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Comparative Photocatalytic Degradation of Rose Bengal Dye under Visible Light by TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ Nanocomposites

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Abstract: Nanocomposites of TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ were prepared by in situ oxidation polymerization method. The prepared TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ Nanocomposites were characterized by the XRD, SEM, TEM, BET, UV-Vis, FTIR, Band gap energy and Photoluminescence. 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 $\text{TiO}_2/\text{PAni}/\text{GO}$ 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 $96.24\text{ m}^2/\text{g}$ were observed for TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ Nanocomposites respectively. The Band gap energy of TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ were calculated by talc plot and obtained 3.0, 2.98 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 photo degradation 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 of photo degradation was investigated for Rose Bengal dye and found first order kinetics. The coating of PAni and GO were enhanced the photocatalytic activity of Titania. Hence TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ are the efficient photocatalyst for the degradation of Rose Bengal dye than pure TiO_2 .

Keyword: Photocatalyst, Photo degradation, Rose Bengal, photocatalysis, nanocomposites, visible light irradiation, Photoluminescence.

I. INTRODUCTION

In recent years, due to industrialization, there is rapid increase in release of pollutants from industries into water bodies [1]. 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 are causing water pollution. About 12% of dyes are used in textile industries in each year. During the synthesis and processing, about 20% dyes are lost in the 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 colour pigments which are causing the carcinogenic effect on the 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 the 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 the human being because it causes the irritation, itchiness, blistering and reddening. It 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. The 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, photo Fenton'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 advanced oxidation process to remove the dye without any side product formation.

Titanium dioxide (TiO_2) is the most used photocatalyst due to its non-toxicity, high activity, photostability, chemical stability, biological inertness, the good absorption, desorption rate of reactants and low cost [4]. TiO_2 photocatalyst has been applied to self-cleaning glasses, antibacterial tiles etc. as it has the strong oxidizing power to decompose most organic compounds to CO_2 [5].

Organic compounds such as halogeno-aliphatic hydrocarbons, halogeno aromatic hydrocarbons, organic acids, coloring matters, nitroaromatic 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 the 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 proposed to overcome the recombination process [10]. It is believed that availability of visible light absorbing photocatalysts would largely solve the technological problems photo reactor considerations. Additionally, harnessing sunlight can be achieved by the scientists recently, most of the researchers 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 photocatalytic 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 $\text{TiO}_2/\text{PAni}/\text{GO}$ 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 photo degradation of Rose Bengal dye in the visible light. The photodegradation of Rose Bengal has been done at different chemical parameters i.e. pH of the solution, the concentration of dye, the amount of photocatalyst, photocatalyst, time of irradiation and recyclability of the photocatalyst. The kinetic study of photodegradation has been performed and found the order of reaction.

II. METHODS AND MATERIALS

All the materials and chemicals used in the study were analytical grade and purchase from Merck without further purification.

A. Synthesis of Titanium Dioxide

TiO_2 nanoparticles were prepared using H_2O_2 solution added to 10 ml of 1 mol/L ethanol solution of titanium tetra-isopropoxide (TTIP). Ethanol was added to the brown colored solution obtained, and the total volume of the solution was adjusted to 100 ml. The solution was then heated at 120°C for 1hr 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 the oven at 60°C for 24 h. The obtained solid was calcined at 600°C for 3hr to get white titanium oxide powder [22-23].

B. 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 sulfate 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 the 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 PAniOligomers. 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].

C. Synthesis of $\text{TiO}_2/\text{PAni}/\text{GO}$ 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 simultaneously 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.

D. 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 $2\theta = 20-80^\circ$. The size of TiO_2 particles was investigated with transmission electron microscope (TEM). The 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.

E. 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].

F. 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, a sample was withdrawn from the reaction mixture and was centrifuged to separate photocatalyst particles. The photoluminescence spectrum of the sample was recorded between 335 and 600 nm at an excitation wavelength of 325 nm and variation in the intensity of the peak at 425 nm was monitored using Perkin Elmer LS 55 Fluorescence Spectrometer [27].

