

# Waste-Water Treatment: Based on Solar-Light-Driven Photo-Catalysis using Semiconducting Nano-Materials

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## Abstract

The development of innovative technologies for effective waste-water treatment is gaining extraordinary importance worldwide. Photocatalysis is one of the most useful, cost-effective and easily manageable methods for decomposition and remediation of organic pollutants in waste-water treatment. In this sense, several semiconducting nano-scaled materials, such as iron sulfide (FeS), CdS, ZnS, CuS, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles (NPs) etc., have been established as effective catalysts for conducting such types of photochemical reactions. When the nano-materials have the ability to absorb solar light energy, i.e., to utilise the most of the solar spectrum, the performance of photo-degradation reactions has increased much more. In this chapter, the photo-catalytic efficacy of the proposed NPs has been elaborated based on its structural modification, increasing surface area, and controlling size and morphology. The possible mechanism of this photo-catalytic procedure has also been deliberated through the recognition of hydroxyl radical (OH•). On the basis of this developed methodology, the unlimited abundance of solar energy can be used in large scale waste-water treatment.

**Keywords:** *Photocatalysis; Semiconducting Nano-Materials; Solar-Light-Driven Reaction Kinetics; Nonlinear Least Square Fitting; Waste-Water Treatment; Hydroxyl Radical (OH•)*

## Introduction

Because of the gradual increase in water pollution, the demand for remediation and restoration of this contaminated water is increasing day by day. Several organic pollutants, such as pesticide products, pharmaceutical products, textile effluents, and supplementary organic products (Hasiya *et al.*, 2019), which have poisonous effects and prolonged persistence in water bodies, have severe adverse impacts on life and the environment of the planet. Considering their high solubility in water and low-biodegradability, complete removal from polluted water is vital and treatment of that waste-water is often difficult by conventional methods.

Several analytical techniques have been developed for the elimination of contaminants, including bio-degradation, adsorption, sedimentation, membrane filtering, and coagulation

(Ge *et al.*, 2018). The photocatalytic degradation process is the more efficient and acceptable method, which involves photochemical reactions in the presence of catalysts under light illumination (Dutta *et al.*, 2012). As a catalyst material, semiconducting nano-scaled materials, which have suitable band-gap energy, have been often used to absorb light energy and accelerate the photo-chemical reaction rate (Hoffmann *et al.*, 1995). As a result, it can decompose numerous environmental pollutants completely within a few hours at room temperature (Rafiq *et al.*, 2021). TiO<sub>2</sub>-based resources are well known catalysts and have been widely used for photo-decomposition of pollutants over the past decade; however, it is catalytically active only under UV radiation ( $\lambda < 400$  nm) as it has widespread band gap energy ( $E_g \approx 3.2$  eV) (Nakata & Fujishima, 2012). Of late, several non-titania-based materials such as CuO, ZnO, FeS, ZnS etc. (Sun *et al.*, 2008) and even doped hetero-nanostructures Bi<sub>2</sub>S<sub>3</sub>/BiOCl, Eu-doped Bi<sub>2</sub>S<sub>3</sub> (Sarkar *et al.*, 2015) have been found to show visible-light-driven catalytic efficiency. Recently, considerable attention has been paid to narrow band-gapped (1.0-2.0 eV but not over 3.0 eV) semiconducting nanomaterials having absorption matches with the solar spectrum exhibit enhanced photocatalytic activity under solar light illumination. So, focus needs to be put on improving environmentally friendly, low-energy, and cost-effective technologies for solar-light-driven photo-catalysis.

