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](image)

![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](image)

**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].
Fig. 5.13. Effect of pH of solution on photodegradation of RB with (a) TiO₂, (b) TiO₂/PAni and (c) TiO₂/PAni/GO nanocomposite

5.3.2.5 Effect of photocatalyst amount

It is clear from the results shown in Fig. 5.14 that TiO₂, TiO₂/PAni, and TiO₂/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].

![Recyclability of Photocatalyst](image)

Fig.5.15. Photodegradation of Rose Bengal by Photocatalyst and recyclable Photocatalyst TiO$_2$, TiO$_2$/PAni, TiO$_2$/PAni/GO

### 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.

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](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
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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, \( h^+_{VB} \) may react with surface-bound \( H_2O \) or \( OH^- \) to produce the hydroxyl radical and \( e^-_{cb} \) is picked up by oxygen to generate superoxide radical anion (\( O_2^- \)), as indicated in the following equations 3-5; absorption of efficient photons by Titania (\( h\nu \geq E_{bg} = 3.2 \text{ eV} \))

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

Formation of superoxide radical anion

\[
O_2 + e^-_{cb} \rightarrow O_2^- \quad (4)
\]

Neutralization of \( OH^- \) group into \( OH \) by the hole

\[
(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^+_{dye} \rightarrow \cdot OH + H^+ \quad (5)
\]

It has been suggested that the hydroxyl radical (\( \cdot OH \)) and superoxide radical anions (\( O_2^- \)) 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 \( OH \) radicals,
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\[
R + \cdot OH \rightarrow R. + H_2O \quad (6)
\]

or by direct reaction with holes

\[
R + h^+ \rightarrow R^+ \rightarrow \text{degradation products} \quad (7)
\]

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\textsubscript{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 (\(\lambda<387\ \text{nm}\)) [61]. Many organic compounds have a potential above that of the TiO\textsubscript{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\textsubscript{2} conduction band.

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

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

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

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

The TiO\textsubscript{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\textsuperscript{+} combines with two electrons and a proton to give its reduced form (RB\textsuperscript{−}). 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\textsubscript{2} and NH\textsubscript{4}.

It is observed that rate constant in the presence of TiO\textsubscript{2}/PAni nanocomposite photocatalyst is larger than that in the presence of pure TiO\textsubscript{2} photocatalyst. The electron from the conduction band of TiO\textsubscript{2} may be transferred to the empty PAni states, making the valence band hole of TiO\textsubscript{2} stable, thus enhancing the oxidative efficiency of the
TiO$_2$ 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 TiO$_2$, it is possible to drive the photogenerated electrons farther away from the TiO$_2$, 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 TiO$_2$ 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 TiO$_2$ 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),

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

(10)

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

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

(11)
\[ \ln \left( \frac{[RB]}{[RB]_0} \right) = k' t = K't \]  

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

Figure 5.20 shows the \( \ln \left( \frac{[RB]}{[RB]_0} \right) \) 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].
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].

\[ \eta = \frac{TB_0 - TB_F}{TB_0} \]  

(13)

where TB$_0$ is the initial absorbance and TB$_F$ is the final sampled absorbance for a given time.
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.

![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.
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, vis (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:

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

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:

\[
r_o = \frac{kK_A C_o}{1 + K_A C_o}
\]  

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]:

<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>
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\[ -\frac{dC}{dt} = kK_{A}C_{o} = \ln \frac{C_{o}}{C} = kK_{A}t \quad (16) \]

\[ C = C_{o}e^{-k_{\text{photo}}t} \quad (17) \]

Where \( k_{f,\text{photo}} \) is \( kK_{A} \). The value of \( k_{f,\text{photo}} \) can be determined from the plot of \( \ln C_{t}/C_{0} \) vs. \( t \) (Fig. 5.24).

\[ \text{Fig. 5.23.} \ % \ \text{Adsorption of Thymol Blue dye under dark condition in presence of (a) TiO}_{2}, \ (b) \ \text{TiO}_{2}/\text{PAni} \ \text{and (c) TiO}_{2}/\text{PAni/GO}} \]

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 \( \text{TiO}_{2} \), \( \text{TiO}_{2}/\text{PAni} \) and \( \text{TiO}_{2}/\text{PAni/GO} \) 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 \( \text{TiO}_{2} \), \( \text{TiO}_{2}/\text{PAni} \), and \( \text{TiO}_{2}/\text{PAni/GO} \).
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, 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 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 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.
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$_2$.

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CHAPTER-6

Photocatalytic degradation of Victoria Blue and Rose Bengal dye in visible light by prepared TiO$_2$/PPy/GO nanocomposite

The present research work describes a proficient method for synthesis of TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites. These nanocomposites were prepared by one-step in situ deposition oxidative polymerization of pyrrole hydrochloride using Ammonium per sulphate (APS) as an oxidant in the presence of ultra fine grade powder of TiO$_2$ nanoparticles cooled in an ice bath. The obtained nanocomposites were characterized by XRD, TEM, SEM, UV-Vis, FTIR, techniques. The obtained results showed that TiO$_2$ nanoparticles have been encapsulated by PPy with a strong effect on the morphology of TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites. The Photocatalytic degradation of Rose Bengal and Victoria blue dye was done at different condition viz concentration of dye, time of illumination, pH and dose of photocatalyst. The maximum photodegradation were found at 7 pH, 20 ppm concentration of Victoria blue and 25 ppm of rose bengal dye solution, 800 mg/L for VB and 1600 mg/L for RB amount of photocatalyst and 120 min irradiation of visible light. Kinetics of photodegradation was investigated for Victoria blue and Rose Bengal dye and found first order kinetics. The coating of PPy and GO were enhanced the photocatalytic activity of Titania. Hence TiO$_2$/PPy and TiO$_2$/PPy/GO are the efficient photocatalyst for the degradation of Rose Bengal and Victoria Blue dye than pure TiO$_2$. 


6.1. Introduction

The waste water released from textile and other colouring industries, containing the various dyes have been badly affecting aquatic life and living organism due to their carcinogenic behaviour. Lots of investigations reported that 10-12% of dyes, such as Rose Bengal, Victoria blue, Thymol blue, Caramine, Indigo Red, Red 120, Rhodamine B, Methylene Blue, Eriochrome Black-T (EBT) etc., have been used every year in textile industries, [1-4]. The major portion (~20%) of these dyes is lost during synthesis and processing operations, which enter into water bodies through effluents, causing water polluted. Rose Bengal (Figure 6.1 a) is a significant xanthene dye used in textile and photochemical industries. It has severe toxic effects on the human health [5-7] and become dangerous in contact with skin, causing itchiness, irritation, reddening and blistering. It also affects to eyes causing inflammation, eye redness, itching etc. [8]. Victoria blue is another triphenylmethane derivatized dye which is extensively used in the textile industry. It has been extensively used as textile dyes for silk, wool, and cotton, in the preparation of inks, in the surface-coating and dyeing of paper [9-11], as colorants in foods, drugs, cosmetics [12], as biological stains, and as anti-infective, antimicrobial and antihelmintic agents [13]. The photocytotoxicity of triphenylmethane dyes is based on the production of the reactive oxygen species and tested extensively with the regard to its photodynamic treatment [14].

In the past several techniques, like coagulation, flocculation, reverse osmosis, adsorption, ion exchange method ultra-filtration and photosensitized oxidation have been used to reduce the toxic dye effluents from wastewater [15-18]. Though methods are fairly effective in removing pollutants, however, the main drawback of these techniques is the formation of the secondary waste product which cannot be treated again and dumped as such [19]. In the recent years, photocatalytic degradation has emerged as an effective technique for complete mineralization of waste water. Titanium dioxide (TiO$_2$) nanoparticles (NPs) are an excellent photocatalyst because of its low cost, simple preparation, good stability, non-toxicity and better photodegradation ability [20]. It has successfully been used in solar cells [21] photocatalysis [22] and photocatalytic hydrogen production [23]. The bare TiO$_2$ nanoparticles have the wide band gap, thus has low sunlight energy conversion efficiency and high rate of (e$^{-}$-h$^{+}$) electron-hole recombination capability. Therefore, improvement of the photocatalytic properties of TiO$_2$ is essential. In order to enhance the
photocatalytic properties of TiO$_2$, number of manipulations, such as metal or non-metal doping [24], compositing with other semiconductors [25], compositing with conductive materials such as graphene [26] or carbon nanotubes [27], sensitization with organic dyes and conductive polymers, such as polyaniline [28], polythiophene [29], and polypyrrole (PPy) have been tested in the past [30]. Among these routes, the coating of conductive polymers is one of the most effective methods for the generation of good photocatalytic activity [31]. The coating of conductive polymers can reduce the recombination rate of electron-hole (e$^-$-h$^+$) simultaneously act as sensitizer making effective large band gap semiconductor like TiO$_2$ [32-33].

Among the various conductive polymers, PPy is one of the most promising coating agents, owing to its good conductivity, high absorption coefficient in the visible part of sunlight, high charge carrier mobility, and good environmental stability [34]. Therefore PPy is suitable conducting polymer and stable photosensitizer to improve the photocatalytic activity of TiO$_2$ in solar light. In the past TiO$_2$/PPy nanocomposite has been successively used in solar cells and for the photocatalytic degradation of organic species; however, its use in photocatalytic degradation of organic dyes is rarely reported.

There are many methods of preparing TiO$_2$/PPy nanocomposite, for example, anodic co-deposition [35], self-assembly techniques [36], photoelectrochemical polymerization [37], and hydrothermal methods [38]. However, in-situ chemical polymerization is a promise method for preparation of TiO$_2$/PPy owing to its simplicity, good reproducibility, and easy scale up.