III. RESULTS AND DISCUSSION

A. Characterisation

1) **XRD:** The XRD patterns of TiO_2 , PANi, TiO_2 /PANi, TiO_2 /PANi/GO nanocomposite are showing in Fig 1. The XRD pattern of TiO_2 showing in Fig. 1(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 TiO_2 (JCPDS file No: 86-1157). Fig.1 (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° 2θ [28]. The peak at $2\theta \sim 25^\circ$ due to the periodicity perpendicular to the polymer chain and other crystal planes at $2\theta \sim 15^\circ$ was absent, which shows that the as-synthesized PANi is highly amorphous in nature. In the XRD pattern of the TiO_2 /PANi nanocomposites (Fig. 1c) the usual broad peak corresponding to the periodicity parallel to the polymer chain encompassing a slight crystalline small peak at 20° 2θ was not observed. All the peaks corresponding to anatase TiO_2 were also present. In the XRD pattern of the TiO_2 /PANi/GO nanocomposites (Fig. 1d), all the peaks corresponding to anatase TiO_2 were also present suggesting that the state of TiO_2 did not change during the polymerization process. On the other hand, a slight reduction in the peak intensity and red shift was observed for TiO_2 peaks in the TiO_2 /PANi nanocomposite [29]. This might be due to the surface coating of PANi on TiO_2 during the polymerization process and the interactions between the TiO_2 nanoparticles and the PANi chain [30].

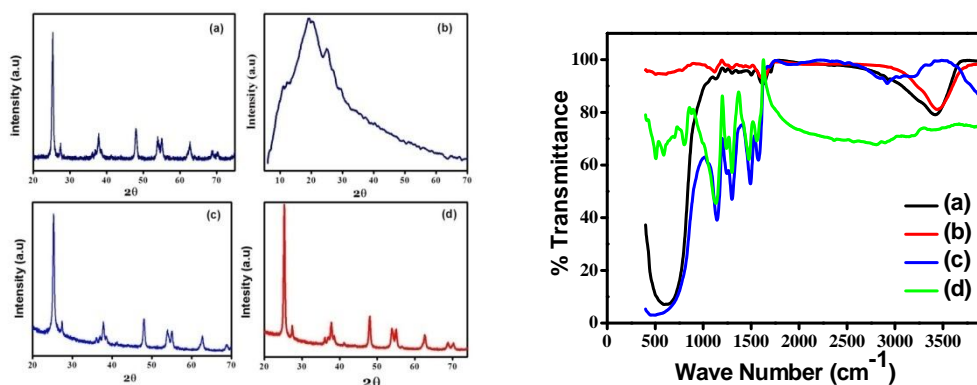


Fig.1 XRD Pattern and FTIR spectra of (a) TiO₂ (b) PANi (c) TiO₂/PANI (d) TiO₂/PANI/GO

- 2) **FTIR:** FT-IR spectra of TiO₂, PANi, TiO₂/PANI and TiO₂/PANI/GO are shown in Figure 3. In Figure 1(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 1b. 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 the ring and N-O asymmetric and 1219 cm⁻¹ C-O stretching and this confirms the presence of PANi and GO in the TiO₂/PANI/GO nanocomposite. Because titanium is a transition metal, it has intense tendency to form coordination compound with the 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 the presence of PANi and GO in nanocomposite [31].
- 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.2 (a, b, c and d) clearly show that all the prepared nanocomposites are obtained in nanodimension which is agglomerate form. The TiO₂, PANi, TiO₂/PANI and TiO₂/PANI/GO are indicating that the particle morphology is in spherical shape and disc shape. The TiO₂ molecule is agglomerate with PANi to form chips like structures which are partially spherical and disc shape. The nanocomposites were found to be in nanometerrange Fig.4 showing the TiO₂/PANI morphology which is in nanodimension with little change in surface morphology. Fig.2 d showing the SEM image of TiO₂/PANI/GO which is in nanodimension and the surface morphology of TiO₂/PANI/GO has been changed slightly, due to the coating of PANi and GO layer on the TiO₂ lattice. The surface of TiO₂/PANI/GO was observed like disk shape and spherical [32, 33].