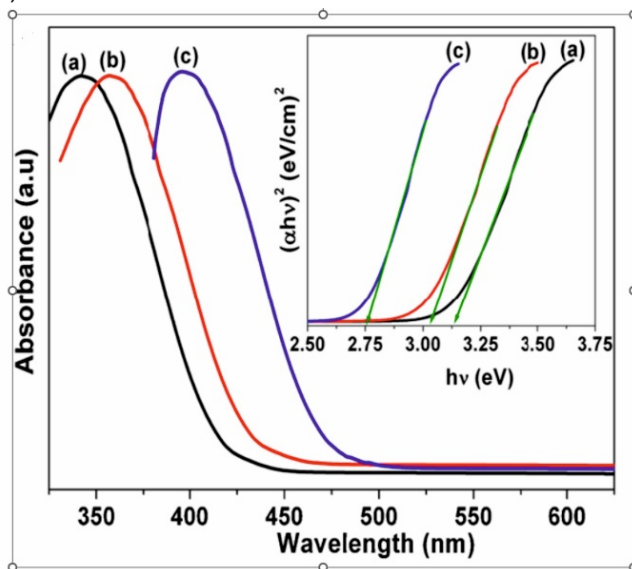
Keeping this in mind, in the following chapter, details have been elaborated on about the photo-catalytic activities of the proposed semiconducting nano-materials and their use as effective photo-active devices for decomposition and remediation of organic pollutants in waste-water treatment. At last, the possible mechanism of the photo-catalytic procedure has also been deliberated through the recognition of hydroxyl radical (OH•).

### ***Nano-Scaled Semiconducting Materials***

As effective heterogeneous photo-catalysts, the most widely studied nano-scaled semiconducting materials include transition metal sulfides, oxides such as iron sulfide (FeS), CdS, ZnS, CuS and iron oxide (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles (NPs). Different synthesis methods are available to prepare different shapes, sizes, morphologies, and even different forms such as nano-spheres, nano-tubes etc., which are important factors that affect their photo-catalytic performances.

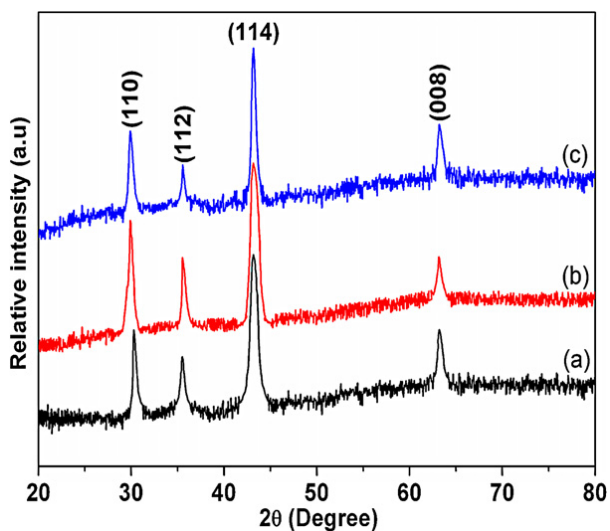
Iron sulfide (FeS) NPs with different morphologies, i.e., nanospheres and nanorods, have been manufactured from a precursor complex [Fe(ACDA)<sub>3</sub>] [where the ligand is 2-aminocyclopentene-1-dithiocarboxylic acid (HACDA)] through a solvothermal way at 120 °C (Maji *et al.*, 2012a) using different nucleophilic solvents: Ethylene glycol (EG), Ethylene diamine (EN) or Ammonia (NH<sub>3</sub>). To improve photo-catalytic performance, the shape, size, and morphology have been controlled during the crystal growing progression, where crystal nuclei favourably grow along a unique route to produce nano-rods in the presence of EN or are combined into quasi sphere-shaped assemblies to produce nano-spheres in the presence of EG and NH<sub>3</sub>. As a result, the band gap energy of different FeS NPs has been automatically

tuned between 2.75 to 3.13 eV which has been measured through UV-Vis absorption spectroscopy (Figure 1).



