Photo induced charge separation mechanism in active $Fe_2O_3/CoTiO_3/TiO_2$ ternary hybrids; structural design, spectral study and degradation study

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Abstract

In this work we have successfully prepared efficient and active $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites for degradation of Reactive Yellow 84 (RY 84) disposed from textile and commercial chemical industrial on aquatic systems. Efficient $CoTiO_3/Fe_2O_3/TiO_2$ based hetero structure was prepared via dispersed method and the results were compared with Fe_2O_3/TiO_2, $CoTiO_3/TiO_2$ heterojunction and bare TiO_2. The $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites were analyzed by X-ray diffraction [XRD], Scanning electron microscopy [SEM], Diffused reflectance spectroscopy [UV-DRS], Photoluminescence [PL] study, which implies the crystal structure, surface morphology, optical properties and quenching of electron role recombination.

The $CoTiO_3/Fe_2O_3/TiO_2$ ternary composite shows excellent photo stability over RY 84. The degradation ability of prepared $CoTiO_3/Fe_2O_3/TiO_2$ ternary nanostructures was compared and evaluated with Fe_2O_3/TiO_2, $CoTiO_3/TiO_2$ and TiO_2. This can be 100% degradation ability at 120 min respectively. Our report will help in the establishment and development of photo catalytic research.

Keywords: Photo catalyst, dye degradation, ternary nanostructure, RY 84, heterostructure.

Introduction

In the recent years, several industries are grown in our country like dyeing, printing, textiles, photography, cosmetics and food industry etc. The problem is our improper waste water management is due to an abundant level of rising population and its basic needs leading to abnormal growth of industrialization and urbanization[1,9,16]. Previously World Health Organization has reported that globally 15% of the people as well as aquatic life is affected due to industrial wastewater.[4,6,11,29]

Nowadays, the industry waste water has been treated for conversion of pure water from waste water under ion exchange, evaporation ultra filter method, micro filtration etc. Photo catalytic degradation method is one of the most essential economical and non-toxic approaches because all dye molecules are completely degraded[12-14,23,25]. Furthermore, in the dye degradation, some heterogeneous catalyst[2,5,15,19] such as Fe_2O_3[28], WO_3[17,24], Bi_2WO_6[27], ZnO[3], Bi_2O_3[18], TiO_2[21], $FeTiO_3$[22], SnO_2[8], $CoTiO_3$[7], CeO_2[26] and Cu_2O[20] are used.

In particular, TiO_2 is a major source of photo catalyst. TiO_2 coupled with other metal oxides will enhance the activity of photocatalytic efficiently and then the synthesized titanate of $FeTiO_3$ utilizes as an excellent photo catalyst when degradation of RB5 occurs without adding any green oxidants as a catalyst[10]. Next, cobalt titanate ($CoTiO_3$) is photocatalytic efficient.

The thermal stability of $CoTiO_3$ greatly improves and also the photo catalytic performance of TiO_2 also improved simultaneously. In the present work, we have synthesized ternary nano structure of $CoTiO_3/Fe_2O_3/TiO_2$ by polar solvent dispersed method. The degradation rates of $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites have been investigated. Furthermore, the crystal structure, surface properties, optical behavior, electron-hole recombination rate and photocatalytic activity were also examined.

Material and Methods

Titanium tetrachloride (99.5%) supplied by Loba Chemie Pvt. Ltd., Ferrous Sulphate hepta hydrate, Ammonia solutions and Cobalt nitrate supplied by Merck are used for the preparation of the photo catalyst. Sodium hydroxide and hydrochloric acid (both AR grades) from Loba Chemie were used as such for adjusting the pH *of* the dye solutions. Double distilled de ionized water was used for the preparation of dye solutions. Reactive Yellow 84 is a widely used anionic *azoic* dye in textile finishing processes with two monochlorotriazine anchor groups supplied by Vexent Dyeaux India Pvt. Ltd., Mumbai. The properties of the dye are given below:

Chemical Formula: $C_{50}H_{24}C_{l2}N_{14}Na_{10}O_{30}S_{10}$
Molecular Weight : 1922.26
Water solubility : 70 g/L at 293 K
Maximum Absorbance: 410 nm in visible and 235 at UV region.

