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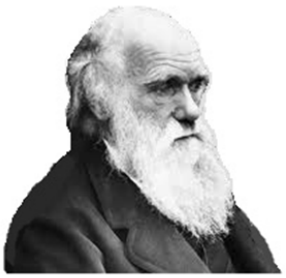

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UV–light assisted photocatalytic activity of activated charcoal-TiO_2 nanomaterial

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ABSTRACT

An activated charcoal-TiO_2 Catalyst was synthesized via the precipitation method and sonication technique, and three dyes: Reactive Black 5 (RB 5), Rhodamine B (Rh B) and Napthol Blue Black (NBB) were used to assess the quality of the product under UV-Light. The nanomaterial was also characterized by High-resolution scanning electron microscopy (HR-SEM), elementary dispersive X-ray (EDX), photoluminescence spectroscopy (PL), and UV-Vis DRS. The photodegradation of the three dyes when exposed to this nanomaterial indicate the superior photocatalytic activity of RB 5 as compared to the other dyes. A mechanism is proposed for the higher activity of AC-TiO_2 than that of TiO_2 nanocomposite material. Overall, this nanocomposite material was found to be highly stable and reusable. The nanomaterial is also economically of very low cost.

***Keywords*:** RB 5 dye, photocatalyst, Activated charcoal-TiO_2

1. INTRODUCTION

TiO_2 is used in plastics paint and paper industries, for an outstanding to excellent optical properties and well-organized environmental pollutants[1-4]. Reactive Black 5 (RB 5), Rhodamine B (Rh B) and Napthol Blue Black (NBB) dyes is commonly used in several industries, such as food, cosmetics, paper and textiles, and such as dye for colorizing the

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foodstuffs. It is a dye degradation product, such as aromatic amines which are greatly carcinogenic and hazardous. The advanced oxidation process is a photocatalysis in a waste water treatment and a technigue used for the total mineralization of organics and photocatalytic application.[5-9] As an alternative approach for degradation methods it is the addition of charcoal or carbon due to its valuable features in the chemical, physical or biological process.[10-12]

2. EXPERIMENT

2. 1. Synthesis of AC-TiO_2 nanomaterial

AC-TiO_2 nanomaterial was synthesized by the precipitation method and sonication technique. The amount of Bi $(NO_3)\cdot 5H_2O$ was first dissolved with deionized water. The resulting solution was added but dropping by drops into tetra isopropyl orthotitanate solution at room temperature.

The above solution was vigorously stirred for 3 h and then three drops of concentrated HNO_3 and 5 mL deionized water were added. The obtained solution was stirred for 2 h and ultra-sonicated for 20 min, until precipitate was formed. The precipitate was washed with deionized water and ethanol. Then it was collected and dried in an oven at 100 °C for 12 h. The resulting powder sample was calcined at 450 °C for 3 h to achieve AC–TiO_2 nanomaterial as economically very low cost and high stability elevated material.

2. 2. Chemicals

Tetra isopropyl orthotitanate ($C_{12}H_{28}O_4Ti$), Bi $(NO_3)\cdot 5H_2O$, and Nitric acid (HNO_3-65%) were used for the studies. Reactive Black 5 (RB 5), Rh B, and NBB as well as ethanol were the guaranteed reagents of Sigma Aldrich. The aqueous solutions were prepared by using double distilled water.