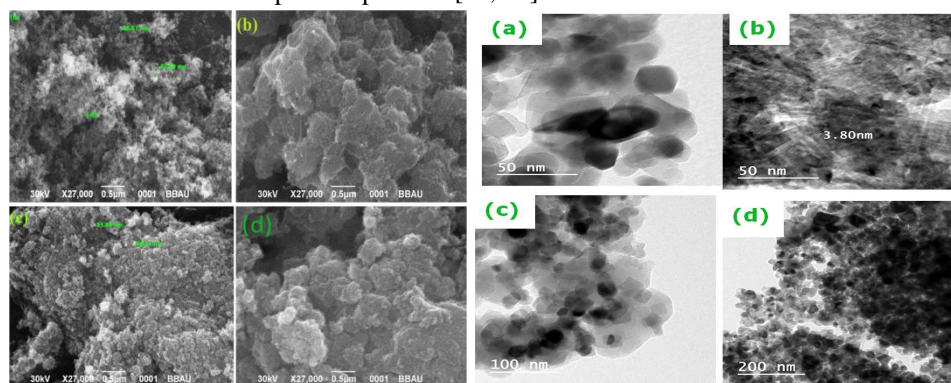


Fig.2 SEM and TEM images of (a) TiO₂ (b) PANi (c) TiO₂/PANI (d) PANi/TiO₂/GO

- 4) **TEM Analysis:** The TEM images of TiO₂, TiO₂/PANI and TiO₂/PANI/GO are shown in Fig 2. In the TEM of TiO₂ hexagonal crystal lattice structure has been observed (Fig.2a). Fig.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 TiO₂ does not change the size of TiO₂ significantly (Fig.2c). The sizes of both modified and TiO₂ 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 TiO₂[34, 35]. Generally, PANi synthesized by a chemical oxidative method in hydrochloric acid solution is the emeraldine salt (ES) form

(Fig. 2), 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.

- 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 $\text{TiO}_2/\text{PANi}/\text{GO}$ nanocomposite. The N_2 adsorption-desorption isotherms of the TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$ nano-composite were measured at 77 K, as shown in Figure 6. The specific surface areas (from BET and Surface area, pore volume and the pore radius of the TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$ nanocomposite are showing in Table 1. The surface area was found 37.52, 76.68 and 96.24 m^2/g for TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$ respectively. There is an increase in pore volume (V_p) of TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$ nanocomposite and pore radius is decreased [36-38].

From these results, it may be concluded that the high surface area of the $\text{TiO}_2/\text{PANi}/\text{GO}$ nanocomposite may favour rapid electron transport and high ion diffusion, allowing improved photochemical performance. Moreover, the BET surface areas increased remarkably in the $\text{TiO}_2/\text{PANi}/\text{GO}$ 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 a unique set of properties [39].

Table 1:- The specific surface area, pore volume and pore radius of the TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)
TiO_2	37.52	0.132	1.84
TiO_2/PANi	76.68	0.512	1.64
$\text{TiO}_2/\text{PANi}/\text{GO}$	96.24	0.512	1.21

- 6) **UV-Vis spectrophotometer:** The absorption spectrum of TiO_2 consists of a single broad intense absorption around 263 nm (shown in Fig.3) in the region of the hypsochromic shift. The PANi (Fig.3b) 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. 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 $\text{TiO}_2/\text{PANi}/\text{GO}$ nanocomposite. This is due to the coating of PANi and Graphene oxide in the Titania and the Titania completely interacted with PANi and GO.

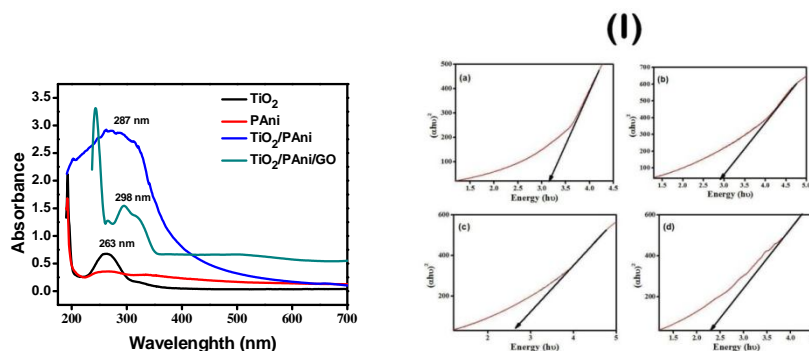


Fig.3. UV spectra of TiO_2 , PANi, TiO_2/PANi , $\text{TiO}_2/\text{PANi}/\text{GO}$