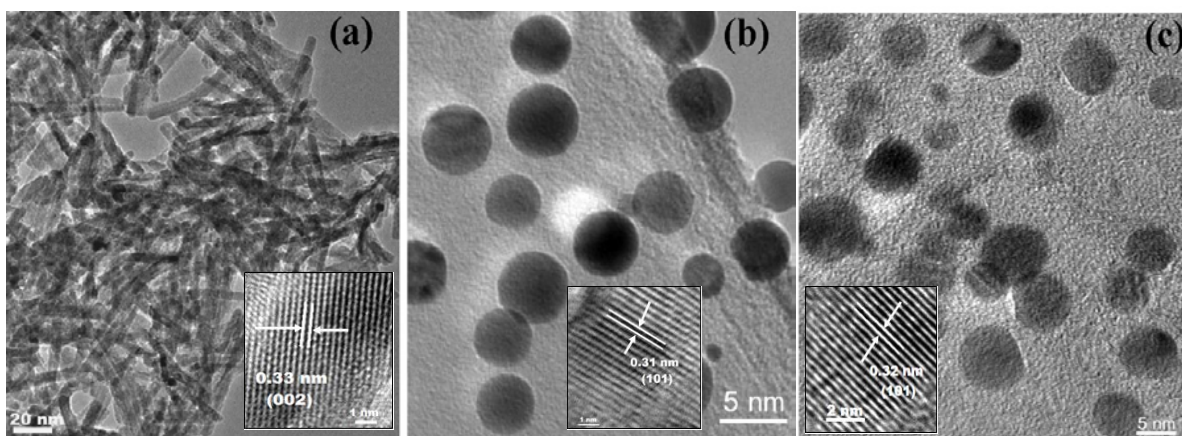
**Figure 1: UV-vis Absorbance Spectra (inset: corresponding Tauc's plots) of FeS NPs, Manufactured in Solvent (a) EG, (b) EN and (c)  $\text{NH}_3$  (S.K. Maji, 2012a)**

The crystalline nature has been examined through powder X-Ray diffraction (XRD) pattern where low crystal defect has been indicated by fairly intense peaks. The diffraction patterns confirmed the formation of hexagonal FeS (JCPDS: 370477) (Figure 2).



**Figure 2: XRD Pattern of FeS Nanoparticles, Manufactured in Presence of (a) EG, (b) EN and (c)  $\text{NH}_3$  (Maji et al., 2012a)**

[Cd(ACDA)<sub>2</sub>] has been used as a precursor material for the manufacturing of CdS NPs with dissimilar morphologies through the same solvothermal route at 120 °C using different nucleophilic solvents EN or hexadecyl-amine (HDA) or dimethyl-sulfoxide (DMSO) (Maji *et al.*, 2012b). The effect of solvents on the morphologies of CdS NPs has been investigated using transmission electron microscopy (TEM), which confirms the presence of rod-like structures with average length and diameter of 70 and 5 nm, respectively (Figure 3a) and spherical structures with average diameters of 4 and 6 nm, (Figure 3b, 3c), respectively. Also, the second important factor to increase the catalytic efficiency, i.e., highly crystalline nature, is indicated by the magnified image of lattice fringes in the live-Fast-Fourier Transform (FFT) (inset Figure 3). Moreover, all CdS NPs possess a high specific surface area (32.1-81.9 m<sup>2</sup>g<sup>-1</sup>) and a mesoporous nature, which are also responsible for high catalyst loading capacity and enhancing the rate of photo-degradation reactions.



**Figure 3: TEM and Inset Magnified Image of Lattice Fringes of CdS NPs, Manufactured in Presence of (a) EN, (b) HDA and (c) DMSO (Maji *et al.*, 2012b)**