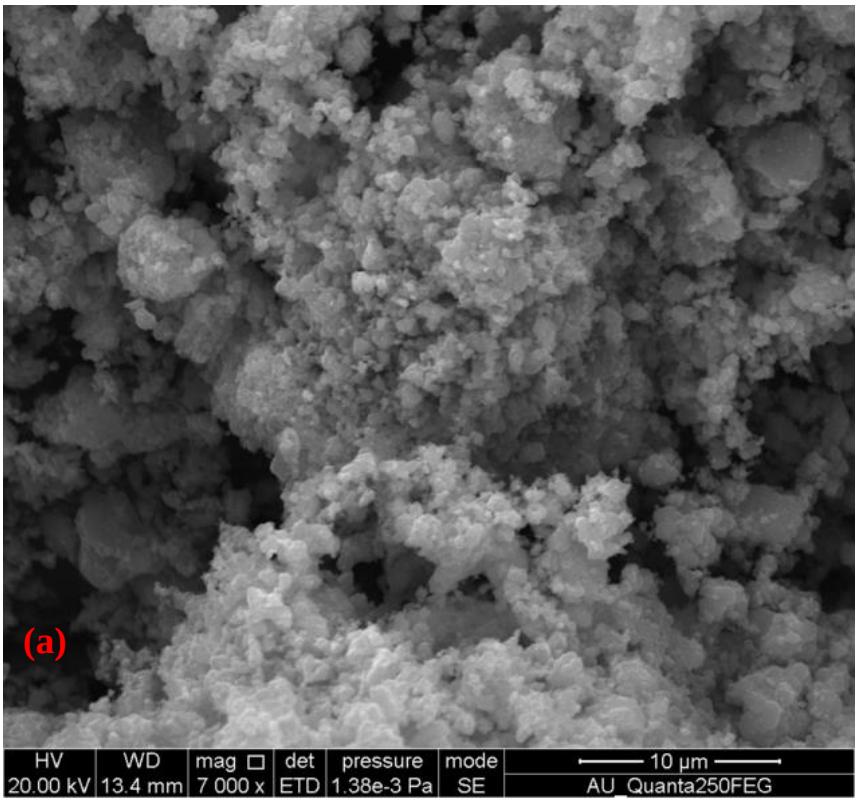
2. 3. Analytical Methods

The Scanning electron microscopy (HR-SEM) with elementary dispersive X-Ray analysis (EDX) was carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The sample was prepared by placing a small quantity of prepared material on a carbon coated copper grid and allowing the solvent to evaporate. Photoluminescence (PL) spectra at a room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. The crystallinity of sample was characterized by an UV-Vis DRS and the direct band gap energy was analyzed by UV–visible (Shimadzu UV-1650 PC) spectrophotometer. UV spectral measurements were done using a Hitachi-U-2001 spectrometer.

3. RESULTS AND DISCUSSION

3. 1. Structural studies (HR-SEM with EDX) – analysis

Scanning electron microscopic image of substracte at temperature at 450 °C was done. The average grain size was 10 μm, as shown in **Fig. 1**(a). SEM micrographs reveal that the particles are nano-spherical in a chain structure. In TiO_2 the small particles have been agglomerated and the particles were slightly better in the size.