- 7) **Determination of Optical Band Gap energy of composites:** The band gap of TiO_2 , TiO_2/PANi and $\text{TiO}_2/\text{PANi}/\text{GO}$ were determined from absorption spectra and Tauc relation (Eq. (2))

$$\alpha h\nu = B(h\nu - E_{gap})^m \quad (2)$$

The band gap energy of prepared materials was calculated by extrapolation of the $(\alpha h\nu)^2$ versus $h\nu$ plots, where α 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.3). Graph yields an E_g value of 3.2 eV for TiO_2 and 2.98 for TiO_2/PAni [41]. The slight decrease in band gap energy in case of TiO_2/PAni is due to the formation of sub-band level between the valence band and the conduction band. In the case of $\text{TiO}_2/\text{PAni}/\text{GO}$ the band gap energy 1.74 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 subband in the Titania [42].

B. Photodegradation

The photo-catalytic degradation of Rose Bengal in the presence of TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ 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.4 and 5.

Photocatalytic degradation efficiencies (h) are obtained by using following equation.

where RB_0 is the initial absorbance and RB_F is the final sampled absorbance.

- 1) *Effect of Irradiation time:* The effect of the irradiation time on photodegradation of RB dye has been studied in presence of TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposite. The UV spectrum has been taken for TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposite at different irradiation time (30, 60, 90, 120 and 180 min) (Fig. 4). It is interesting to remark that the absorbance decreases with the increase of time with the photocatalyst. At 120 minutes the photodegradation efficiency observed was 14, 93 and 97 % for TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposite respectively. The Titania was showed very low photodegradation efficiency in visible light. This is due to the high band gap energy (3.2 eV) which is not active in the visible light region. Whereas TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ 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].

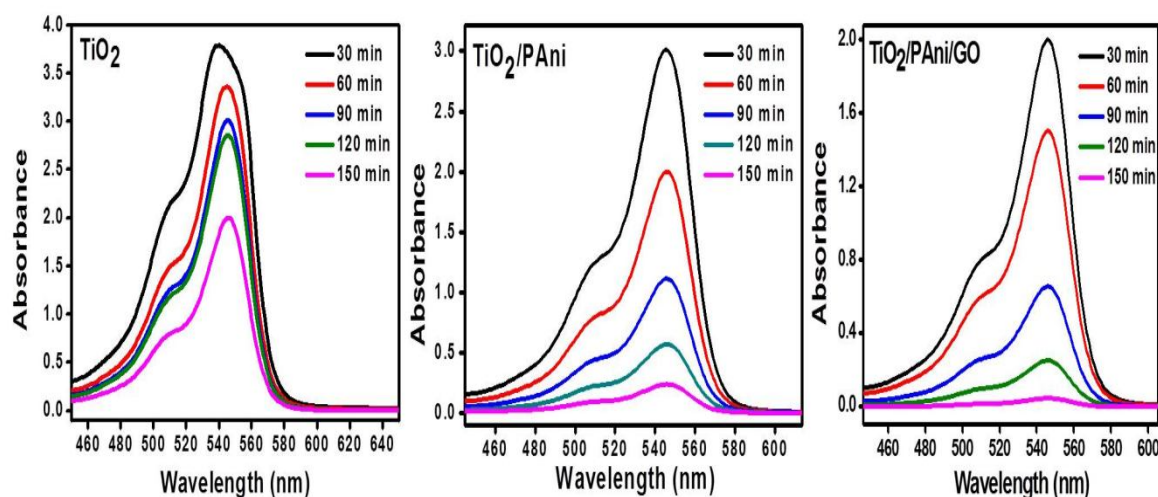


Fig.4 UV spectrum showing the effect of irradiation time on photodegradation with TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposite

- 2) *Effect Of Photocatalyst:* The effect of photocatalyst was investigated. It is clear from the results shown in Fig.5 that TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposites are proving as an effective photocatalyst for the degradation of Rose Bengal dye. However, $\text{TiO}_2/\text{PAni}/\text{GO}$ seems to be more effective as the photocatalyst for the degradation of Rose Bengal. The prominent degradation of Rose Bengal was found in 120 min study in the presence of $\text{TiO}_2/\text{PAni}/\text{GO}$ in comparison to the prepared TiO_2 and TiO_2/PAni . This is due to the coating of polyaniline of Titania surface which provides the electron from the HOMO to LUMO. The electrons of HOMO get excited into LUMO which is further jumping into the conduction band of Titania [44].