![Molecular Structure of dyes](attachment://figures/fig6.1.jpg)

(a) Victoria Blue
(b) Rose Bengal

Fig.6.1. Molecular Structure of dyes (a) Victoria Blue (b) Rose Bengal
In the present study, TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites have been prepared by one-step *in situ* polymerization of pyrrole in the reaction medium. The photocatalytic degradation of Victoria Blue and Rose Bengal have been studied in the presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites at the different parameters i.e. concentration of dye, the dose of the photocatalyst, pH of the reaction mixture and irradiation time. The kinetics for the photodegradation process has also been investigated in this work.

Table 6.1. Showing the structure and properties of dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Victoria Blue</th>
<th>Rose Bengal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>[C$<em>{33}$H$</em>{40}$N$_3$]Cl.</td>
<td>C$<em>{20}$H$</em>{4}$Cl$<em>{4}$I$</em>{4}$O$_{5}$</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>507.5 g/mol</td>
<td>973.67 g/mol</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>614 nm</td>
<td>547 nm</td>
</tr>
</tbody>
</table>

6.2. Experimental

6.2.1 Materials

Pyrrole monomer, having molar mass of 67 g/mol and density of 0.97 g/cm$^3$ (Merck India) was triply distilled until a colourless liquid was obtained. The distilled pyrrole was stored at lower than 5 °C temperature in the absence of light. All other chemicals were analytical grade.
6.2.2 Preparation of PPy

1.727 ml pyrrole was dissolved in 50 ml of de-ionized water and stirred for 15 min using a magnetic stirrer. 2.717 ml dilute H\textsubscript{2}SO\textsubscript{4} was added slowly using dropper to the pyrrole monomer solution. 2.28 g ammonium per sulphate was dissolved in 50 ml of de-ionised water and slowly added drop-by-drop from a burette to the above prepared solution with constant stirring for half an hour. After stirring for 4 h, the solution was filtered and the residue was washed with double distilled water, methanol and acetone, and dried in oven at 60°C. Subsequently, the product was grinded to get powder of polypyrrole [39].

6.2.3. Preparation of graphene oxide

Graphene oxide was synthesized from graphite powder using a modified Hummer’s method. In brief, first, 0.5 g of powdered flake of graphite and 0.5 g of NaNO\textsubscript{3} were added into 24 mL of H\textsubscript{2}SO\textsubscript{4} and were stirred until dissolved. Then, 3 g of KMnO\textsubscript{4} was added slowly, preventing the temperature of the suspension from exceeding 20 °C. After continuous stirring, the mixture for 1 h at 35 °C, 40 ml of distilled water was slowly added to dilute the mixture and the temperature was raised to 90 °C. To reduce the residual permanganate and manganese dioxide to colourless soluble manganese sulphate, 5 ml of 34.5% H\textsubscript{2}O\textsubscript{2} was added and the suspension was filtered with distilled water until pH 7.0. The obtained yellow-brown suspension was exfoliated to produce single layer graphene oxide using a sonicator, and the unexfoliated precipitation was removed by centrifugation. Finally, we obtained a brown dispersion of homogeneously exfoliated graphene oxide [40].

6.2.4. Preparation of TiO\textsubscript{2}/PPy nanocomposites

TiO\textsubscript{2} nanoparticles, with an average particle size of 50 nm, were prepared by previous reported method [41]. 3.454 ml pyrrole and 5.434 ml dilute H\textsubscript{2}SO\textsubscript{4} were stirred with 100 ml double distilled water and 1.036 g TiO\textsubscript{2} added in the pyrrole reaction medium. 4.56 g ammonium per sulphate was dissolved in 100 ml of de-ionized water and slowly added drop by drop from a burette to the above prepared solution for half an hour. After stirring for 4 h, the solution was filtered and the residue was washed with double distilled water, methanol and acetone, dried in an oven at 60°C and grinded into powder [42].
6.2.5 Preparation of TiO$_2$/PPy/GO nanocomposites

3.454 ml pyrrole and 5.434 ml dilute H$_2$SO$_4$ were stirred with double distilled water. 1.0362 g TiO$_2$ and 60 mg graphene oxide was added in the pyrrole reaction medium and the mass ratio of TiO$_2$: PPy: GO was maintain at 8: 17.5: 1. The amount of 4.56 g ammonium per sulphate was dissolved in 100 ml of de-ionized water and slowly added drop by drop using burette to the above prepared solution for half an hour. After stirring for 4 h, the solution was filtered and the residue was washed with double distilled water, methanol and acetone, dried in an oven at 90 ºC and grinded into powder form [43].

6.2.6. Characterizations

The phase and purity of as-synthesized TiO$_2$, PPy, TiO$_2$/PPy and TiO$_2$/PPy/GO materials were determined by X-ray diffraction (XRD) pattern recorded on analytical X’Pert Pro X-ray diffractometer in the 2θ range 10 to 80º with the step size of 0.025º. The particle size of TiO$_2$ and morphology of particles was investigated with transmission electron microscope (TEM) images observed on JEOL JEM 200 CX equipment. The morphology of neat TiO$_2$, PPy, and TiO$_2$/PPy nanocomposites was investigated by scanning electron microscopy images recorded on JEOL 6490 LB equipment. Diffused Reflectance spectroscopy study was done on Carry 100 spectrophotometer and graphs were used to determine band gap energy of prepared nanocomposites. Photoluminescence spectra (recorded on Perkin Elmer LS 55 spectrofluorometer) were used to study emission behaviour and e$^-$$h^+$ recombination determination of the samples.

6.2.7. Determination of the point zero charge of powdered Titania Nanocomposites

The point zero charge (PZC) of the Titania nanocomposites was determined employing the solid addition method using 0.1 mol L$^{-1}$ KCl and 0.002 mol L$^{-1}$ citrimide (C$_{19}$H$_{42}$BrN) surfactant solutions. Fifty millilitres of KCl and citrimide solution was taken in 100 mL stoppered conical flask. The initial pH values of the solutions were roughly adjusted to be between 2 and 12 by adding either 0.1 mol L$^{-1}$ HCl or 0.1 mol L$^{-1}$NaOH. The initial pH of the solution was then accurately recorded. One gram of the prepared Titania based nanomaterials was added to each flask. The suspensions were shaken and allowed to equilibrate with intermittent shaking. The final pH of the supernatant liquid was recorded. The difference between the initial and final pH values (pH = pHi – pHf) were plotted against
the initial pH value. The point of intersection of the resulting curve where the change in pH is zero gives the value of the PZC [44].

6.2.8. Irradiation Procedure

The solutions of dyes were prepared in 10:1 (V/V) ratio of water and alcohol. The known amount of photocatalyst was dispersed in the dye solution (20 ml). The desired concentrations of Victoria Blue and Rose Bengal dye (20 mL) were taken in a 100 mL beaker and 1 g of each photocatalyst; TiO$_2$, PPy, TiO$_2$/PPy and TiO$_2$/PPy/GO were mixed to dye solutions and resulting suspensions were stirred on the magnetic stirrer in dark for 30 min to reach adsorption equilibrium. The visible light was irradiation was done by putting xenon lamp (1000 W) vertically on the surface of the reaction medium with constant stirring. After desired time interval, an aliquot of the solution was isolated, centrifuged, filtered through a Millipore filter to separate the photocatalysts and their UV-Vis absorption spectra were recorded to determine the residual concentration.

The % degradation efficiency of the samples was calculated using equation 1 [45-46].

$$\eta \% = \frac{A_0 - A_F}{A_0} \times 100$$  \hspace{1cm} (1)

Where $\eta$ is the degradation efficiency, $A_0$ is the initial absorbance and $A_F$ is the final absorbance

6.3. Results and Discussion

6.3.1 XRD patterns of nanocomposites

XRD patterns of pure TiO$_2$, PPy, TiO$_2$/PPy and the TiO$_2$/PPy/GO synthesized nanocomposites are presented in Figure 6.2. In the case of pure TiO$_2$ nanoparticles the main diffraction peaks observed at 25, 38, 48, 55.1 and 63.2 $^\circ$ are respectively (101), (103), (200), (211) and (204) planes of TiO$_2$ (JCPDS file No: 86-1157) (Figure 6.2 a). In the XRD pattern of GO obtained via the improved Hummers’ method, the (0 0 1) crystal plane of GO was observed, with a spacing of 8.33 Å which is typical for GO. In the XRD pattern of pure PPy (Figure 6.2 b) the observance of a broad peak in the 20 region 20 to 50$^\circ$ revealed that the as-synthesized PPy is amorphous in absence of TiO$_2$. Broad peaks in the region 15$^\circ$ < 20 < 30$^\circ$ is revealing that the resulting polypyrrole powders are amorphous in nature.
Fig. 6.2. X-Ray diffraction of (a) TiO$_2$ (b) Pure PPy (c) pure graphene oxide (d) TiO$_2$/PPy (e) TiO$_2$/PPy/GO

This agrees well with the structure reported in literature [16]. Such broad peak usually indicates short range arrangement of chains. It can be seen from Figure 6.2 c & d that the main peaks of TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites are similar to those of neat TiO$_2$ nanoparticles but broad weak diffraction peak of PPy still exists, however, its intensity has been decreased. It implies that when pyrrole is polymerized on TiO$_2$, each phase maintains its initial structure [47-48].
6.3.2 Determination of Average size of Particles/Grains in samples

Utilizing the observed X-ray diffraction data of samples, Scherrer’s calculations were attempted to know the average size of Crystal in the samples [49]. Although, Scherrer’s calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the Crystal in the samples, which may be quite accurate, provided the size of Crystal is below 100 nm.

\[
B = \frac{0.9\lambda}{t \cos \theta}
\]

The mean size of TiO\(_2\), TiO\(_2\)/PPy, and TiO\(_2\)/PPy/GO nanocomposites, calculated by Scherrer’s Equation, are about 19, 24 nm and 30 nm, respectively. The results of Scherrer’s calculations are presented in Table 2. The results suggest average size of the Crystal in the samples lying in nm range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>19</td>
</tr>
<tr>
<td>TiO(_2)/PPy</td>
<td>24</td>
</tr>
<tr>
<td>TiO(_2)/PPy/GO</td>
<td>30</td>
</tr>
</tbody>
</table>

6.3.3 SEM and TEM analyses

The morphology and shape of pure TiO\(_2\) nanoparticles, neat PPy, TiO\(_2\)/PPy and TiO\(_2\)/PPy/GO nanocomposites were characterized by SEM instrument and the obtained pictures are presented in Figure 6.3. As shown in Figure 6.3 b, TiO\(_2\) nanoparticles were aggregated due to their high surface energy. In the corresponding TEM image (Figure 6.4 a) 30±10 nm diameter polygonal prism like structures have been observed. In the SEM image (Figure 6.3 a) and TEM image (Figure 6.4 b), cloud like image of pure PPy has been observed.
Fig. 6.3. SEM images of (a) TiO$_2$ (b) pure PPy, (c) pure GO (d) TiO$_2$/PPy (e) TiO$_2$/PPy/GO nanocomposites.