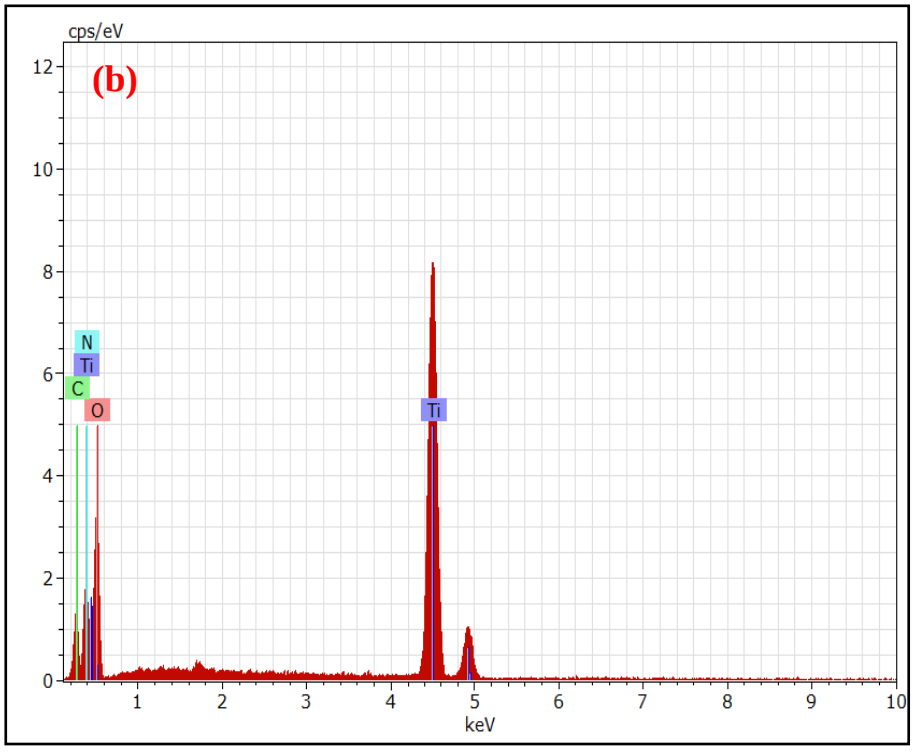


Fig. 1. HR-SEM image of **(a)** AC-TiO_2 nanomaterial and **(b)** EDX analysis

The average particle size of AC-TiO_2 is effective due to less agglomeration which produces them more in the surface area so with the high photocatalytic activity. EDX analysis is shown in (**Fig. 1**b). The presence of Ti, C, and O was confirmed from the catalyst.

3. 2. The PL spectrum

The PL spectrum of prepared TiO_2 and AC-TiO_2 were emission band at 525 nm. The PL emission intensity decreases in AC-TiO_2 when compared to prepared TiO_2, as shown in **Fig. 2**a and b, respectively. This activity electron transfer is faster than the recombination of electron and hole in the valence band with this lower energy state of AC. Thus due to a definite quenching of electron and hole pairs in the mixed catalyst of TiO_2, the calculated result confirmed the photocatalytic activity has increased.

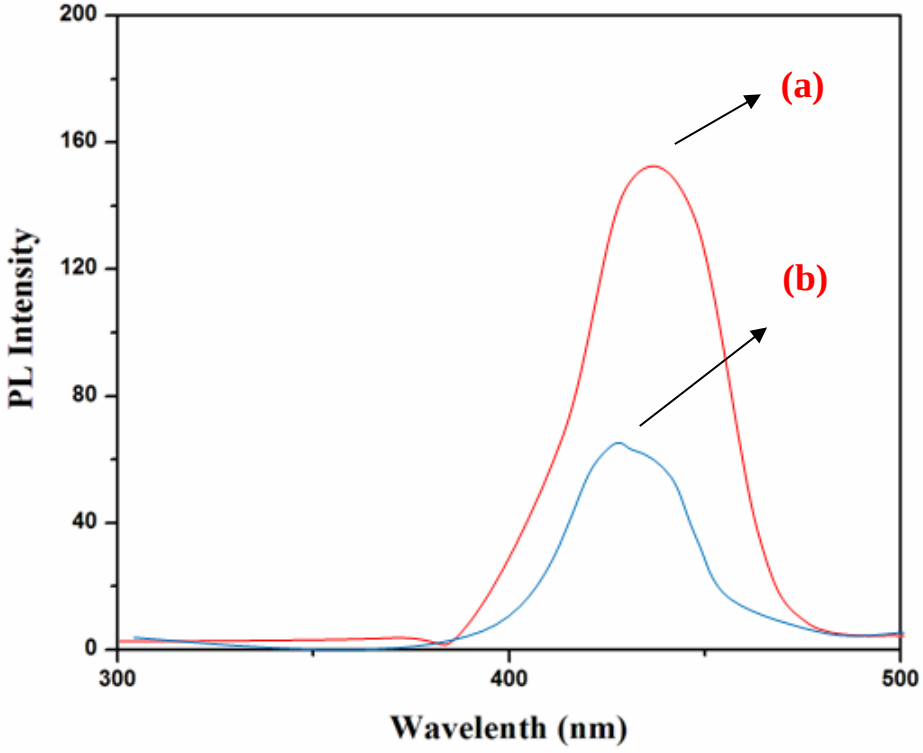


Fig. 2. Photoluminescence spectra of: (a) TiO_2, and (b) AC-TiO_2 nanomaterial

3. 3. UV-vis DRS Spectrum

The UV-vis DRS Spectrum of prepared TiO_2 and AC-TiO_2, as shown **Fig. 3** a and b, reveals the strength covalently interacts with TiO_2 and decreases its band gap. AC-TiO_2 caused the red shift in absorption edge from 400 to 422. The results indicated in UV-vis spectrum in the diffuse reflectance mode (R) were tranceformed to the Kubelka-Munk function F(R) to the whole the degree of light absorption from diffusion. The band gap energy was obtained from the plot of the modified Kubelka- Munk function $(F(R)E)^{1/2}$ vs. the energy of the absorbed light (E), (eqn. 1), as shown in **Fig 3**.

$$(F(R)\cdot E)^{\frac{1}{2}} = \frac{(1-R)^{1/2}}{2R} Xh\nu \qquad (1)$$

The final result indicates the band gap energies of the synthesized TiO_2 and AC-TiO_2 are 3.4 eV and 3.0 eV, correspondingly. The lower band gap energy supports the higher photocatalytic activity [9, 13-14].