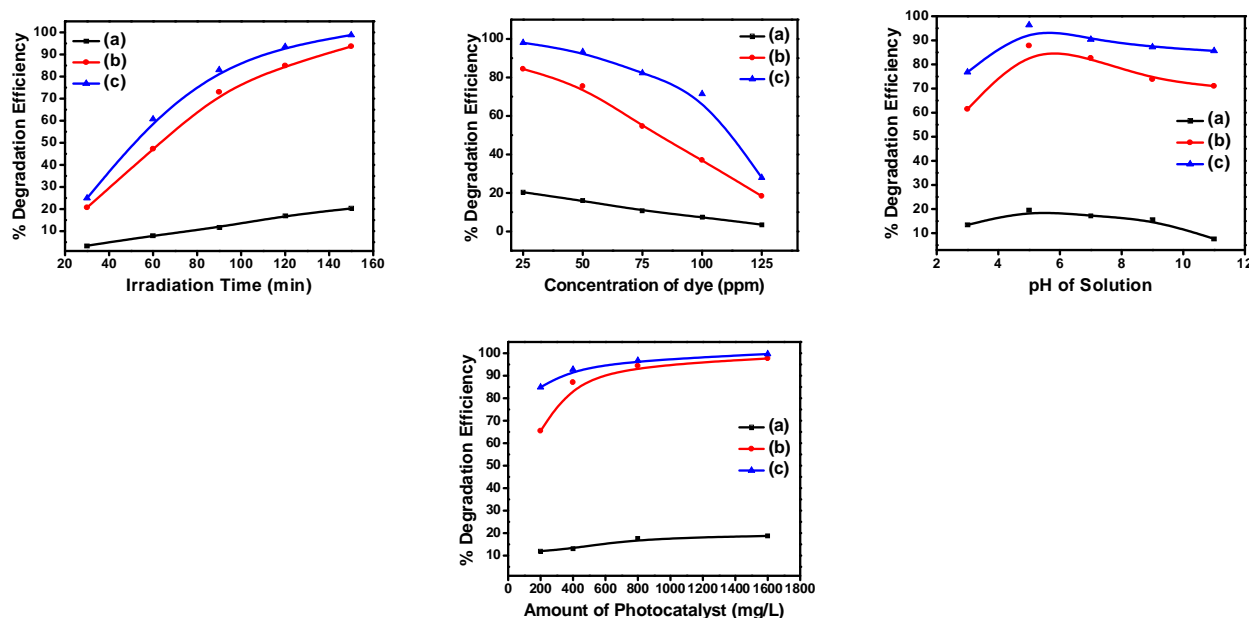


Fig. 5 Photodegradation of Rose bengal at different parameters with (a) TiO_2 , (b) TiO_2/PAni and (c) $\text{TiO}_2/\text{PAni}/\text{GO}$

- 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. The rate of photodegradation was decreased 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].
- 4) *Effect of Ph:* The photodegradation was carried out under varying pH conditions from (3 to 11), by adjusting with H_2SO_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). 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.. Fig. 5 Effect of pH of solution on photodegradation of Rose Bengal with photocatalyst Hence highly acidic and basic condition is not encouraging for the degradation of rose bengal. This implies that neutral conditions are good 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) *Effect of photocatalyst Amount:* It is clear from the results shown in Fig.14 that TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni}/\text{GO}$ nanocomposites are proving as an effective photocatalyst for the degradation of rose bengal dyes. The photodegradation of Rose Bengal was increasing with increases the amount of photocatalyst. It is observed that $\text{TiO}_2/\text{PAni}/\text{GO}$ 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 $\text{TiO}_2/\text{PAni}/\text{GO}$ respectively [49].

C. 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 centrifuged to remove the photocatalyst. The obtained 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 Rose Bengal. The photodegradation of Rose Bengal by the recycled Photocatalyst are showing in Fig. 6. The result shows that the recycled photocatalyst efficiency is decreasing due to the loss of some active sites and decrease of the collection efficiency of photon [50, 51].