Synthesis of anatase TiO_2: The anatase phase TiO_2 was successfully synthesized from $TiCl_4$ as reported elsewhere[1]. In the typical synthesis of TiO_2, 5mL of $TiCl_4$ was

added in 50 ml of ice cold distilled water with stirring for 2 h and a clear solution was obtained after stirring, then to that solution, aqueous ammonia was added drop wise till the formation of a gel. The gel solution was washed repeatedly with distilled water to remove the entire chloride ions in the solution, then kept for drying at 100° C to remove part of the absorbed water. The dry gel was milled and calcinated at 450°C for 4 h to obtain crystalline TiO_2. The same synthetic methods were carried out to synthesise Fe_2O_3 and $CoTiO_3$. The starting material and calcinations temperature of Fe_2O_3 and $CoTiO_3$ were Ferrous sulphate hepta hydrate and Cobalt chloride and 500ºC for 4 hrs and 550°C for 7 hours respectively.

Preparation of Ternary Composite Photo catalysts: In the preparation of 0.5 *wt* % $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites, 0.05 g of $CoTiO_3$ and 0.995 g of Fe_2O_3/TiO_2 was mixed with pistil mortar and ground gently to get fine powder. This ternary mixture was subsequently annealed at 300°C for 3 hours in a Muffle furnace. The $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites with 1, 2, 3 and 4 *wt*% of $CoTiO_3$ were prepared by varying Fe_2O_3/TiO_2 ratios and labeled as CFT-1, CFT -2, CFT-3 and CFT-4 respectively. The binary composites such as Fe_2O_3/TiO_2 and $CoTiO_3/TiO_2$ were mentioned in the same protocol. The Fe_2O_3/TiO_2 and $CoTiO_3/TiO_2$ binary were labeled as FT and CT.

Evaluation of Photo catalytic Activity: The photocatalytic studies were carried out under *a* natural solar light on plain sky atmosphere days during the period of February to May-2019. In a typical experiment, 50 ml of Reactive Yellow 84 solutions were taken in 250-ml glass beaker with 50 mg of photocatalyst added and saturated with oxygen by aerated with an air-pump up to 1 hour to attain adsorption equilibrium. Then the dye solution (Model pollutant) was set aside in direct sunlight. Continuous aeration and the concentration/absorbance of the dye remains were measured gradually. Then the light absorbance was measured at the visible λ max by using an Elico UV-Visible spectrophotometer.

In order to avoid the difference in results due to oscillation in the intensity of the sunlight, a set of experiments has been carried out simultaneously. For pH studies, the pH of the dye solutions was modified to different pH such as using 0.1M HCl and NaOH solution. For concentration studies, the degradation of dye solution of various concentrations at pH 3 was treated using the photo catalyst and the efficiency of the catalyst was calculated from the percentage of degradation of the dye solution.

The percentage of degradation was calculated using the following relation:

$$\% \text{ of Degradation} = \left(\frac{C_0 - C}{C_0}\right) \times 100$$

where C_0 is the initial concentration of the dye solution and C is the concentration of the dye remains after degradation.

Characterization: A Bruker AXS D8 Diffraction meter was utilized to study the X-ray diffraction patterns of prepared nano structure with the range of wave length=0.15406nm, 2θ range and $3\text{-}80^0$ at laboratory temperature The surface morphology of the catalyst was analyzed using the Scanning electron microscope JEOL Model JSM-6390LV. UV-diffuse reflectance data were collected over the spectral range 200-800nm with a Varian Cary-500 UV–Vis–NIR spectrometer equipped with an integrating sphere attachment and Gamma alumina was used as the reference material. The photoluminescence emission spectra of the samples were measured at room temperature using a Perkin-Elmer LS 55 Luminescence spectrophotometer.

Results and Discussion

UV-Visible absorbance analysis of dye: The UV-Visible spectrum of the dye RY-84 is shown in the figure 1. The dye shows maximum visible absorption at 410 nm and also extended visible absorbance up to 510 nm. The UV absorption maximum was at 235 nm. The visible absorbance at 410 nm has been used to calculate the concentration of dye solution before and after photo catalytic degradation experiments are by using the Beer–Lambert law (Figure 1).