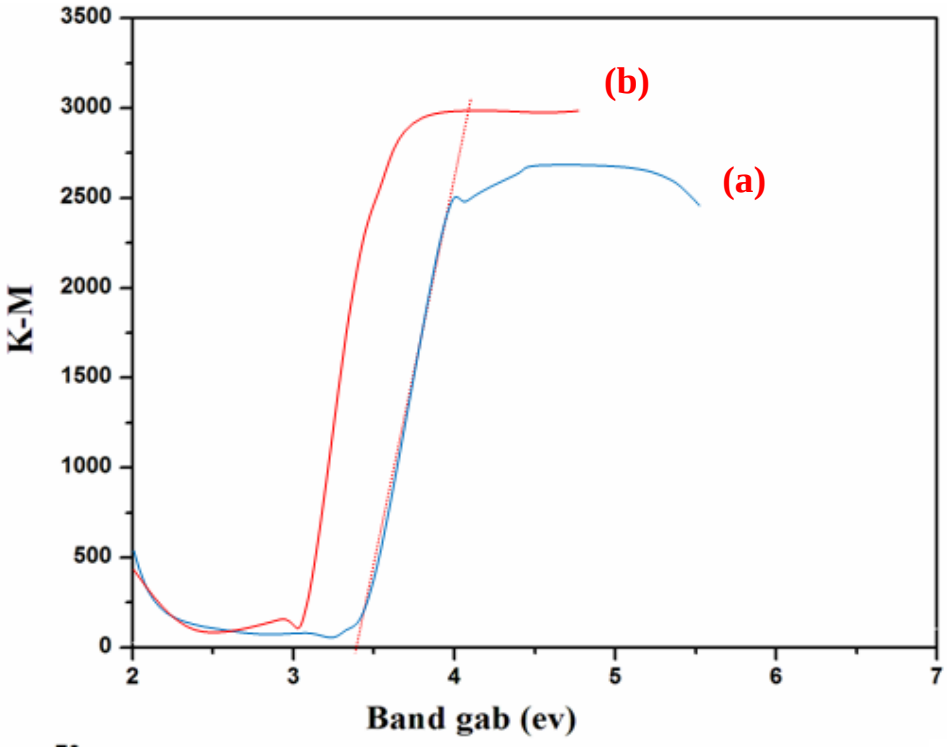


Fig. 3. Plot of Kubelka−Munk versus energy of the light absorbed of the (a) TiO_2 and (b) AC-TiO_2 nanomaterial

3. 4. Photocatalytic study

3. 4. 1. Degradation of RB 5 dye

AC-TiO_2 can be degraded with the RB 5 in aqueous solution up to 98% when compared that of TiO_2 (60%). The reaction of RB 5 undergoes (%) degradation under UV-light at 365 nm by measuring the time dependent degradation efficiency of RB 5. The photocatalytic degradation is in the order of the catalyst material used AC-TiO_2 > TiO_2, as shown in **Fig. 4** a.

3. 4. 2. Degradation of Rh B dye

AC-TiO_2 can degraded with the Rh B in aqueous solution up to 82% when compared that of TiO_2 (51%)**.** The reaction of Rh B undergoes (%) degradation under UV-light at 365 nm by measuring the time dependent degradation efficiency of Rh B. The photocatalytic degradation is in the order of the catalyst material used AC-TiO_2 > TiO_2, as shown in Fig. 4 b.

3. 4. 3. Degradation of NBB dye

AC-TiO_2 can be degraded with the NBB in aqueous solution up to 73% when compared that of TiO_2 (43%). The reaction of NBB undergoes (%) degradation under UV-light at 365 nm by measuring the time dependent degradation efficiency of NBB. The photocatalytic degradation is in the order of the catalyst material used AC-TiO_2 > TiO_2, as shown in Fig. 4 c.