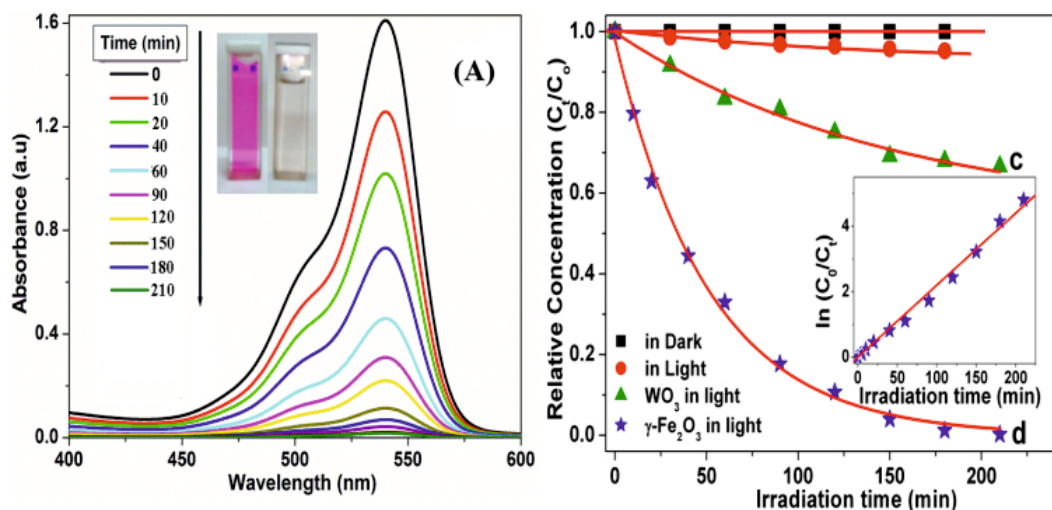
To prepare another semiconducting nano-materials, ZnS NPs, an important II–VI semiconductor, Maji *et al.* (2011) has chosen the same solvothermal decomposition of precursor [Zn(ACDA)<sub>2</sub>] using different nucleophilic solvents. Nanorods (diameter ~6 nm and length ~50 nm) and Nano-sphere (~5 nm) have been deposited in presence of EN (20 ml) and [HDA (15 ml) + TOP (5 ml)], respectively.

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs (Dutta, Maji & Adhikary, 2014) has been prepared from a Fe(III) starting material, where the complex in solid state just burned inside a quartz tube of a horizontal tubular furnace at 670°C for 1 h.

Recently, Eu-doped Bi<sub>2</sub>S<sub>3</sub> hetero-nanostructures (1.8 %, 2.3 % and 4.3 % Eu-doped) (Sarkar *et al.*, 2015) have been synthesized through the same solvothermal process but a mixture of precursor materials [Bi(ACDA)<sub>3</sub>] and [Eu(ACDA)<sub>3</sub>·H<sub>2</sub>O] in different ratios have been decomposed at 140 °C for 5 h.

### Photo-Catalytic Action Measurements

To measure the photo-catalytic performances of the proposed nano-scaled materials, water-soluble and non-biodegradable organic pollutants, such as rose bengal (RB), methylene blue (MB) dyes, and phenol-based pollutants, have been chosen as examples because they are commonly used in industries. The catalytic performances have been investigated spectrophotometrically through the degradation of RB in the wavelength range 400–600 nm under visible light illumination. The UV–vis absorption curves decrease rapidly with the irradiation time (Figure 4A), catalysed by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs and the corresponding solution becomes colorless (Figure 4A inset) within a few hours. A comparative performance has been illustrated in Figure 4B with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs and commercial TiO<sub>2</sub> or commercial tungsten (VI) oxide (WO<sub>3</sub>) as an example.



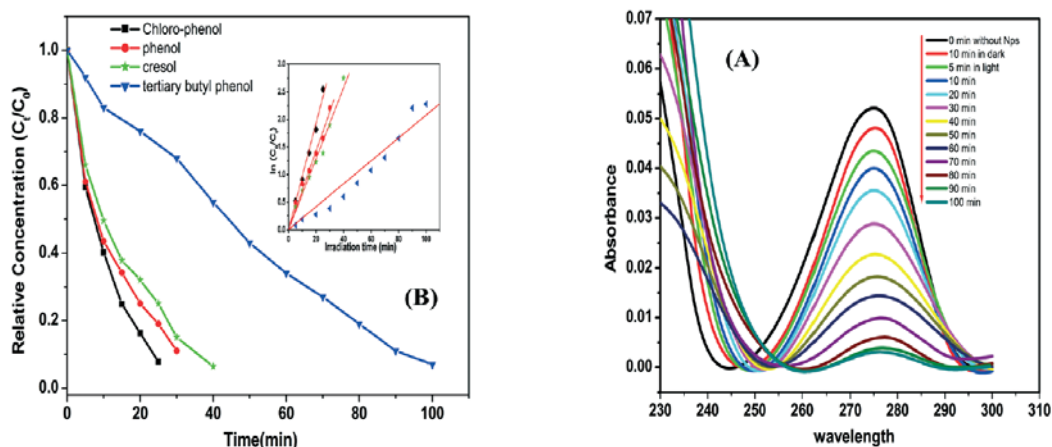
**Figure 4:** (A) Spectro-photometric Variations of RB with Time in Presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nano-catalyst under Light Illumination. Inset: Photography of Corresponding Colour Changes Before and After Decomposition Process, (B) Corresponding Reaction Profile with Pseudo-First Order Kinetics Fitting (Dutta, Maji & Adhikary, 2014)