Fig. 6.4. TEM of (a) TiO$_2$ (b) Pure PPy (c) Graphene Oxide (GO) (d) TiO$_2$/PPy (e) TiO$_2$/PPy/GO

The SEM and TEM images (Figure 6.3 c and Figure 6.4 c) show that the morphology of TiO$_2$/PPy composite is similar to pure PPy. In the SEM image (Figure 6.3 d), aggregates
of TiO$_2$/PPy/GO observed, however in the TEM image (Figure 6.4 d), multi facet polygonal prismatic structures, with diameter 40±15 nm have been observed. Above data indicate that PPy polymerizes in presence of GO. The SEM images help us draw a conclusion that the doping of TiO$_2$ has no effect on PPy’s morphology, however, presence of TiO$_2$ along with GO retain the similar structure for TiO$_2$/PPy/GO as observed in case of pure TiO$_2$ [50].

6.3.4 Bruner Ernst Teller Surface area analysis

Nitrogen adsorption–desorption isotherms were used to determine the structural characteristics and surface area of TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO nanocomposite. The N$_2$ adsorption desorption isotherms of the TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO nanocomposite were measured at 77 K, as shown in Figure 6.5. The specific surface areas (from BET and Surface area, pore volume and pore radius of the TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposite are showing in Table 6.3. The surface area was found 37.52, 76.68 and 96.24 m$^2$/g for TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO respectively. There is an increase in Vp and pore radius of the TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposite respectively [51]. From these results, it may be concluded that the high surface area of the TiO$_2$/PPy/GO nanocomposite may favour rapid electron transport and high ion diffusion, allowing improved photochemical performance.

Table 6.3. The specific surface area, pore volume and pore radius of the TiO$_2$, TiO$_2$/PPy and PPy/TiO$_2$/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>1.21</td>
</tr>
<tr>
<td>PPy</td>
<td>19.83</td>
<td>2.632</td>
<td>1.12</td>
</tr>
<tr>
<td>GO</td>
<td>14.86</td>
<td>2.142</td>
<td>1.02</td>
</tr>
<tr>
<td>TiO$_2$/PPy</td>
<td>76.68</td>
<td>6.5124</td>
<td>1.64</td>
</tr>
<tr>
<td>TiO$_2$/PPy/GO</td>
<td>96.24</td>
<td>9.5124</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Moreover, the BET surface areas increased remarkably in the TiO$_2$/PPy/GO nanocomposite, which suggests that TiO$_2$ is well intercalated in PPy matrix and may also provide direct conduction pathway for electrons. The formation of TiO$_2$ with PPy by co-deposition
oxidation synthesis resulted in the generation of well dispersed TiO$_2$ in PPy Matrix giving one TiO$_2$/PPy system with unique set of properties [52].
6.3.5 UV-Visible spectra of nanocomposites

The prepared nanocomposites aqueous suspensions were used for the UV absorption studies. The absorption spectrum of TiO\textsubscript{2} consists of a single broad intense absorption between 250 to 400 nm due to the charge-transfer from the valence band to the conduction band [53]. The TiO\textsubscript{2} showed absorbance in the shorter wavelength region while PPy, GO, TiO\textsubscript{2}/PPy and PPy/TiO\textsubscript{2}/GO result showed slight red shift in the absorption edge. The absorption spectrum of TiO\textsubscript{2} consists of a single broad intense absorption around 383 nm (shown in Fig.6.6) in the region of the hypsochromic shift. The TiO\textsubscript{2}/PPy results showed a red shift in the absorption onset value and the broad peak observed at 410 nm. This is due to the coating of PPy layer on the surface of Titania [54]. The red shift that is observed at 410 nm in the absorption spectra with the decrease in particle size has been reported in TiO\textsubscript{2}/PPy/GO nanocomposite. This is due to the coating of PANi and Graphene oxide in the Titania and the Titania completely interacted with PPy and GO.
6.3.6. Determination of optical band gap of nanocomposites

The UV-Vis spectra of the Titania based nanocomposites have been recorded and data were used to determine band gap values. The band gap of materials was determined by the Tauc relation (Eq. 3)

$$\alpha \nu = B(\nu - E_{\text{gap}})^m$$  

where $\alpha$ is the absorption coefficient, $\nu$ is the photon energy and $m = 1/2$ for direct band gap material shown in Figure 6.7. To describe a direct method for fitting and determination of band gap using Tauc relation [53-54], we can re-write the equation (3) as:

$$\left( \frac{\text{Abs.}}{\lambda} \right)^{1/m} = B \left( \frac{1}{\lambda} - \frac{1}{\lambda_{\text{gap}}} \right)$$  \hspace{1cm} (4)

where $\lambda$ is the wavelength and Abs. the corresponding value of measured absorbance. $\lambda_{\text{gap}}$ can be easily obtained from curve $(\text{Abs.}/\lambda)^{1/m}$ vs. $1/\lambda$ plot at condition $(\text{Abs.}/\lambda)^{1/m} = 0$. The band gap value is obtained from relation $E_{\text{gap}} = 1239.83/\lambda_{\text{gap}}$. The band gap of samples was calculated by extrapolation of the $(\alpha \nu)^2$ versus $\nu$ plots, where $\alpha$ is the absorption coefficient and $\nu$ is the photon energy; $\nu = (1239/\lambda)$ eV. The value of $\nu$ extrapolated to $\alpha = \ldots$
0 gives an absorption energy, which is correspond to a band gap \((E_g)\). Figure 6.8 yields an \(E_g\) value of 3.2 eV for TiO\(_2\), 2.98 eV for pure PPy, 2.65 eV for TiO\(_2\)/PPy and 2.45 eV for TiO\(_2\)/PPy/GO [55]. The band gap values of nanocomposites slightly decrease compared to pure TiO\(_2\) because the electrons of pure PPy are excited from the HOMO to the LUMO of PPy whereas holes were left in the HOMO of PPy. The excited-state electrons can be readily injected into the conduction band of TiO\(_2\) [56].

![Fig. 6.7 Band Gap energy of (a) pure TiO\(_2\) (b) pure PPy (c) Graphene oxide (d) TiO\(_2\)/PPy (e) TiO\(_2\)/PPy/GO nanocomposites.](image)

Fig. 6.7. Band Gap energy of (a) pure TiO\(_2\) (b) pure PPy (c) Graphene oxide (d) TiO\(_2\)/PPy (e) TiO\(_2\)/PPy/GO nanocomposites.
6.3.7. Determination of PZC of Nanocomposites

The point zero charge (PZC) of the Titania nanocomposites was determined employing the solid addition method. The point zero charge (PZC) was found 6.4, 6.6 and 6.9 for the TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO. It is shown in the Fig.6.8.

Fig.6.8. Determination of PZC of nanocomposites (a) TiO$_2$ (b) TiO$_2$/PPy (c) TiO$_2$/PPy/Go

6.3.8. Photodegradation

6.3.8.1. Effect of pH

The Photodegradation of dyes are affected by the pH of the solution. The variation of solution pH changes the surface charge of TiO$_2$ particles and shifts the potentials of catalytic reactions. As a result, the adsorption of dye on the surface is altered thereby causing a change in the reaction rate. Titania has point of zero charge (pzc) at 6.9. Under acidic or alkaline condition the surface of Titania can be protonated or deprotonated according to the following reactions [57]:

$$\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \quad (9)$$

$$\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (10)$$

Thus Titania surface will remain positively charged in acidic medium (pH < 6.9) and negatively charged in alkaline medium (pH > 6.9). Titanium dioxide is reported to have higher oxidizing activity at lower pH, but excess H$^+$ can decrease reaction rate. TiO$_2$ behaves as a strong Lewis acid due to the surface positive charge. In other words, the anionic dye acts
as a strong Lewis base and can easily adsorb on the positively charged catalyst surface. This favours the adsorption of the dye under acidic conditions, while in the alkaline conditions this complexation process is not favoured presumably because of competitive adsorption by hydroxyl groups and the dye molecule in addition to the Coulombic repulsion due to the negatively charged catalyst with the dye molecule [58]. The extent of dye adsorption depends on the initial dye concentration, nature of the dye, surface area of photocatalyst and pH of the solution. The pH determines the surface charge of the photocatalyst. Adsorption of the dye is minimum when the pH of the solution is at the isoelectric point (point of zero charge [44]. The surface of the photocatalyst is positively charged below isoelectric point and carries a negative charge above it.