The final result indicates a high photocatalytic activity of RB 5 that of Rh B and NBB by the nanomaterial used.

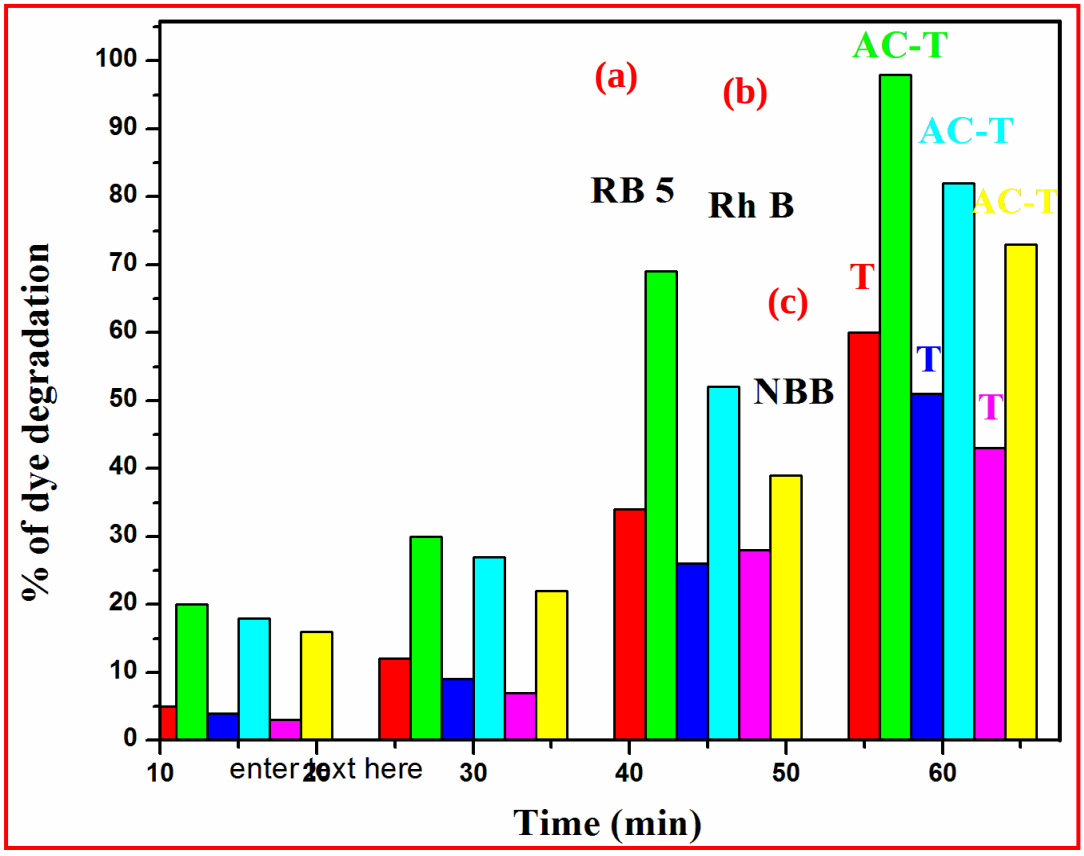


Fig. 4. Primary analysis under natural UV-light irradiation by TiO_2 and AC-TiO_2 nanomaterial on degradation of three dyes.

3. 4. 4. Re-usability of the catalyst

The most important advantage of the nanomaterial is its stability and re-usability. The re-usability of AC-TiO_2 was phtodegradation tested by transporation out four successive cycles of RB 5 that of Rh B and NBB photodegradation under UV-light result are shown in **Fig. 5**. The whole degradation was obtained in 60 min for the RB 5 I^{st} (100), II^{nd} (98), but III^{th} and IV^{th} runs gave 96%, Rh B I^{st} (100), II^{nd} (96), but III th and IV^{th} runs gave 93% and NBB I^{st} (100), II^{nd} (93), but III th and IV^{th} runs gave 90% degradation. There is no considerable loss of activity up to IV^{th} and V^{th} runs, the catalyst is stable and re-usable.