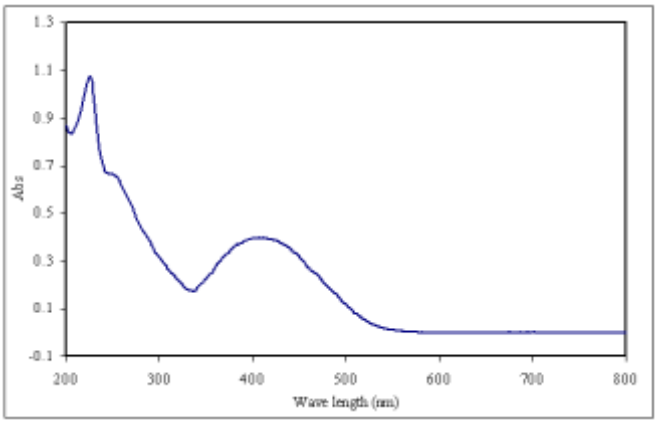


Figure 1: UV-Visible absorbance spectrum of Reactive Yellow 84.

XRD pattern of Ternary Semiconductors Photo catalysts: XRD patterns of Pure Fe_2O_3, $CoTiO_3$, TiO_2, 6 *wt*% FT, 7 *wt*% CT, 4wt % CFT and 6wt % CFT ternary composites were shown in the figure 2.

The XRD pattern of Fe_2O_3 indicates in illmenite phase respectively. The diffraction patterns of TiO_2 match the patterns in JCPDS Card No. 21-1272, which indicate that TiO_2 was in pure anatase phase. The $CoTiO_3$ structure exactly matches the JCPDS card no. 89-2944 and it has good crystalline phase. The diffraction patterns of $CoTiO_3/TiO_2$ and Fe_2O_3/TiO_2 heterojunctions are similar like the patterns of anatase TiO_2. The diffraction peaks of Fe_2O_3 and $CoTiO_3$ were undetectable in the diffraction patterns of the CFT ternary heterojunction; this could be attributed to the high degree of dispersion of Fe_2O_3 and $CoTiO_3$ in the matrix of TiO_2 forming solid solution. But the intensity of CFT ternary composites highly decreased, it might be due to the coating of low crystalline phase $CoTiO_3$ and Fe_2O_3 semiconductors.

SEM Analysis: Scanning electron microscopic technique is used for the determination of morphologies and dispersion of the photo catalyst. The Scanning electron micrographs of pure TiO_2, 6 wt% FT, 7 wt% CT were shown in figure 3 (a, b and c). These morphologies consist of irregular agglomerated particles and were in the form of bulky particles. Figure 3 (d) – (f) shows the images of the CFT ternary composites photo catalysts. Further the formation of ternary composites shows different morphologies compared to binary and pure TiO_2 photo catalysts.

2 wt% CFT morphology indicates Fe_2O_3 and $CoTiO_3$ growing on the platform of TiO_2 and CFT. From these results, 6 wt % CFT photo catalysts show suitable surface morphology for photocatalytic degradation of reactive dyes. The reason is formed of small size irregular particles.

DRS Analysis: The diffuse reflectance spectra of synthesized TiO_2, 6 wt% FT, 7 wt% CT, 2 wt % CFT, 3 wt % CFT and 5 wt % CFT ternary heterojunction are displayed in figure 4. Fe_2O_3/TiO_2 shows larger absorption than synthesized TiO_2 in the visible region; $CoTiO_3/TiO_2$ also shows the better absorbance band in the visible region such as 500 nm to 700 nm. Both the results reveal increase of the visible light activity of the TiO_2 photo catalyst. The ternary CFT completely shifts to in the whole of visible light absorption. This indicates coupling of narrow band gap semiconductors like $CoTiO_3$ and Fe_2O_3 with TiO_2.

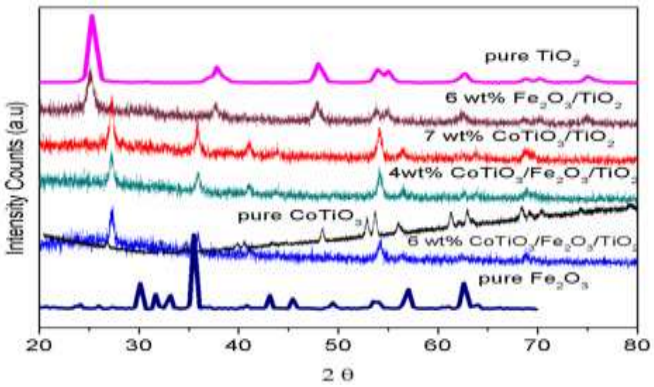


Figure 2: XRD patterns of Pure Fe_2O_3, $CoTiO_3$ and TiO2, 6 wt% FT, 7 wt% CT, 4wt % CFT and 6wt % CFT ternary heterojunction.