To investigate the kinetics of the above photo-chemical reactions, the decomposition processes have been modelled as a pseudo-first order reaction kinetics expressed by the equation (1)

$$\ln(C_0/C_t) = k t \quad (1)$$

$C_0$  = initial concentration,  $C_t$  = concentration at a reaction time ' $t$ ', and  $k$  = reaction rate constant. The data have been fitted to the above model using a nonlinear least square fitting method, and the corresponding rate constant values have been summarized in Table 1. By comparison with commercial photo-catalyst, TiO<sub>2</sub> (Degussa P-25) and WO<sub>3</sub>, it has been recognised that pollutant decomposition happens in a quicker way in the presence of the proposed NPs. It has also been established that, photocatalytic activities of the different CdS NPs increase with the order of CdS NPs manufactured in solvents from NH<sub>3</sub> < DMSO < EN < HT based on the increase in specific surface area and crystallinity of the NPs.

In another study, the photo-degradation of phenol-based compounds was carried out using another photo-catalyst, Eu-doped Bi<sub>2</sub>S<sub>3</sub> hetero-nanostructure (Figure 5).



**Figure 5: (A) UV-Vis Spectral Changes of 4-tert-butylphenol with Time in Absence and Presence of 4.26% Eu-doped Bi<sub>2</sub>S<sub>3</sub> NPs, (B) Corresponding Reaction Profile with Kinetics Fitting (Sarkar et al., 2015)**

**Table 1: Comparison of the Kinetic Parameters for the Photo-Catalytic Activity of the Proposed Nano-Scaled Materials**

Nano-catalyst	Rate constant (min <sup>-1</sup> ) for RB degradation	Rate constant (min <sup>-1</sup> ) for MB degradation	Reference
γ-Fe <sub>2</sub> O <sub>3</sub>	2.15×10 <sup>-2</sup>	8.80×10 <sup>-2</sup>	Dutta, Maji & Adhikary, 2014
WO <sub>3</sub>	3.3 × 10 <sup>-3</sup>	4.5 × 10 <sup>-3</sup>	Dutta, Maji & Adhikary, 2014
TiO <sub>2</sub> (Degussa P-25)	1.7 × 10 <sup>-3</sup>	1.16 × 10 <sup>-3</sup>	Maji et al., 2012b
CdS (from HDA)	2.2 × 10 <sup>-2</sup>	–	Maji et al., 2012b
ZnS (from HDA)	2.17×10 <sup>-2</sup>	–	Maji et al., 2011
FeS (from EG)	–	2.71 × 10 <sup>-2</sup>	Maji et al., 2012a
FeS	6.02×10 <sup>-2</sup>	5.73×10 <sup>-2</sup>	Dutta et al., 2012
FeSe	3.39×10 <sup>-2</sup>	2.32×10 <sup>-2</sup>	Dutta et al., 2012

### Photo-Catalytic Mechanism

To understand the mechanism of the photo-catalytic activity of the proposed semiconducting nano-materials, it has been established that during light irradiation, the nano-materials use the light energy to excite electrons from their valance band (VB) to the conduction band (CB), thus leaving behind holes (Figure 6). This hole can capture electrons from water bodies to generate hydroxyl radical ( $\text{OH}\cdot$ ) (Al-Ekabi, 1989). These radicals actually oxidize or decompose the pollutants.