Bubacz et al [59] observed an increase in the rate of the photocatalytic degradation of methylene blue with an increase in pH. According to Ling et al [60], basic pH electrostatic interactions between negative TiO\(^-\) and Methylene blue cation leads to strong adsorption with a corresponding high rate of degradation. Ling et al [60] noted that basic pH electrostatic interactions between negative TiO\(^-\) and methylene blue cation leads to strong adsorption with a corresponding high rate of degradation. The surface charge properties of TiO\(_2\) were also found to change with a change of pH value due to the amphoteric behaviour of semi conducting TiO\(_2\) (Guillard et al [61], Zielin’ska et al [62], Senthilkumaar et al [63]). Kansal et al [64] also found that the degradation of Reactive Black 5 and Reactive Orange 4 dyes was favored in acidic medium with TiO\(_2\). Tanaka et al. [65] found that positively charged TiO\(_2\) surface adsorbed more Acid Orange 7 at lower pH value, and more decomposition was achieved. The acid black 1 has a sulfuric group in its structure, which is negatively charged. So the acidic solution favours adsorption of dye onto photocatalyst surface as TiO\(_2\) surface is positively charged in acidic solution (Grzechulska and Morawski [66]).

The photodegradation of cationic dyes (Victoria blue) and anionic dye (Rose Bengal) was carried out under varying pH conditions from (2 to 9), by the addition of H\(_2\)SO\(_4\) and NaOH, keeping other parameters constant (concentration = 50 ppm, the amount of catalysts = 800 mg/L and irradiation time = 120 min). The results show that degradation of dye Victoria blue is highest in basic medium (at pH = 10) shown in Figure 6.9. Under acidic conditions, it was found difficult to adsorb the cationic VB dye onto the TiO\(_2\) surface. The active •OH radicals, formed in low concentrations, and hence the photodegradation process of VB
remained slow. With higher pH values, the formation of active •OH species is favoured, due to not only improved transfer of holes to the adsorbed hydroxyls, but also electrostatic abstractive effects between the negatively charged TiO\(_2\) particles and the operating cationic dyes. Although the VB dye can adsorb onto the TiO\(_2\) surface to some extent in alkaline media, when the pH value is too high (pH 11), the VB dye molecules will change to a leuco-compound. Our results indicate that the TiO\(_2\) surface is negatively charged, and the VB adsorbs onto the TiO\(_2\) surface through the positive ammonium groups. This is characteristic of heterogeneous photocatalysts, and the results are in agreement with the earlier studies [67].

The photodegradation of Rose Bengal is highest in acidic medium at pH 5 shown in Figure 6.10. This implies that the acidic condition is favourable for the formation of the reactive intermediate hydroxyl radicals for Rose Bengal. This further helps in enhancing the reaction rate. On the other hand in the neutral condition, the formation of reactive intermediate is relatively less favourable and hence not feasible [68]. The rate of photodegradation increases with increases in pH of the solution. At lower pH (3) values, surface of catalyst is negatively charged and dye molecules are positively charged. So dye molecules and catalyst particles will attract to each other. Thus catalytic reaction on the surface of TiO\(_2\) will take place to greater extent. But it is reported to have higher oxidizing activity at lower pH, but excess H\(^+\) can decrease reaction rate of photodegradation of dye. But the maximum photodegradation of Rose Bengal dye was found at pH 5, this is because that decrease in H\(^+\) concentration and adsorption of Rose Bengal (anionic dye) is higher at pH 5, because the force of attraction between catalyst surface and dye molecules will start operating thus resulting in increase in rate of dye degradation [69].

6.3.8.2 Effect of photocatalyst and dose

The effect of photocatalysts and their doses on the degradation of dyes Victoria Blue and Rose Bengal is shown in Figure 6.10 and Figure 6.11. It is clear from the results that the TiO\(_2\), TiO\(_2\)/PPy and TiO\(_2\)/PPy/Go are effective photocatalyst for degradation of Victoria Blue and Rose Bengal dye; however TiO\(_2\)/PPy/Go seems to be the most effective photocatalyst for degradation of Victoria Blue and Rose Bengal. Further photodegradation efficiency of the catalysts follows the trend TiO\(_2\) < TiO\(_2\)/PPy < TiO\(_2\)/PPy/GO.
Chapter 6  
Photocatalytic degradation of Victoria Blue and Rose Bengal dye......

![Graph](image1)

Fig.6.9. Effect of pH on photodegradation efficiency of dyes Victoria Blue and Rose Bengal (a) TiO$_2$ (b) TiO$_2$/PPy and (c) TiO$_2$/PPy/Go

![Graph](image2)

Fig.6.10. Effect of irradiation time on photodegradation efficiency of dyes Victoria blue and Rose Bengal (a) TiO$_2$ (b) TiO$_2$/PPy and (c) TiO$_2$/PPy/GO

The effect of photocatalyst dose on the photodegradation of Victoria Blue and Rose Bengal was studied by applying different concentrations (from 50 mg/L to 800 mg/L) of the photocatalyst is shown in Figure 6.11. Initially (from 50 mg/L to 200mg/L) the rate of degradation of the dyes Victoria Blue and Rose Bengal was very rapid, after that, it became slow and attained plateau at 800 mg/L due to occupancy of all active sites at this concentration. When the PPy is coated in TiO$_2$, the band gap energy is decreased which enhanced the photo-efficiency, the surface area of photocatalyst also increased the photo-efficiency of the photocatalyst.
Fig. 6.11. Effect of photocatalyst amount on efficiency of dyes Victoria blue and Rose Bengal (a) TiO$_2$ (b) TiO$_2$/PPy and (c) TiO$_2$/PPy/GO

6.3.8.3 Effect of dye concentration

The effect of dye concentration on photocatalytic degradation was studied in presence of TiO$_2$/TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites materials, keeping the amount of catalyst constant. A known concentration of dye solution was prepared in water: alcohol 10:1 (V: V) ratio. The 800 mg/L of photocatalyst was dispersed in the different concentration of dye solution (20, 40, 60, 80 and 100 ppm for Victoria blue and 25, 50, 75, 100 and 125 ppm Rose Bengal) and the reaction mixture was irradiated by visible light. The effect of photocatalytic degradation with time was measured and results are shown in Figure 6.12. The highest photodegradation efficiency (97 %) of both dyes was found in presence of TiO$_2$/PPy/GO nanocomposite while in presence of TiO$_2$/PPy and neat TiO$_2$ it was 86% and 16% respectively. When the concentration of solution increased, the number of dye molecule also increased, therefore, the effective number of photon penetrating the dye reached at the catalyst surface also reduced, owing to hindrance in the path of light, thereby reducing the reactive hydroxyl and superoxide radicals and decreasing the % degradation [67-69].
Fig. 6.12. Effect of concentration on photodegradation efficiency of dyes Victoria blue and Rose Bengal (a) TiO$_2$ (b) TiO$_2$/PPy and (c) TiO$_2$/PPy/GO

6.3.9. GC-MS of VB and RB photodegradation products

The photodegradation of the Victoria blue and Rose Bengal takes place by irradiating under visible-light in the presence of TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO nanocomposite. The photodegraded products of photodegradation of Victoria blue and Rose Bengal have been determined by GC-MS analysis (Fig. 6.13 and 6.14). It has been found that MS chromatograph (Fig. 6.15 and 6.16) and correspondingly mass chromatographs of Victoria blue and Rose Bengal (after 2 h of irradiation) in the presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO are almost similar, except in their respective intensities (Fig. 6.15 and 6.16). Among the number of degraded products of Victoria blue and Rose Bengal, seven products formed in the photodegradation, shown in mass chromatograph (Fig. 6.15 and 6.16) have been identified, as listed in Table 6.4.

Fig. 6.13. GC chromatogram of Victoria blue dye in presence of TiO$_2$/PPy/GO
The mechanism for the photodegradation of Victoria blue and Rose Bengal using Titania nanocomposites is believed to take place by the photo produced e- and h+, that results into formation of highly oxidative species such as hydroxyl and superoxide radicals, which on reaction with Victoria blue and Rose Bengal results into its decomposition to smaller molecules [70].

Table.6.4 Different intermediate products form in the photodegradation of Victoria Blue dye
The mass spectroscopy has been studied to identify the possible reaction intermediates after 180 min of reaction, as shown in Fig. 6.17. The RB dye solution displays a prominent mass signal at m/z = 1022 in Fig. 6.13 i.e. very close to the formula mass of RB dye. Noticeably,
no mass signals are detected about the formation of the reaction intermediates, which clearly reveal the removal by adsorption. The m/z = 1022 signal is weaken after 180 min of photocatalytic reaction over the TiO2/PPy/GO nanocomposites and multiple mass signals have appeared (Fig.6.17, indicates the formation of reaction intermediates during the photocatalytic degradation. Fig.6.17 depicts the molecular structures of possible reaction intermediates from fragmentations of the main skeleton of RB dye which have the oxy groups in their rings. It is believed that the formations of these reaction intermediates are crucial to determine the degree of degradation of the organic compounds to complete mineralization [71].

6.3.10. Recyclability of Photocatalyst

In order to observe reusability, the photocatalyst recyclability has been studied in this work. The photocatalyst and Victoria Blue and Rose Bengal mixture was agitated, illuminated with visible light and after desired time, the mixture was centrifuged to remove the photocatalyst.

[Graph showing photodegradation efficiency vs. time for different catalysts]

Fig.6.18. Photodegradation of Victoria Blue by Photocatalyst and recyclable Photocatalyst (a) TiO2 (b) Recyclized TiO2 (c) TiO2/PPy (d) Recyclized TiO2/PPy (e) TiO2/PPy/GO (f) Recyclized TiO2/PPy/GO

The obtained photocatalysts were washed three times with distilled water and finally kept in oven for 24 h at 60 °C temperature and further, it is reused for the degradation of dyes. The photodegradation of Victoria Blue and Rose Bengal by the recyclized
Photocatalyst are showing in Figure 6.18 and 6.19. The results show that the recyclized photocatalyst efficiency is decreased due to the loss of some active sites and decrease of collection efficiency of photon [72].