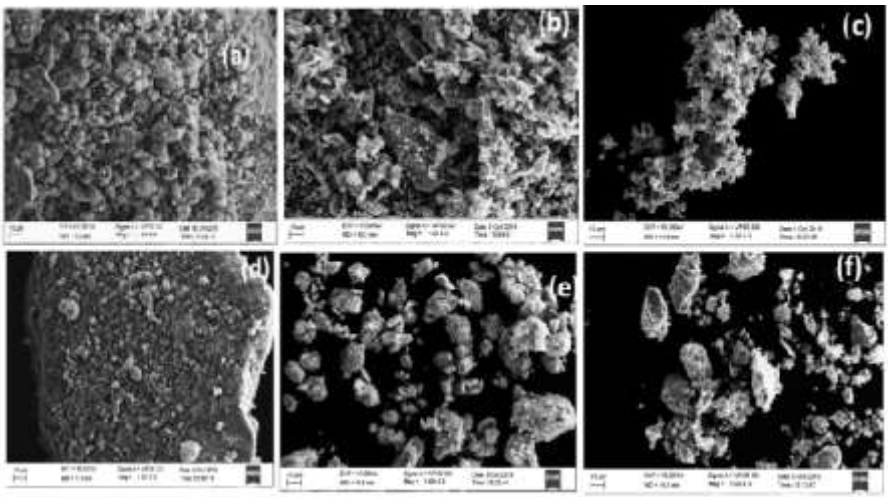


Figure 3: Scanning Electronic Micrograph of TiO_2, 6 wt% FT, 7 wt% CT, 2 wt % CFT, 3 wt % CFT and 5 wt % CFT ternary heterojunction.

Photoluminescence Study: Among different samples, pure anatase TiO_2 has a highest PL intensity followed by FT, CT and ternary CFT (Figure 5).

The PL intensities mainly depend on the extent of photo induced charge carrier separation. Efficient electron hole separation resulting from a wider band gap and smaller crystallite size makes ternary CFT less luminescent in comparison to FT, CT and TiO_2. The lower PL intensity of ternary CFT can be explained on the basis of better electron hole separation resulting from the electron transfer from the conduction band of TiO_2 to the Fe_2O_3. The red shift of the PL band observed for ternary CFT may be due to the presence of narrowband semiconductors

Photo degradability of Reactive yellow 84: The photocatalytic activity of the TiO_2, Fe_2O_3, $CoTiO_3$, FT, CT and CFT photocatalyst has been evaluated on RY 84 in the presence of UV-visible light irradiation as shown in figure 6. This dye has been chosen for the studies, since it has a strong light absorption in UV-visible region. The UV-visible transmittance spectrum of the RY 84 solution shows that more than 80% of incident light in the wavelength range 320-530 nm was absorbed by 50 mg/l dye solution in a path length of 1 cm.

Hence, the degradation of the RY 84 solution with concentration above 50 mg/l in a simple photocatalytic process over a RY 84 photo catalyst like TiO_2 is difficult and will take more treatment time for complete degradation.

The photo catalytic activities of Fe_2O_3/TiO_2 and $CoTiO_3/TiO_2$ heterojunction photo catalyst were shown in Figure 7. The photocatalytic activity of the Fe_2O_3/TiO_2 and $CoTiO_3/TiO_2$ heterojunction photo catalyst exhibited better photocatalytic activity than bare TiO_2. It could be clearly seen that the photocatalytic degradation rate of Reactive Yellow 84 gradually increased with increase of Fe_2O_3 and $CoTiO_3$ in TiO_2. It was interesting to note that the 3 weight% Fe_2O_3/TiO_2 and 8wt% $CoTiO_3/TiO_2$ heterojunction shows the highest photocatalytic degradation efficiency.

But at the higher Fe_2O_3 and $CoTiO_3$ content, fabrication on TiO_2 the photocatalytic activity decreased suggesting that the optimal Fe_2O_3 and $CoTiO_3$ on TiO_2 existed when the weight ratio was 3 and 8 wt%. Further the photo catalytic study has been extended to improve the photocatalytic efficiency of TiO_2.

