\)/PAni/GO showing in Fig.5.24.

The rate constant values for the photocatalytic degradation of Thymol Blue follow the first order kinetic for the both photocatalyst. This is confirmed that photocatalytic degradation of Thymol Blue follows first order kinetic in presence of TiO\(_2\), TiO\(_2\)/PAni, and TiO\(_2\)/PAni/GO.
Fig. 5.24. Linear first order reaction of Langmuir Hinshelwood kinetics of Thymol Blue dye vs. time (a) TiO$_2$ (b) TiO$_2$/PAni (c) TiO$_2$/PAni/GO

**Conclusion**

In this work, nanocomposites materials were prepared by the in situ co-deposition oxidative method. Different techniques were used for the characterisation of the TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO nanocomposite such as XRD, BET, SEM, TEM, FTIR, Photolumiscence, band gap energy and UV spectrophotometer. The XRD confirmed the presence of anatase and rutile phase were observed in the prepared materials nanocomposites. The SEM study confirms that spherical morphology of the nanocomposite. The TEM analysis confirms that the size of nanocomposite. The FTIR characterisation confirms that the TiO$_2$/PAni/GO molecules are well combined with polyaniline and graphene oxide structure. EDEX confirms about the elements which are present in the prepared sample by x-ray emission spectrum. The surface area 37.52, 76.68 and 96.24 m$^2$/g were observed for TiO$_2$, TiO$_2$/PAni and TiO$_2$/PAni/GO Nanocomposites respectively. The Band gap energy of TiO$_2$, TiO$_2$/PAni, and TiO$_2$/PAni/GO were calculated by t alc plot and obtained 3.0, 2.86 and 1.76 eV respectively. The Photocatalytic degradation of Rose Bengal dye was done at different condition viz concentration of dye, time of illumination, pH, and dose of photocatalyst. The maximum photodegradation were found at neutral pH, 6.25 ppm concentration of dye solution, 800 mg/L amount of photocatalyst and 120 min irradiation of visible light.
Kinetics study was investigated for the photodegradation of Rose Bengal dye and found first order kinetics. The maximum photodegradation of Thymol blue was found in TiO$_2$/PAni/GO at 25 ppm concentration of dye, 1600 mg/L amount of photocatalyst, pH 7 and 120 min irradiation of visible light. Hence, the photocatalytic activity of Titania has been increased by the coating of PAni and Graphene oxide. The coating of PAni and GO were enhanced the photocatalytic activity of Titania. Hence TiO$_2$/PAni and TiO$_2$/PAni/GO is the efficient photocatalyst for the degradation of Rose Bengal dye than pure TiO$_2$.

References

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