![Photodegradation of Rose Bengal by Photocatalyst and recyclable Photocatalyst](image)

**Fig.6.19. Photodegradation of Rose Bengal by Photocatalyst and recyclable Photocatalyst (a) TiO$_2$ (b) Recyclized TiO$_2$ (c) TiO$_2$/PPy (d) Recyclized TiO$_2$/PPy (e) TiO$_2$/PPy/GO (f) Recyclized TiO$_2$/PPy/GO**

### 6.3.11. TOC Analysis of photodegraded dyes

In order to measure the complete mineralization of Victoria blue and Rose Bengal dyes, a TOC analysis was performed. During the initial stage of recirculation in the dark (30 min), the chemisorptions of the dyes on the catalyst surface caused a TOC depletion of 5-8%. The experimental data obtained by using either TiO$_2$ or TiO$_2$/PPy and TiO$_2$/PPy/GO are shown in Figure 6.20. The Blank test of dye (without photocatalyst) is also reported for comparison for photocatalytic activity of nanocomposites, a maximum decrease of the TOC percentage is observed in the presence of the TiO$_2$/PPy/GO nanocomposites [73].

The TOC analysis of photodegraded Victoria Blue and Rose Bengal dye in presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO were done. The TOC of Victoria blue is showing in Figure 6.21. The Victoria blue was photodegraded for 3 h in presence of photocatalyst. The TOC of Victoria blue was observed 100, 92, 26 and 4% for the blank, TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO. The polypyrrole modified Titania material shows the good photocatalytic
activity. Similarly, The TOC was observed for the Rose Bengal dye shown in Figure 21. The TOC photodegraded Rose Bengal was found 100, 94, 34 and 16 % for blank, TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO. It means that polypyrrole modified Titania shows the good photocatalytic activity due to formation of heterostructures [74].

Fig.6.20. % TOC of dye after adsorption (keep in under dark for 30 min)

Fig.6.21. % TOC of dyes after photodegradation with TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO

6.3.12. Hydroxyl radical formation

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 method, alkaline solution of terephthalic acid, having TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/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
Chapter 6  Photocatalytic degradation of Victoria Blue and Rose Bengal dye……

intensity of a peak at 425 nm was monitored using Perkin Elmer LS 55 Fluorescence Spectrometer.

As hydroxyl radical performs the key role for the decomposition of the organic pollutants, it is necessary to investigate a number 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. Figure 6.22 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. If the generation of hydroxyl radical is higher, the yield of TAOH will be more and hence more intense will be the fluorescence peak. Thus, TiO$_2$/PPy/GO with the highest intensity confirms the generation number of hydroxyl radicals compared to other photocatalysts. The fluorescence intensity follows the trend (i.e. TiO$_2$, < TiO$_2$/PPy < TiO$_2$/PPy/GO) of photocatalytic performance of all the photocatalyst [75].

![Fig.6.22. PL spectra of photocatalyst with terephthalic acid (0.001M) TiO$_2$, TiO$_2$/PPy, and TiO$_2$/PPy/GO](image)

6.3.13. 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. Figure 6.23 shows the photoluminescence spectra of synthesized photocatalysts. It means TiO$_2$ and TiO$_2$/PPy with strong PL intensity have high recombination of charge carriers whereas TiO$_2$/PPy/GO has weak intensity. The weak PL intensity of TiO$_2$/PPy/GO may arise due to the coating of polypyrrole on Titania lattice, so that decrease in the band gap of TiO$_2$/PPy/GO was found which results in the decolourisation of photoexcited electrons. This delays the electrons-holes recombination process and hence is utilized in the redox reaction leading to improved photocatalytic activity [75].

![Figure 6.23](image_url)

**Fig.6.23. Photoluminescence Spectra of TiO$_2$, TiO$_2$/PPy, TiO$_2$/PPy/GO, Polypyrrole (PPy) and Graphene Oxide (GO)**

### 6.3.14. Adsorption of dyes

The Photodegradation of Victoria Blue and Rose Bengal dyes were done under visible light irradiation in presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites. It is an example of heterogeneous catalysis. Rate laws in such reactions seldom follow proper law
Chapter 6  Photocatalytic degradation of Victoria Blue and Rose Bengal dye……

model and hence are inherently more difficult to formulate from the data. It has been widely accepted that heterogeneous catalytic reactions can be analyzed with the help of Langmuir Hinshelwood (LH) Model [76-77], satisfying, the following assumptions (i) there are limited number of adsorption sites on the catalyst and its surface is homogeneous, (ii) only one molecule can be adsorbed on one site and monolayer formation occurs (iii) the adsorption reaction is reversible in nature, and (iv) the adsorbed molecules do not react amongst themselves [78-79]. According to LH Model, following three steps take place in the kinetics mechanism [80–81], these steps are of adsorption, surface reaction and desorption of products from the surface.

Step 1: D (Dye) + C (catalyst) $\leftrightarrow$ D.C (Adsorption)

Step 2: D.C $\leftrightarrow$ E.C + Other products (Surface reaction)

Step 3: E.C $\leftrightarrow$ E + C (Desorption)

The Freundlich isotherm [82] is employed, assuming a heterogeneous surface with a non uniform distribution of heat of adsorption over the surface and it may be written as:-

$$q_e = K_F C_e^{\frac{1}{n}} \quad (11)$$

The above equation can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (12)$$

Where $q_e$ (mg/g) is the amount of solute adsorbed per unit weight of adsorbent, $C_e$ (mg/l) is the equilibrium concentration of solute, $K_F$ (mg/g) is the Freundlich constant (which indicate the relative adsorption capacity of the adsorbent) and $1/n$ is the constant indicate the intensity of adsorption. Since the photocatalyst is covered by both Dye as well as water molecules ($C_{water}$) by hydrogen bonding, their competition for the active sites cannot be ignored. Langmuir adsorption model [83] can be applied to the aqueous solutions of dyes with the help of the following expression:

$$q = \frac{q_t}{q_{max}} = \frac{K_L C}{1 + K_L C + K_{water} C_{water}} \quad (13)$$
Where $q$ is the fractional sites covered by the dye, $q_t$ is the absorbed quantity of dye at any time, $q_{\text{max}}$ shows the maximum quantity of dye that can be adsorbed, $K_L$ is the Langmuir adsorption constant for reactant and $K_{\text{water}}$ is the adsorption constant for water.

$$q = \frac{K_L C}{1 + K_L C} \quad (14)$$

The quantity adsorbed at a particular time can also be expressed

$$q_t = \frac{(\text{Reactor Volume} \times (\text{Change in concentration}))}{\text{Mass of catalyst}} \quad (15)$$

The equilibrium adsorption quantity $q_{eq}$ can be written as:

$$q_e = q_{\text{Max}} \left[ \frac{K_L C_e}{1 + K_L C_e} \right] \quad (16)$$

where $C_e$ is the equilibrium concentration of the dye. On transforming Eq. (16), a function can be derived as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{K_L q_{\text{max}}} \quad (17)$$

The intercept on the vertical axis gives $1/K_L q_{\text{max}}$ and the reciprocal of slope gives $q_{\text{max}}$. 

Fig. 6.24. % Adsorption of Victoria Blue and Rose Bengal dye under dark condition in presence of (a) TiO$_2$, (b) TiO$_2$/PPy and (c) TiO$_2$/PPy/GO

The value of $C_{\text{water}} \gg C$, hence $C_{\text{water}}$ remains almost same throughout the reaction and the catalyst coverage by water molecules remains almost constant. Thus, we can ignore the quantity $K_{\text{water}}$, $C_{\text{water}}$ and rewrite Eq. (13) as:

$$q = \frac{K_L C}{1 + K_L C} \quad (14)$$
6.3.15. Kinetic study of Photocatalytic degradation

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 (Figure 24). 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 (Figure 6.24). 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:

\[
\text{Rate (r)} = \frac{dC}{dt} = k\theta = \frac{kK_AC}{1+K_AC}
\]  

(18)

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 the reaction, the initial pH, the amount of catalyst, and photo intensity 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:

\[
r_o = \frac{kK_AC_o}{1+K_AC_o}
\]  

(19)

Where \(r_o\) is the initial rate of degradation of Victoria Blue and Rose Bengal 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. (19) can be simplified as first-order equation [84-85]:

\[
-\frac{dC}{dt} = kK_AC_o = \frac{\ln C_o}{C} = kK_A t
\]  

(20)

\[C = C_o e^{-k_fphoto t}\]  

(21)

Where

\(k_{f, \text{Photo}} = k_A \)
The value of $k_{f,\text{photo}}$ can be determined from the plot of $\ln \frac{C_0}{C_t}$ vs. $t$ (Figure 6.25).

![Graph of ln(C0/Ct) vs. Time for Victoria Blue and Rose Bengal dye](image)

Fig. 6.25. Linear first order reaction of Langmuir Hinshelwood kinetics of Victoria Blue and Rose Bengal dye vs. time (a) TiO$_2$ (b) TiO$_2$/PPy (c) TiO$_2$/PPy/GO

The slope of the straight line obtained will be the value of first order rate constant [86]. The Value of apparent rate constant was determined at definite concentrations of dye solution for photocatalysis reaction in presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO showing in Fig.6.26. The rate constant values for the photocatalytic degradation of Victoria Blue and Rose Bengal follow the first order kinetic for the both photocatalyst. This is confirmed that photocatalytic degradation of Victoria Blue and Rose Bengal follows first order kinetic in presence of TiO$_2$, TiO$_2$/PPy and TiO$_2$/PPy/GO.