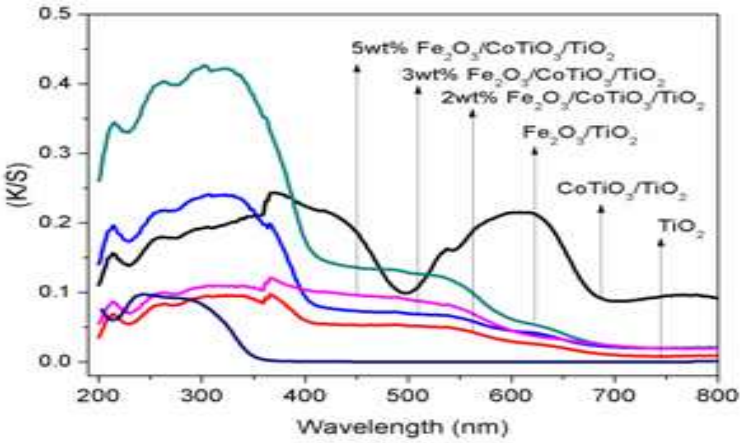


Figure 4: UV-visible diffused reflectance spectra of TiO_2, 6 wt% FT, 7 wt% CT, 2 wt % CFT 3 wt % CFT and 5 wt % CFT ternary composites.

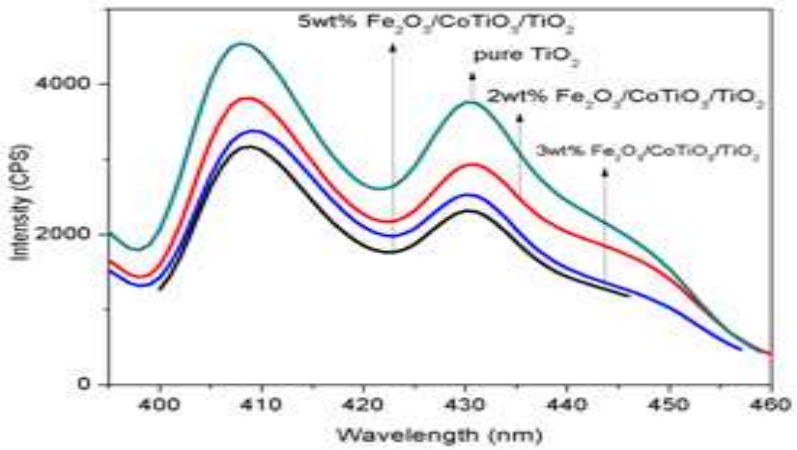


Figure 5: PL intensity of TiO_2, FT, CT and ternary CFT

The photocatalytic activity of TiO_2 improved by the formation of ternary composites with various weight ratios of Fe_2O_3 on $CoTiO_3/TiO_2$ hetero junctions in the presence of UV-visible light irradiations. In this study, the optimized 8 wt% $CoTiO_3/TiO_2$ hetero junctions coupled with Fe_2O3 at various weight ratios. After 60 min of UV-visible light illumination, the Reactive Yellow 84 degrades over Fe_2O_3/TiO_2; $CoTiO_3/TiO_2$ hetero junctions are only 60% and 70% respectively. However, CFT ternary composites show higher photocatalytic degradation rate (71–99%) in the presence of same experimental conditions.

It is worth noting that CFT ternary composites could be inducing notable photo degradation efficiency from 70% to 99% beyond the increases of 8 wt% of Fe_2O_3. This shows that the photocatalytic activity of CFT ternary composites increases with the increase in $CoTiO_3$ content up to 8 wt %. Further it increases the rate content, the photo catalytic efficiency was slightly decreased (90%). As a result, 8 wt% of $CoTiO_3$ is the optimum dosage ratio in the CFT ternary composites.

