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. Such as dye for colorizaing the
foodstuffs. It is a dye degradation products such as aromatic amines which are greatly carcinogenic and hazardous. The advanced oxidation process is a photocatalysis in a waste water treatment is a technique and it is used for the total mineralization of organics and photocatalytic application. 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.

2. EXPERIMENT

2.1. Synthesis of AC-TiO₂ nanomaterial

AC-TiO₂ nanomaterial was synthesized by the precipitation method and sonication technique. The amount of Bi (NO₃). 5 H₂O 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 vigorous stirring for 3h and than three drops of con HNO₃ and 5 mL deionized water were added. The obtained solution was stirred for 2h and ultra-sonication for 20 min, until precipitate was formed. The precipitate was washed with deionized water and ethanol. Than it was collected and dried in an oven at 100 °C for 12h. The resulting powder sample was calcined 450 °C for 3h to achieve AC–TiO₂ nanomaterial is economically very low cost and high stability elevated material.

2.2. Chemicals

Tetra isopropyl orthotitanate (C₁₂H₂₈O₄Ti), Bi (NO₃), 5 H₂O, Nitric acid (HNO₃-65%), were used as such. Reactive Black 5 (RB 5), Rh B and NBB are used, 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 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 supstrat temperature at 450 °C respectively. The average grain size 10 µm as show in Fig. 1(a). SEM micrographs reveal that the particles are nano spherical in chain structure. In TiO₂ 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$_2$, hence AC-TiO$_2$ is effective due to less agglomeration which produces is more in the surface area so the high photocatalytic activity. EDX analysis is shown in (Fig. 1b). The presence of Ti, C and O is confirmed from 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 decrease in AC-TiO$_2$ when compared to prepared TiO$_2$ is shown in Fig. 2a and b respectively. This activity electron transfer is faster than the recombination of electron and hole in the valence band this lower energy state of AC. Thus due to definite quenching of electron and hole pairs in mixed catalyst of TiO$_2$ and calculated by was confirmed photocatalytic activity is increased.

![Photoluminescence spectra of (a) TiO$_2$ (b) AC-TiO$_2$ nanomaterial](image)

**Fig. 2.** Photoluminescence spectra of (a) TiO$_2$ (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 W strength covalently interacts with TiO$_2$ and decreases its band gap. AC-TiO$_2$ caused is a red shift in absorption edge from 400 to 422. The result indicate in UV-vis spectrum in the diffuse reflectance mode (R) were trance formed to the Kubelka-Munk function $F(R)$ to the wole 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 $E$) (eq 1) is shown in Fig 3.
\[(F(R) \cdot E)^\frac{1}{2} = \frac{(1-R)^{1/2}}{2R} Xhν \]

\[\text{-------------------------- - (1)}\]

The final result indicates was band gap energy of the synthesized TiO\textsubscript{2} and AC-TiO\textsubscript{2} are 3.4 eV and 3.0 eV correspondingly. The lower band gap energy supports the higher photocatalytic activity [9,13-14].

\[\text{Fig. 3. Plot of Kubelka–Munk versus energy of the light absorbed of the (a) TiO}_2\text{ and (b) AC-TiO}_2\text{ nanomaterial}\]

3. 4. Photocatalytic study

3. 4. 1. Degradation of RB 5 dye

AC-TiO\textsubscript{2} can be degradation of the RB 5 in aqueous solution up to 98 % when compared that of TiO\textsubscript{2} (60 %). The reaction of RB 5 undergoes % of 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\textsubscript{2} > TiO\textsubscript{2} shown in Fig. 4 a.

3. 4. 2. Degradation of Rh B dye

AC-TiO\textsubscript{2} can be degradation of the Rh B in aqueous solution up to 82 % when compared that of TiO\textsubscript{2} (51 %). The reaction of Rh B undergoes % of 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$_2$ shown in Fig. 4 b.

3. 4. 3. Degradation of NBB dye

AC-TiO$_2$ can be degradation of the NBB in aqueous solution up to 73% when compared that of TiO$_2$ (43 %), The reaction of NBB on % of 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$_2$ shown in Fig. 4c.

The final result indicate high photocatalytic activity of RB 5 that of Rh B and NBB by nanomaterial.

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. Reusability of the catalyst

The most important advantage of nanomaterial stability and reusability. The reusability of AC-TiO$_2$ was photodegradation 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 $1^{st}$ (100), $2^{nd}$ (98), but $3^{rd}$ and $4^{th}$ runs
gave 96 %, Rh B I\textsuperscript{st} (100), II\textsuperscript{nd} (96), but III \textsuperscript{th} and IV\textsuperscript{th} runs gave 93 % and NBB I\textsuperscript{st} (100), II\textsuperscript{nd} (93), but III \textsuperscript{th} and IV\textsuperscript{th} runs gave 90 %, degradation. There no considerable loss of activity up to IV\textsuperscript{th} and V\textsuperscript{th} runs, the catalyst is stable and reusable.

![Graph showing degradation percentage over runs](image)

**Fig. 5.** Stability and Reusability on RB 5, Rh B and NBB dye degradation; by AC-TiO\textsubscript{2} nanomaterial

### 3. 4. 5. Mechanism for photocatalytic effect of AC-TiO\textsubscript{2} nanocomposite material

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

* Dye - RB 5 that of Rh B and NBB

\begin{align*}
1\text{Dye}_0 + \text{hv} & \rightarrow 1\text{Dye}_1 & \ldots(1) \\
1\text{Dye}_1 + \text{ISC} & \rightarrow 3\text{Dye}_1 & \ldots(2) \\
\text{AC-TiO}_2 (\text{SC}) + \text{hv} & \rightarrow e^- (\text{CB}) + h^+ (\text{VB}) & \ldots(3) \\
\text{OH}^- + h^+ & \rightarrow \cdot\text{OH} & \ldots(4) \\
\cdot\text{OH} + 3\text{Dye}_1 & \rightarrow \text{Leuco Dye} & \ldots(5) \\
\text{Leuco Dye} & \rightarrow \text{Products} & \ldots(6)
\end{align*}
Scheme 1. Dyes absorbs radiation of desired wavelength and it forms excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the semiconducting AC-TiO\(_2\) (SC) also utilizes this energy to excite its electron from 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 OH radical. This hydroxyl radical will oxidize methyl green to its leuco form, which may ultimately degrade to 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 presence of hydroxyl radical scavenger (2-propanol) [15].

4. CONCLUSION

AC-TiO\(_2\) nanomaterial was synthesized by precipitation method. It was characterized by HR-SEM image showed spherical shaped structure with EDX spectra revealed 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 was higher photocatalytic activity when compared that of TiO\(_2\) nanomaterial on RB 5 that of Rh B and NBB dye under UV-light irradiation. The final result indicate high photocatalytic activity of RB 5 that of Rh B and NBB by nanomaterial. AC-TiO\(_2\) nanomaterial is economically very low cost and high stability and nanomaterial shows elevated for expanded important industrial applications. The result indicates that the prepared AC-TiO\(_2\) nanomaterial is stable and reusable.
References