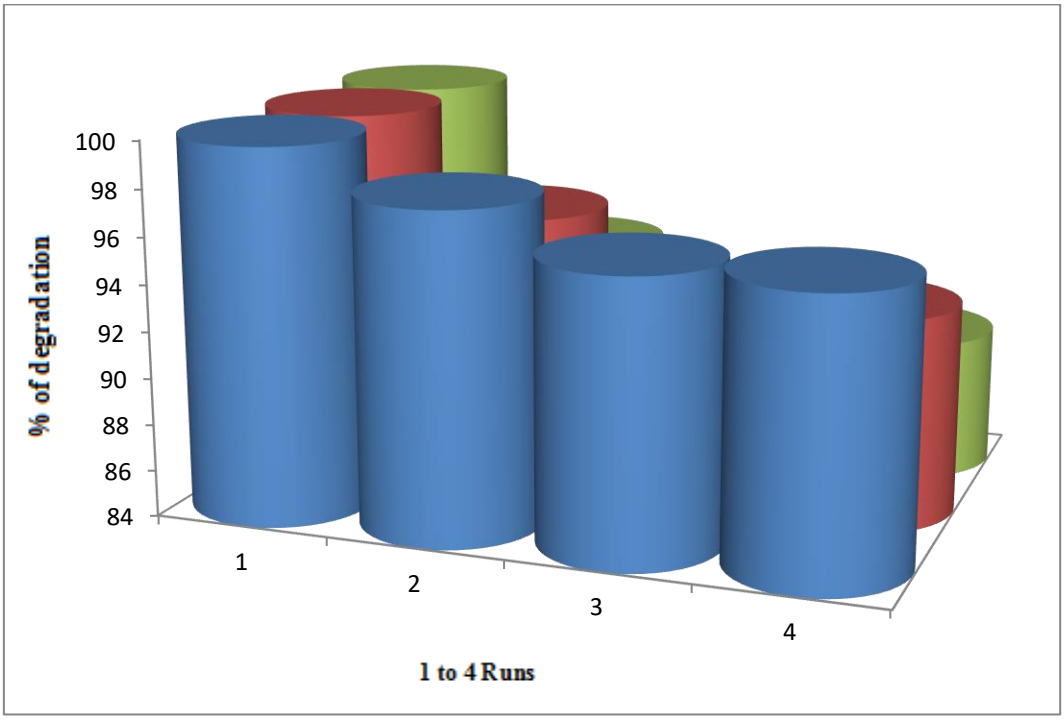


Fig. 5. Stability and Reusability on RB 5, Rh B and NBB dye degradation; by AC-TiO_2 nanomaterial

3. 4. 5. Mechanism for photocatalytic effect of AC-TiO_2 nanocomposite material

On the base of these observations, a mechanism in favor of photocatalytic degradation of dyes is proposed as follows:

* Dye - RB 5 that of Rh B and NBB

$$^{1}Dye_{0} + h\nu \rightarrow Dye_{1} \quad (1)$$

$$^{1}Dye_{1} + ISC \rightarrow {}^{3}Dye_{1} \quad (2)$$

$$AC\text{-}TiO_2\ (SC) + h\nu \rightarrow e^{-}\ (CB) + h^{+}\ (VB) \quad (3)$$

$$^{-}OH + h^{+} \rightarrow {}^{\bullet}OH \quad (4)$$

$$^{\bullet}OH + {}^{3}Dye_{1} \rightarrow \text{Leuco Dye} \quad (5)$$

$$\text{Leuco Dye} \rightarrow \text{Products} \quad (6)$$

Figure 6 presents the dyes absorbing radiation of desired wavelength and its form of excited singlet state. Further, it undergoes an intersystem crossing (ISC) to give a more stable triplet state. Along with this, the semiconducting AC-TiO_2 (SC) also utilizes this energy to excite its electron from the valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h^{+}) present in the valence band of semiconductor generating $^{\bullet}OH$ radical. This hydroxyl radical will oxidize methyl green to its leuco form, which may ultimately degrade to the

products. It was confirmed that the •OH radical participates as an active oxidizing species in the degradation of dyes, as the rate of degradation was appreciably reduced in the presence of hydroxyl radical scavenger (2-propanol) [15].