The photocatalytic degradation kinetics of Reactive Yellow 84 was investigated under the influence of FT, CT heterojunctions and CFT ternary composites were shown in the figure 7 (a2), (b2) and (c2). The data obtained from the degradation studies were analyzed with the Langmuir–Hinshelwood kinetic model:

$$r_s = \frac{kKc}{1+KC}$$

where r_S is the specific degradation reaction rate the dye ($mgl^{-1}min^{-1}$), C the concentration of the dye (mgl^{-1}), k is the reaction rate constant (min^{-1}) and K is the dye adsorption constant. When the concentration (C) is small enough, the above equation can be simplified in an apparent pseudo first-order equation:

$$r_s = kKC = K_{app}C\left(=-\frac{dc}{dt}\right)$$

After integration, we will get

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}\,t$$

where C_0 is the initial concentration ($mg\,l^{-1}$), C is the concentration of the dye after (t) minutes of illumination. The data obtained from the degradation of Reactive Yellow 84 fits well the apparent pseudo first order kinetics. The electrons in the conduction band can be transferred to surface adsorbed oxygen molecules and form superoxide anions which can further transform to $OH^{\bullet}$ and initiate the degradation of Reactive Yellow 84.

The photocatalytic activity also tested for Fe_2O_3 and $CoTiO_3$. This study shows that Fe_2O_3 and $CoTiO_3$ have very low photocatalytic activity in UV-visible light when compared to TiO_2, binary heterojunction and ternary composites even though its band gap was only 2.5(*ev*). This shows that the Fe_2O_3 and $CoTiO_3$ have a smaller electron-hole diffusion length than TiO_2 which leads to the recombination of most of the photo generated electron-hole pairs inside the Fe_2O_3 and $CoTiO_3$ particle before reaching its surface[34].

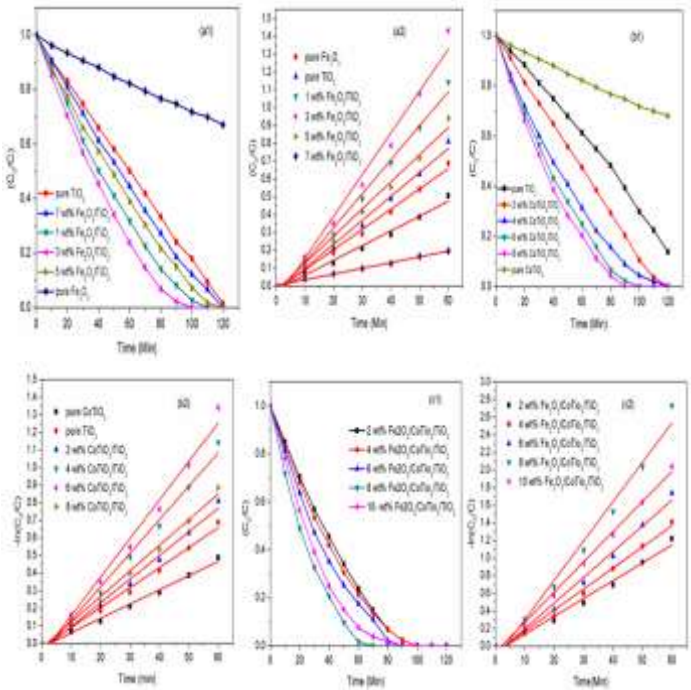
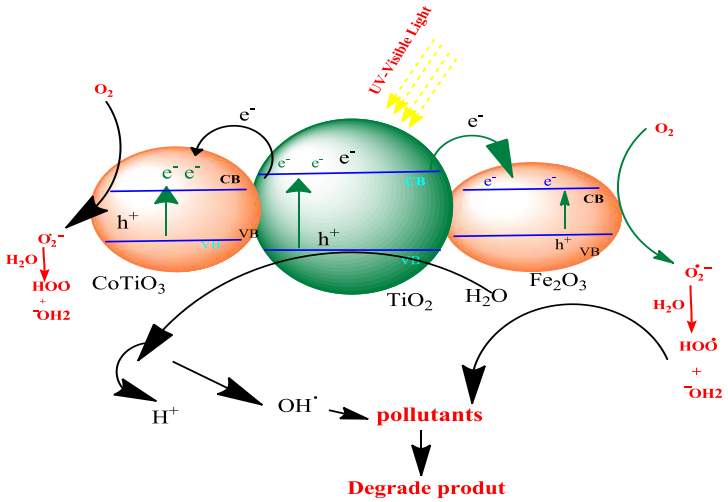


Figure 6: Photocatalytic degradation and kinetic plots of Reactive Yellow 84 over various photo catalysts.