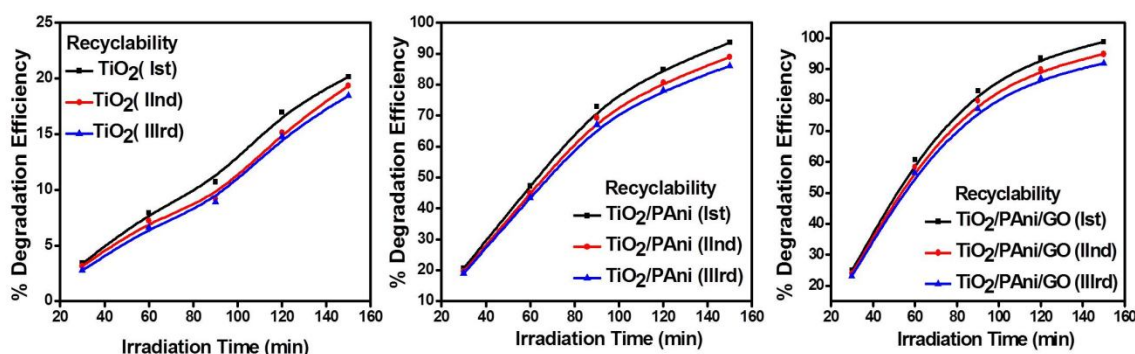


Fig.6. Photodegradation of Rose Bengal by Photocatalyst and recyclable Photocatalyst TiO_2 , TiO_2/PAni , $\text{TiO}_2/\text{PAni/GO}$

D. Lowering of electron-hole recombination

Photoluminescence spectra have been utilized to look at the mobility of the charge carriers to the surface and in addition, the recombination process required by the electron-hole pair in semiconductor particles. PL emission comes about because of the radiative recombination of energized electrons and holes. It is a basic need of a decent photocatalyst to have least electron-hole recombination. To concentrate the recombination of charge carriers, PL investigations of incorporated materials have been attempted. PL emission intensity is directly related to recombination of excited electrons and holes. Fig. 7 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 $\text{TiO}_2/\text{PAni/GO}$ has weak intensity. The weak PL intensity of $\text{TiO}_2/\text{PAni/GO}$ 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].

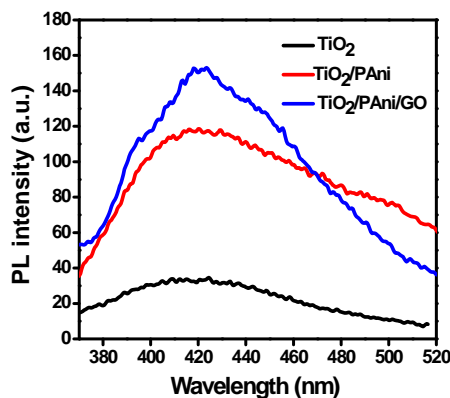
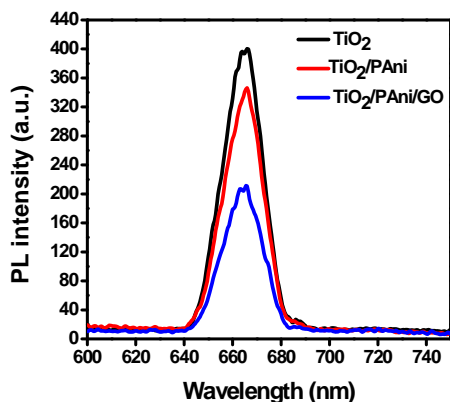


Fig.7 Photoluminescence Spectra of TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni/GO}$ Fig.8 PL spectra of photocatalyst with terephthalic acid (0.001M) TiO_2 , TiO_2/PAni and $\text{TiO}_2/\text{PAni/GO}$

E. Hydroxyl radical formation

As the hydroxyl radical plays important role in the decomposition of the organic pollutants. It is important to explore the measure of hydroxyl radicals created by each photocatalyst. In this way, there is a strategy to build up the arrangement of hydroxyl radicals utilizing terephthalic acid (TA) as a probe molecule. In this technique, TA was reacting with OH radical forming 2-hydroxyl terephthalic acid (TAOH) which gives fluorescence peak at 426 nm. Fig. 8 denoted the fluorescent signal of all the photocatalysts after reacting with TA arrangement. The fluorescent intensity is linearly related to the number of hydroxyl radicals formed by the photocatalysts. It implies higher is the formation of hydroxyl radical, yield of TAOH will be high and subsequently more intense will be the fluorescence peak. Thus, $\text{TiO}_2/\text{PAni/GO}$ with highest intensity confirms the generation more number of hydroxyl radicals compared to other photocatalysts. The fluorescence intensity follows the trend (i.e. $\text{TiO}_2 < \text{TiO}_2/\text{PAni} < \text{TiO}_2/\text{PAni/GO}$) of photocatalytic performance of all the photocatalyst [54, 55].