### 6.3.16. 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, 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 (Victoria Blue and Rose Bengal) and it’s largely vacant conduction band (CB), which is commonly characterized by the band gap energy ($E_{bg}$). The semiconductors may be
photo-excited to form electron-donor sites (reducing sites) and electron acceptor sites (oxidizing sites), providing great scope for the redox reaction. When the semiconductor is illuminated with light (hv) of greater energy than that of the band gap, an electron is promoted from the Victoria Blue and Rose Bengal to the CB leaving a positive hole in the valence band and an electron in the conduction band as illustrated in Figure 6.26 and 6.27.

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+ and dyes (Victoria Blue and Rose Bengal) may react with surface-bound H2O or OH⁻ to produce the hydroxyl radical and e_cb is picked up by oxygen to generate superoxide radical anion (O2⁻), as indicated in the following equations 6-8; absorption of efficient photons by Titania

(hv ≥ E_{bg} = 3.2 eV)

\[ \text{TiO}_2 + h\nu \rightarrow e_{cb} + h^+_{dye} \] (22)

Formation of superoxide radical anion

\[ O_2 + e_{cb} \rightarrow O_2^- \] (23)

Neutralization of OH⁻ group into OH by the hole

\[ (\text{H}_2\text{O} \Leftrightarrow H^+ + \text{OH}^-)_{\text{ads}} + h^+_{dye} \rightarrow \cdot\text{OH} + H^+ \] (24)

It has been suggested that the hydroxyl radical (\cdot\text{OH}) and superoxide radical anions (O2⁻) are the primary oxidizing species in the photocatalytic oxidation processes [87-88]. These oxidative reactions would results in the degradation of the pollutants as shown in the following equations 23-24;

Oxidation of the organic pollutants via successive attack by OH radicals

\[ R + \cdot\text{OH} \rightarrow R^- + \text{H}_2\text{O} \] (25)

or by direct reaction with holes

\[ R + h^+ \rightarrow R^+ \rightarrow \text{degradation products} \] (26)
Conclusions

The present research work describes a proficient method for synthesis of TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites. These nanocomposites were prepared by one-step in situ deposition oxidative polymerization of pyrrole hydrochloride using Ammonium persulphate (APS) as an oxidant in the presence of ultra-fine grade powder of TiO$_2$ nanoparticles cooled in an ice bath. The obtained nanocomposites were characterized by XRD, TEM, SEM, and UV-Vis for band gap determination. The obtained results showed that TiO$_2$ nanoparticles have been encapsulated by PPy with a strong effect on the morphology of TiO$_2$/PPy and TiO$_2$/PPy/GO nanocomposites. The Photocatalytic degradation of Rose Bengal and Victoria blue dye was done at different condition viz concentration of dye, time of illumination, pH and dose of the photocatalyst. The maximum photodegradation was found at 7 pH, 20 ppm concentration of Victoria blue and 25 ppm of Rose Bengal dye solution, 800
mg/L for VB and 1600 mg/L for RB amount of photocatalyst and 120 min irradiation of visible light. Kinetics of photodegradation was investigated for Victoria blue and Rose Bengal dye and found first order kinetics. The coating of PPy and GO has enhanced the photocatalytic activity of Titania. Hence TiO$_2$/PPy and TiO$_2$/PPy/GO are the efficient photocatalyst for the degradation of Rose Bengal and Victoria Blue dye than pure TiO$_2$.

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Preparation and Photocatalytic activity of Co:La:TiO$_2$ nanocomposites for the degradation of Methyl Blue in Visible light

In this study, prepared the nanocomposites of Co:La:TiO$_2$ by the wet chemical method. Synthesized TiO$_2$ and Co:La:TiO$_2$ were characterized by X-Ray Diffractometer, SEM,TEM, UV-vis, FT-IR, Band gap energy and BET. The TiO$_2$ and Co:La:TiO$_2$ were used as photocatalyst for the degradation of Methyl Blue. The XRD pattern confirmed the presence of anatase and rutile phase in the catalyst. The particle size was estimated by the Scherrer’s and found 68 and 32 nm for TiO$_2$ and Co:La:TiO$_2$ respectively. The particle morphology of the photocatalysts was found in nanodimension. The surface area of the photocatalysts were found 37.52 and 106.68 m$^2$/g for TiO$_2$ and Co:La.TiO$_2$ respectively . The band gap energy of TiO$_2$ and Co:La.TiO$_2$ were 3.2 and 3.0 eV. The FT-IR spectra of Co:La:TiO$_2$ were recorded and found Co bonded with Titania. The photodegradation of Methyl Blue has been found maximum at 5 pH, 25 ppm concentration of dye, 800 mg/L amount of photocatalyst and 180 min illumination of visible light. The photodegradation was following
Chapter 7  Preparation and Photocatalytic activity of Co:La:TiO2 nanocomposites

7.1. Introduction

Photodegradation of dyes, for example, Methylene blue [1] and methyl orange [2] on Titania under UV light illumination is known. However, simulated UV light sources devour a lot of electrical energy and the toxicity of UV light requires safety of the eyes and skin [3-4]. Consequently, the conversion of the light absorption properties of Titania remains an important challenge [5]. Titanium dioxide TiO$_2$ is a most important nanomaterials which has attracted a great attention due to its unique properties. Titanium dioxide TiO$_2$ have excellent merits in solar energy transferring and photocatalysis of poison compounds in environment [6]. The chemical inertness and the non-toxicity of TiO$_2$ have also made it a superior photocatalyst [7-8]. Titania has a large band gap (3.20 eV for anatase TiO$_2$) and therefore, only a small fraction of solar light can be absorbed [9]. The codoping of metal and non-metal into the Titania has shown affirmative results in extending the photoresponse of Titania into the visible light region and getting better charge separation [10]. This leads to improved photocatalytic activity of codoped Titania compared to single doped and undoped Titania [11]. Variation of Titania with non-metal for example sulphur, nitrogen, phosphorus, carbon, etc., introduces mid-band gap states within the band gap of titania leading to band gap narrowing and visible light absorption [12-13]. The impregnation of metallic species such as palladium, gadolinium, lanthanum, iron, samarium, cobalt, silver, etc., has been found to improve charge separation in titania by acting as electron scavengers [14-16].

Many attempts have been made to sensitize titanium dioxide to the whole visible region, such as doping with transition metals [17], transition metal ions [18], non-metal atoms [19] and organic materials [20]. Introduction of dopant allows Titania to absorb in the visible region but this does not necessarily mean that the doped catalyst has a better photocatalytic activity [21].

In photocatalysis, light is absorbed by an adsorbed substrate. Today, semiconductors are usually selected as photocatalysts, because semiconductors have a
narrow gap between the valence and conduction bands [22]. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. When TiO$_2$ is irradiated by UV light (400 nm or less), electron is excited to generate electron (e$^-$) hole (h$^+$) pairs. This movement of electrons forms e$^-$/h$^+$ or negatively charged electron/positively charged hole pairs [23]. The hole can oxidize donor molecules. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals able to undergo secondary reactions [24].

![Methyl Blue molecule](image)

**Fig. 7.1. molecular structure of Methyl Blue**

### 7.2. Methodology

#### 7.2.1 Synthesis of Titania by wet chemical method.

In this method, both TiCl$_4$ solution (1000 mg/l) and NaOH solution (64.5 g/l) was added drop wise to water with stirring. After the resulting solution reaches pH to 7, the slurry was filtered, and the filter cake of TiO$_2$ was washed and redispersed in water to prepare 1 M of TiO$_2$ slurry. Resulting TiO$_2$ slurry and an aqueous solution of HNO$_3$ were refluxed at 95°C for 2 h, cooled to room temperature and neutralized with 28% of aqueous ammonia. Then, it was filtered, washed and calcined at 400 ºC [25, 26].
7.2.2 Synthesis of Co:La:TiO$_2$ nanocomposite

In this study, Co:La:TiO$_2$ nanocomposites were prepared by solution impregnation method. In this method, suitable quantity of prepared TiO$_2$ (2 g) was dispersed in alcoholic cobalt acetate 10% (w/v) and lanthanum nitrate 5% (w/v). The dispersion is agitated continuously for 4 hour at 80 °C temperature. After the treatment, the residue was removed through filtration and was sintered for 4 hour in presence of air at 600 °C by kipping it in a silica crucible inside the muffle furnace. After sintering and slow anilling to room temperature, content was taken out from furnace and was stored in air tight bottles and was used as photocatalyst [27].

\[
\text{TiCl}_4 + 4\text{NaOH} + \text{NH}_3 \rightarrow \text{Ti(OH)}_4 + 4\text{NaCl} \\
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}
\]

7.2.3. Characterization

The physical properties of metal oxide semiconductor nanocomposites that may influence significantly their use as photocatalyst are dependent on nature of crystalline phase present. Thus, phase analysis is an important parameter for this study and the prepared samples were subjected to x-ray diffraction analysis on Powder X-Ray Diffractometer. The observed X-Ray diffractogram of samples were analyzed further to estimate average grain size in the sample by Scherrer’s calculation. Since the absorption of light by photocatalyst is the most crucial step in any photocatalysed reaction and is decided primarily by the band gap energy of material. The morphology and size of the Titania particles were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
7.2.4. Photo-degradation of dyes

In this work, the photo-catalytic degradation of Methyl Blue was investigated. A solution of dye in water: alcohol (10:1 V/V) was prepared and in this solution, a suitable quantity of photocatalyst (100 to 800 mg/L) was dispersed. The dispersion was subjected to Visible light irradiation for varying duration and after desired irradiation, the residual concentration of dye in the solution was determine spectrophotometrically by taken out suitable aliquot of dispersion and removal of photocatalyst by centrifugation. For quantitative estimation of dye concentration, initially calibration curve was obtained and it was utilized to measure the concentration in different sample aliquot obtained at different time. A quantitative estimation of dye concentration spectrometric observation when recorded only at the experimental determines $\lambda$ max value which is 670 nm [28-30].