Photo catalytic Mechanism: The work mechanism of these CFT ternary composites is illustrated in scheme 1. As shown in scheme 1, Fe_2O_3 and $CoTiO_3$ as an electron acceptor can prevent the e- and H^+ from recombination in the UV-visible photo excitation of TiO_2. This function of electron acceptance can promote the decomposition of organic pollutants by the oxidation of the H^+. Then, Fe_2O_3 and $CoTiO_3$ can fabricate onto TiO_2 and shift the absorbency of the system to the visible light region due to its narrow band gap behavior. In addition, illuminated Fe_2O_3 and $CoTiO_3$ might donate the electron and were supported to degrade RY 84.

Furthermore, the combination of $CoTiO_3$, TiO_2 and Fe_2O_3 which the photocurrent is produced by transferring e^- from TiO_2 to Fe_2O_3 and $CoTiO_3$ when exposed to visible light. This process can also prevent the e^- and H^+ from recombination. Finally, it is worthy of pointing out that the transformation of e^- from Fe_2O_3 is possible by photo-oxidizing which makes the ternary composite in system un-losing. Thus, the 6 wt% CFT ternary composites is a hopeful form for further improving the practicability of $CoTiO_3$, Fe_2O_3 and TiO_2.

Reusability of 6 wt% $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites: Reusability is a very important parameter in assessing the practical application of photocatalysts in wastewater treatment. It can contribute significantly to lowering the operational cost of the process. Hence the reusability of the CFT ternary composites was studied for the degradation of 100 mg l^{-1} RY 84 solution at pH 3. The photo catalyst was carefully separated from the degraded dye solution by centrifugation and added to the fresh 100 ml dye solution. The results of the analysis were shown in figure 7. It has been found that 6 wt% CFT ternary composites completely degraded the RY 84 solution in 120 minutes even in its third reuse, this shows that the composites have good stability in the acidic conditions. Hence application of 8wt% $CoTiO_3/TiO_2$ for the treatment of textile effluents will be cost effective.



Scheme 1: Photocatalytic mechanism of prevention of electron-hole recombination and electron injection process of CFT ternary composites

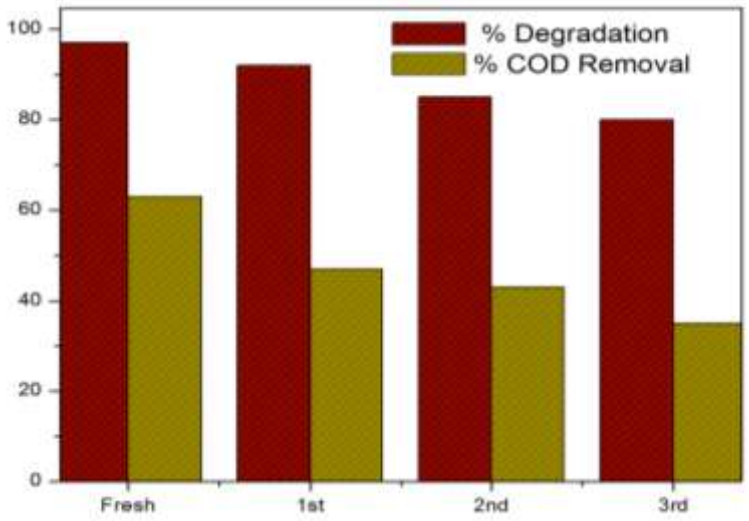


Figure 7: Reusability of $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites.

Conclusion

The heterojunction composites such as $CoTiO_3/TiO_2$, Fe_2O_3/TiO_2 and $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites were prepared in a simple dispersed method from the metal oxides synthesized from the sol - gel method. This synthesized all the composites showing anatase phase. From the degradation result, $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites showed higher photocatalytic activity than that of Fe_2O_3/TiO_2 and $CoTiO_3/TiO_2$ heterojunctions. The mineralization of reactive dyes with *triazine* groups has been reported to be more difficult in most treatment methods. However, at higher concentrations, the dye solutions especially chlorotriazine dye solutions transmit only very small portion of photons to reach the photo catalyst surface. Hence, degradation of these dyes at higher concentration levels is more difficult in the binary system.

However, in most cases, combinations of two or more metal oxides are found to be more efficient than the individual photo catalyst for the degradation of higher concentration dyes. In our study we did not use any green oxidant for the improvement of photocatalytic material without any oxidant. We achieved great photo degradation results in presence of natural solar light. Hence, the optimized heterojunction composites like 6 wt% $CoTiO_3/Fe_2O_3/TiO_2$ ternary composites have been used for the degradation of Reactive Yellow 84.

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