F. Kinetics of photodegradation

For the 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. 9). 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].

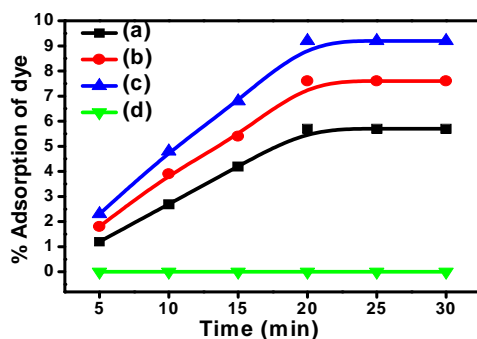


Fig.9 % Adsorption under dark condition (a) TiO₂ (b) TiO₂/PAni (c) TiO₂/PAni/GO (d) Dye + visible light without photocatalyst

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:

$$r = -\frac{d[RB]}{dt} = -\frac{kK[RB]}{1+K[RB]} \quad (2)$$

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.(3) :

$$\ln \frac{[RB]}{[RB]_0} + k ([RB] - [RB]_0) = -kKt \quad (3)$$

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. (3) 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. (2) leads to Eq. (4) :

$$r = -\frac{d[RB]}{dt} = kK[RB] = K'[RB] \quad (4)$$

Integration of eq. (4) yields eq. (5)

$$[RB] = [RB]_0 e^{-K't} \quad (5)$$

$$\ln \frac{[RB]}{[RB]_0} = -K't = -k't \quad (6)$$

Where k' is the pseudo rate constant and is in units of time^{-1} . Figure 20 shows the $\ln [RB]_0 - [RB]$ vs. time plots for TiO₂, TiO₂/PAni and TiO₂/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. 10 [61-62]. The rates constant were found 6.5×10^{-3} , 20.9×10^{-3} and 30.5×10^{-3} for the TiO₂, TiO₂/PAni and TiO₂/PAni/GO nanocomposite respectively.

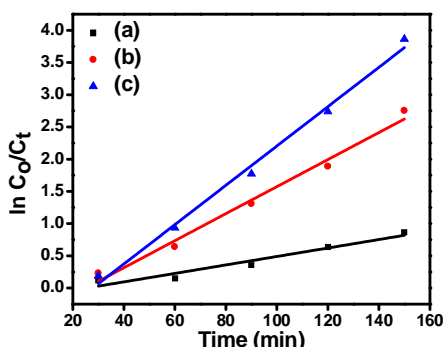


Fig.10 kinetics of photodegradation of RB with (a) TiO₂ (b) TiO₂/PAni (c) TiO₂/PAni/GO

III. CONCLUSION

In this study, nanocomposites materials were prepared by the insitu co-deposition oxidative methods. Different techniques were used for the characterisation of the TiO_2 , TiO_2/PANI and $\text{TiO}_2/\text{PANI}/\text{GO}$ nanocomposite such as XRD, BET, SEM, TEM, FTIR, Photoluminescence, 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 the nanocomposite. The FTIR characterization confirms that the $\text{TiO}_2/\text{PANI}/\text{GO}$ 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 $\text{TiO}_2/\text{PANI}/\text{GO}$ Nanocomposites respectively. The Band gap energy of TiO_2 , TiO_2/PANI and $\text{TiO}_2/\text{PANI}/\text{GO}$ were calculated by tauc 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 the dose of the photocatalyst. The maximum photodegradation was 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 coating of PANi and GO has enhanced the photocatalytic activity of Titania. Hence TiO_2/PANI and $\text{TiO}_2/\text{PANI}/\text{GO}$ is the efficient photocatalyst for the degradation of Rose Bengal dye than pure TiO_2 .

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