7.3. Results

7.3.1. Phase identification by X-ray diffraction analysis

The obtained X-Ray diffraction patterns of Titania and Co:La:TiO$_2$ are shown in Figures 7.2 (a) and (b). The observed pattern of peaks, when compared with the standard JCPDS database, suggested that, in prepared TiO$_2$ sample, major peaks at $2\theta = 25.5, 37.2, 48.3,$ and $54.4,$ which can be indexed to the (101), (004), (200), and (211) crystal facets of anatase TiO$_2$ (JCPDS File number: 21-1272). Whereas major peaks at $2\theta = 26.9^\circ$ and $28.2^\circ$ indicate the presence of rutile phase which can indexed to the (110), (121), respectively. In case of Co:La:TiO$_2$ sample, the observed XRD pattern indicates not only a change in the peak intensity, compared to TiO$_2$ but even the absence of some originally observed TiO$_2$ peaks [31]. This is, probably, due to the change in the crystallinity and grain fragmentation, when the samples were wet impregnated by cobalt and Lanthanum.

7.3.1.1. Determination of Average size of Particles/ Grains in samples

The Scherrer’s calculations were attempted to know the average size of particles/grains in the samples [32]. Although, Scherrer’s calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the
particles/ grains in the samples, which may be quite accurate, provided the size of particles/ grains is below 100 nm. The results of Scherrer’s calculations are presented in Table 7.1. The results suggest average size of the particles/ grains in the samples lying in nm range.

![XRD pattern](image)

**Fig. 7.2.** Observed XRD pattern (A) TiO$_2$ (B) Co:La:TiO$_2$

**Table 7.1.** Average size of particles/grains in the samples of TiO$_2$ and Co:La:TiO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>68</td>
</tr>
<tr>
<td>Co:La:TiO$_2$</td>
<td>32</td>
</tr>
</tbody>
</table>

### 7.3.2. Scanning Electron Microscopy (SEM)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Fig. 7.3 (a) and 7.3 (b) clearly show that both the prepared samples are obtained in nanometric dimension. The doping of cobalt and lanthanum is indicating that the particle size reduce due the penetration of cobalt and lanthanum in the lattice of titanium dioxide [33].
7.3.3. Transmission Electron Microscope (TEM)

TEM images were clearly displayed the morphology and particle size of neat TiO$_2$ and Cobalt and lanthanum doped TiO$_2$. It is observed from the Fig. 7.4 that Cobalt and lanthanum doped modified TiO$_2$ change the size of neat TiO$_2$ significantly. The sizes of both modified and neat TiO$_2$ are mono disperse was found 100–200 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 [34].

7.3.4. Surface Area Analysis (BET)

Figure 7.5 shown the BET and adsorption and desorption plot for the TiO$_2$ and Co:La:TiO$_2$. With the help of Figure 7.5, we can determine the specific surface area, pore volume and average pore size of the TiO$_2$ and Co:La:TiO$_2$ photocatalyst. Table 7.2 shown the physical properties of TiO$_2$ and Co:La:TiO$_2$. The TiO$_2$ modified by Cobalt and Lanthanum are fragmentation to some extent during thermal treatment, leading to a marked increase of the BET surface areas and the average pore radius size and decreasing of the pore volume [35, 36].

Table.7.2. The specific surface area, pore volume and pore radius of the TiO$_2$ and Co:La:TiO$_2$

<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>10.132</td>
<td>1.21</td>
</tr>
<tr>
<td>Co:La:TiO$_2$</td>
<td>106.68</td>
<td>9.5124</td>
<td>1.64</td>
</tr>
</tbody>
</table>
Fig. 7.5. BET and Adsorption desorption plot for TiO$_2$ and Co:La:TiO$_2$

### 7.3.5. FT-IR spectroscopy

FT-IR spectra of TiO$_2$ and 10\% Co and \% La doped TiO$_2$ samples (Fig. 7.6) show peaks corresponding to stretching vibrations of the O-H and bending vibrations of the adsorbed water molecules around 3350-3450 cm$^{-1}$ and 1620-1635 cm$^{-1}$, respectively. The broad intense band below 820, 804, 592 and 456 cm$^{-1}$ is due to Ti-O-Ti vibrations. The shift to the higher wave numbers and sharpening of the Ti-O-Ti band may be due to decrease in size of the catalyst nanoparticles.

Fig. 7.6. FT-IR spectra of (a) TiO$_2$ (b) Co:La:TiO$_2$

In addition, the surface hydroxyl groups in TiO$_2$ increased with the increasing of Co and La loading, which is confirmed by increase in intensity of the corresponding
peaks. The FT-IR spectra of Co:La:TiO$_2$ show strong band at 616 cm$^{-1}$, corresponds to the vibration of Co–O bond and confirms the penetration of Cobalt in Titania [37].

### 7.3.6. UV-Vis spectra

Aqueous suspensions solution of the photocatalysts was used for the UV absorption studies. The absorption spectrum of TiO$_2$ consists of a single broad intense absorption at 371nm due to the charge-transfer from the valence band to the conduction band. The undoped TiO$_2$ showed absorbance in the shorter wavelength region while Co:La:TiO$_2$ result showed a broad peak at 407 nm in the higher wavelength (shown in Fig.7.7). The doping of Co and La ions into TiO$_2$ could shift optical absorption edge from UV to visible range, but prominent change in TiO$_2$ band gap was observed [38].

![Fig.7.7. UV- spectra of (a) TiO$_2$ (b) Co:La:TiO$_2$](image)

### 7.3.7. Band gap energy determination

The band gap of samples 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, $h\nu = \frac{1239}{\lambda}$ eV. The value of $h\nu$ extrapolated to $\alpha = 0$ gives an absorption energy, which corresponds to a band gap ($E_g$). Fig.7.8 yields an $E_g$ value of 3.2 eV for TiO$_2$ and 3.0 for Co:La:TiO$_2$ [39]. The slight decrease in band gap energy in case of Co:La:TiO$_2$, is due to formation of sub-band level between valence band and conduction band caused doping of Co$^{2+}$ and La$^{3+}$ in TiO$_2$ host.
Fig. 7.8. Band gap energy of (a) TiO$_2$ (b) Co:La:TiO$_2$

7.3.8. Photo-degradation of Dyes

The photo-catalytic degradation of Methyl Blue in the presence of TiO$_2$ and Co:La:TiO$_2$ has been studied. The solution of dye was prepared in 10:1 (V/V) ratio of water and alcohol. The known amount of photocatalyst 800 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 temperature. The residual concentration of dye in the reaction mixture was measured spectrophotometrically. The results obtained for the degradation of Methyl Blue is shown in Fig. 7.9 - 7.11.

7.3.8.1. Effect of Temperature

The effect of system temperature on photocatalysis has not attracted enough attention. But in present research, it is found that the temperature has a great effect on the photodegradation of Methyl Blue. The photocatalytic efficiency can be increased about 2-3 times if the temperature increased from 30 °C to 40 °C. Because the solar energy include UV light, which can be used to activate the photocatalytic course, which is increase the temperature of photocatalytic system. The experiments showed that Methyl Blue were photodegraded in presence of photocatalyst and Visible light. The Methyl Blue was
efficiently degraded shown in Fig.7.9. The obvious decrease of concentration of dye shows that the TiO$_2$ and Co:La:TiO$_2$ can serve as an effective photocatalyst [40].

![Graph showing photodegradation efficiency over reaction time]

Fig.7.9. Photodegradation of Methyl Blue at initial concentration 50 ppm (a) TiO$_2$ at 30°C (b) TiO$_2$ at 40°C (c) Co:La:TiO$_2$ at 30°C (d) Co:La:TiO$_2$ at 40°C.

7.3.8.2. Effect of concentration of dye

Effect of dye concentration Keeping the catalyst loading concentration constant at 800 g/liter of the dye solution, the effect of varying concentration of the dye was studied on its rate of degradation (from 25 ppm to 100 ppm) as given in Fig.7.10. With increasing concentration of Methyl Blue the rate of degradation was found to decrease. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating 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 [41].
7.3.8.3. Effect of irradiation Time on photodegradation

The effect of irradiation time on the photodegradation of methyl blue has been studied in presence of TiO$_2$ and Co:La:TiO$_2$. The photodegradation of methyl blue was
increased with increase irradiation time. The photodegradation was found maximum in case of Co:La:TiO\textsubscript{2} for 180 min irradiation of visible light. Fig.7.11 shows the effect of irradiation time on photocatalytic degradation of methyl blue. This is due to the interaction of dye molecule with the surface of photocatalyst as well as the time of irradiation increase the interaction increased. Therefore the photodegradation efficiency of photocatalyst was increased.

### 7.3.8.4. Effect of pH of solution

The photodegradation reaction was also carried out under varying pH conditions from (2 to 9), by adjusting with H\textsubscript{2}SO\textsubscript{4} and NaOH, with TiO\textsubscript{2} kept at constant amounts of 800 mg/L of dye solutions (Fig.7.12). The reaction was found to have low rates at acidic ranges of pH. While at pH 5 photodegradation was found maximum. This implies that less acidic 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 highly acidic medium conditions for the formation of reactive intermediates is relatively less favourable and hence less spontaneous [42].

![Fig.7.12. Effect of pH (a) TiO\textsubscript{2} (b) Co:La:TiO\textsubscript{2}](image-url)
7.3.8.5. Effect of photocatalyst amount

The effect of photocatalyst amount has been studied by applying the different amount (100 ppm to 800 ppm) of the photocatalyst. The photodegradation rate was found to increase by increasing the amount of photocatalyst. It is clear from the results shown in Fig.7.13, the photodegradation increased rapidly with increase of amount of Co:La:TiO$_2$. This is due to the fact that introduction of Co$^{2+}$ and La$^{3+}$ the band gap energy decreased up to 3.0 eV which enhance the photocatalytic activity [43].