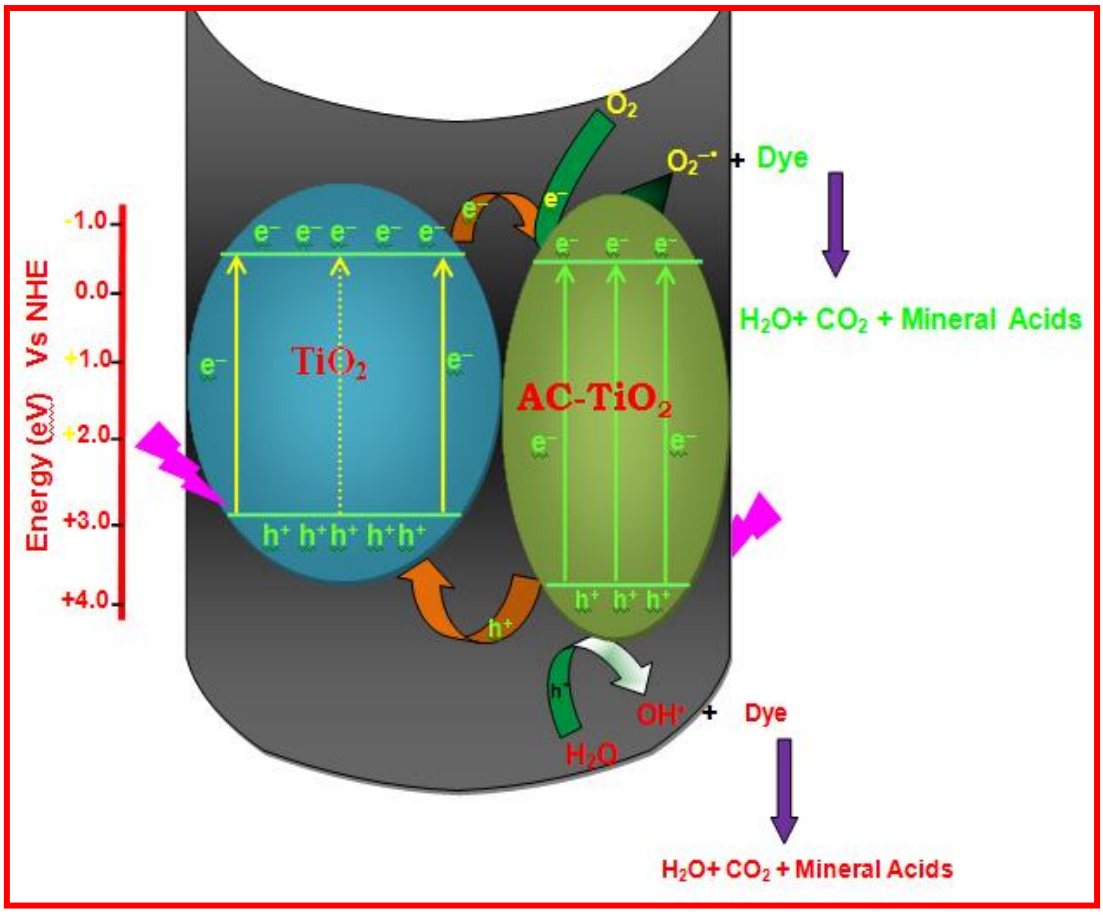


Figure 6. Degradation mechanism.

4. CONCLUSION

AC-TiO_2 nanomaterial was synthesized by precipitation method. It was characterized by HR -SEM image showing spherical shaped structure with EDX spectra revealing the presence of Ti, C and O in the catalyst. PL analysis of a low electron and hole recombination rate implies a lower luminescence emission intensity and higher photocatalytic activity. AC-TiO_2 nanomaterial has a higher photocatalytic activity when compared that of TiO_2 nnomaterial on RB 5 that of Rh B and NBB dye under UV-light irradiation.

The final result indicates a high photocatalytic activity of RB 5 that of Rh B and NBB by nanomaterial. AC-TiO_2 nanomaterial is economically of very low cost and high stability; this nanomaterial shows elevated use for expanded important industrial applications. The result indicates that the prepared AC-TiO_2 nanomaterial is stable and re-usable.

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