![Graph showing photodegradation vs dose of photocatalyst](image)

Fig.7.13. Effect of photocatalyst amount on photodegradation of Methyl Blue

7.3.8.6. Effect of photocatalyst

It is clear from the results shown in Fig.7.9-7.12 that both TiO$_2$ and Co:La:TiO$_2$ are effective photo-catalyst for the degradation of Methyl Blue (MB) dye. However Co:La:TiO$_2$ seems to be more effective as photo-catalyst for the degradation of Methyl Blue (MB). The prominent degradation of Methyl Blue was found in 3 hour study in the presence of Co:La:TiO$_2$ in comparison to the prepared TiO$_2$ [44].

7.3.9. Recyclability of photocatalyst

The photocatalyst and Methyl Blue mixture was agitated, illuminated with visible light and after desired time, the mixture was centrifuge to remove the photocatalyst. The
obtained photocatalyst was washed three times with distilled water and kept in oven for 24 h at 60 °C and reused for the degradation of Methyl Blue. The photodegradation of Methyl Blue by the recyclized Photocatalyst are showing in Fig.7.14. The result shows that the recyclized photocatalyst efficiency is slightly decreased probably due to the loss of some active sites and decrease of collection efficiency of photon [45].

![Graph showing photodegradation of Methyl Blue by recyclable photocatalyst TiO₂ and Co:La:TiO₂](image)

Fig.7.14. Photodegradation of Methyl Blue by recyclable photocatalyst TiO₂ and Co:La:TiO₂

**7.3.10. 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.7.15 shows the photoluminescence spectra of synthesized photocatalysts. In the PL spectra the
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intensity of TiO\textsubscript{2} is higher than Co:La:TiO\textsubscript{2} indicating rate of recombination of e\textsuperscript{−} h\textsuperscript{+} is higher in TiO\textsubscript{2} than that of Co:La:TiO\textsubscript{2}. The weak PL intensity of Co:La:TiO\textsubscript{2} may arise due to the impregnation of Ni in Titania lattice, which for sub band level in band gap region of TiO\textsubscript{2}. This delays the electrons- holes recombination process and hence utilized in the redox, reaction leading to improved photocatalytic activity [46].

Fig.7.15. Photolumiscence Spectra of (a) TiO\textsubscript{2} (b) Co:La:TiO\textsubscript{2}

7.3.11. 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. In this study, terephthalic acid (TA) has been used as a probe reagent to evaluate \( ^{\bullet}\text{OH} \) radical present in the photoreaction pathway. Fig.7.16 shows the PL spectra of TiO\textsubscript{2} and Co:La:TiO\textsubscript{2} recorded Methyl Blue solution in presence of \( 10^{-3} \)M Terephthalic solution. OH radical attack Terephthalic, forming 2- hydroxyl terephthalic acid (TAOH) which gives a fluorescence signal at 426 nm. The fluorescent intensity is linearly related to the number of hydroxyl radicals formed by the photocatalysts. Higher the generation of hydroxyl radical, more will be yield of TAOH and hence more intense will be the
fluorescence peak [47]. The spectra show that the intensity of peak indicating in presence of Co:La:TiO$_2$ higher generation of more number of hydroxyl radicals compared to TiO$_2$.

![PL spectra of photocatalysed Methyl Blue solution in presence of terephthalic acid (0.001M) (a) TiO$_2$ (b) Co:La:TiO$_2$](image)

**Fig. 7.16.** PL spectra of photocatalysed Methyl Blue solution in presence of terephthalic acid (0.001M) (a) TiO$_2$ (b) Co:La:TiO$_2$

### 7.3.12. Mechanism of photooxidation process

The photocatalytic mechanism is initiated by the absorption of the photon $h\nu$ with energy equal to or greater than the band gap of TiO$_2$ (3.3 eV for the anatase phase) producing an electron hole pair on the surface of TiO$_2$ nanoparticles. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). Excited state electrons and holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After the reaction with water, these holes can produce hydroxyl radicals with high redox oxidizing potential [48-50]. Depending upon the exact conditions, the holes, OH radicals, O$_2$, H$_2$O$_2$ and O$_2$ itself, 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 ($h^+$) in the valence
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band and an electron ($e^-$) in the conduction band as illustrated in Fig.7.17. If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, $h^+_{vb}$ may react with surface-bound H$_2$O or OH$^-$ to produce the hydroxyl radical and $e^-_{cb}$ is picked up by oxygen to generate superoxide radical anion ($O_2^-$), as indicated in the following equations 6-8;

Absorption of efficient photons by titania ($h\nu \geq E_{bg} = 3.2$ ev)

$$TiO_2 + h\nu \rightarrow e_{cb} + h^+_{vb}$$  \hspace{1cm} (6)

Formation of superoxide radical anion

$$O_2 + e_{cb} \rightarrow O_2^-$$  \hspace{1cm} (7)

Neutralization of OH$^-$ group into OH by the hole

$$(H_2O \square H^+ + OH^-)_{ads} + h^+_{vb} \rightarrow \cdot OH + H^+$$  \hspace{1cm} (8)

It has been suggested that the hydroxyl radical ($\cdot OH$) and superoxide radical anions ($O_2^-$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would results in the degradation of the pollutants as shown in the following equations 9-10;

Oxidation of the organic pollutants via successive attack by OH radicals

$$R + \cdot OH \rightarrow R^- + H_2O$$  \hspace{1cm} (9)

or by direct reaction with holes

$$R + h^+ \rightarrow R^{+} \rightarrow \text{degradation products}$$  \hspace{1cm} (10)
7.3.13. Kinetic study

The pseudo-first-order rate constant \(k\), \(\text{min}^{-1}\) for the photodegradation reaction of Methyl Blue was determined through the following relation where \(k\) can be calculated from the plot of \(\ln(C_o/C_t)\) against time \(t\), \(C_o\) and \(C_t\) denote the initial concentration and reaction concentration, respectively.

\[
k t = \ln \frac{C_o}{C_t}
\]

In addition, the linear feature of plots of \(\ln(C_o/C_t)\) versus time (Fig.7.18 and 7.19) indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law [51-54]. The rate constant of the photocatalysis at 30 °C is 0.04260 to 0.0234 \(\text{min}^{-1}\). The effect of temperature and concentration are showing in table 7.3.

Fig.7.17. Mechanism of photodegradation of Titania and formation of free radical.
Fig. 7.18. The straight line relationship between the ln (C₀/Cₜ) and irradiation time indicates photodegradation rate of Methyl Blue (50 ppm) can be approximated by a pseudo first order reaction (a) TiO₂ at 30°C (b) TiO₂ at 40°C (c) Co:La:TiO₂ at 30°C (d) Co:La:TiO₂ at 40°C.

Fig. 7.19. The straight line relationship between the ln (C₀/Cₜ) and irradiation time indicates photodegradation rate of Methyl Blue (100 ppm) can be approximated by a pseudo first order reaction (a) TiO₂ at 30°C (b) TiO₂ at 40°C (c) Co:La:TiO₂ at 30°C (d) Co:La:TiO₂ at 40°C.
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Table 7.3. The effect of concentration and temperature on rate constant

<table>
<thead>
<tr>
<th>Sample</th>
<th>100 ppm</th>
<th></th>
<th>50 ppm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min(^{-1}))</td>
<td>R(^2)</td>
<td>k (min(^{-1}))</td>
<td>R(^2)</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.006</td>
<td>0.969</td>
<td>0.008</td>
<td>0.999</td>
</tr>
<tr>
<td>Co:La:TiO(_2)</td>
<td>0.008</td>
<td>0.988</td>
<td>0.012</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Conclusion
Prepared nanocomposites of Co:La:TiO\(_2\) were characterized by X-Ray Diffractometer, SEM, TEM, UV-Vis, FT-IR, Band gap energy and BET. The TiO\(_2\) and Co:La:TiO\(_2\) were used as photocatalyst for the degradation of Methyl Blue. The particle size was estimated by the Scherrer’s and found 68 and 32 nm for TiO\(_2\) and Co:La:TiO\(_2\) respectively. The surface area of the photocatalysts were found 37.52 and 106.68 m\(^2\)/g for TiO\(_2\) and Co:La:TiO\(_2\) respectively. The band gap energy of TiO\(_2\) and Co:La:TiO\(_2\) were 3.2 and 3.0 eV. The photodegradation of Methyl Blue has been found maximum at 5 pH, 25 ppm concentration of dye, 800 mg/L amount of photocatalyst and 180 min illumination of visible light. The photodegradation was following the first order kinetics.

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Titanium dioxide (TiO₂), commonly known as Titania, is one of the most commonly used photocatalysts. Because of its high oxidative power, stability, and non-toxicity, it promises a broad range of uses as a photocatalysts.

Advantage of using TiO₂ as photo-catalyst are: (a) using TiO₂, the process occurs under ambient conditions, (b) using TiO₂, the oxidation of the substrate to CO₂ is complete in most cases and (c) it is comparatively inexpensive and remains quite stable in contact with different substrate. TiO₂ has also played a leading role in the active research for the utilization of solar energy. In this thesis, prepared the different nanocomposites by the doping of metals in Titania and polymer based nanocomposites. The prepared materials were characterized by the XRD, FTIR, UV-Vis, BET, SEM, TEM, PL and LCMS. The Photodegradation of Eriochrome Black T, Acetic Acid, Methyl Green, Victoria Blue, Thymol Blue, Methyl Blue and Rose Bengal have been done. In this study, investigate the effect of different parameters on the photodegradation.