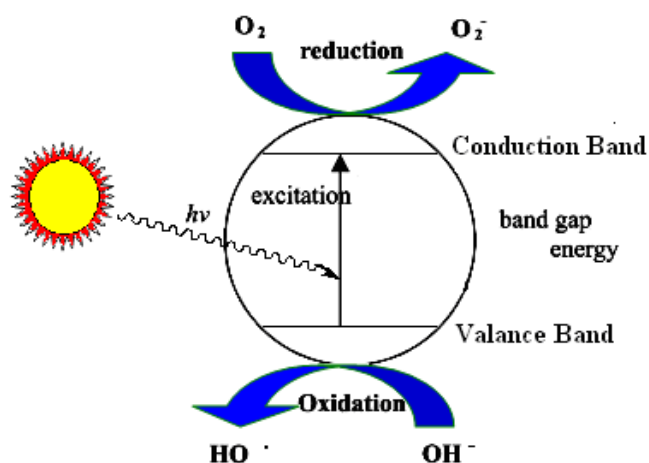
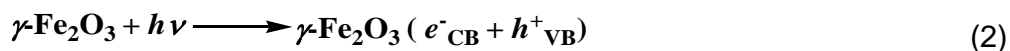


Figure 6: Illustration of Photo-Catalytic Mechanism (Dutta, Maji & Adhikary, 2014)

If that band gap energy becomes tremendously short, the lifetime of the produced electrons and holes on its surface also becomes short, there is a possibility of recombination of electron-hole pairs, and hence the photocatalytic activity is decreased. In that case, doped hetero-nanostructures have been used, where the dopant operates as an electron scavenger on the surface of the nano-structures, defeating the recombination of electron-hole pairs and enhancing their lifetime.

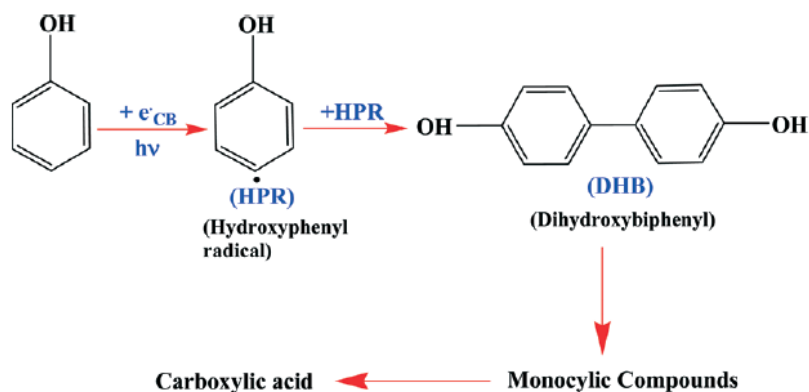
The overall reactions are presented in equations (2)–(5).



The aromatic dyes have been further degraded by  $\text{O}_2^-$  active species, which was generated on the surface of the proposed NPs according to following equations.

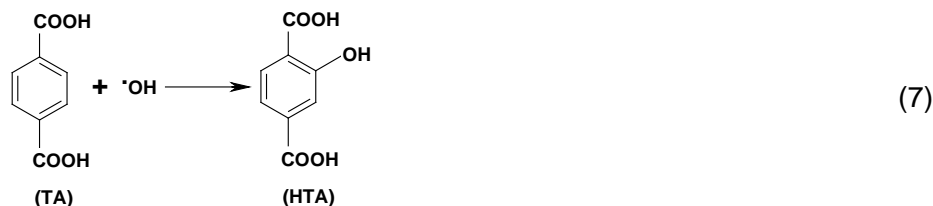


The final product after the photo-catalytic decomposition process has been investigated through LC-MS spectrum, where a significant peak at  $m/z = 113.1$  corresponds to the chlorobenzene group, indicating the total breakage of the RB molecule into very small fragments. In the case of phenol-based pollutants, the decomposition process occurs through the formation of a hydroxy-phenyl radical (HPR) and various intermediates like dihydroxybiphenyl (DHB) or catechol (CC) or hydroquinone (HQ) followed by photo-catalytic oxidation and ring cleavage to yield carboxylic acids or aldehydes, which are further degraded to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Figure 7) (Sarkar *et al.*, 2015).



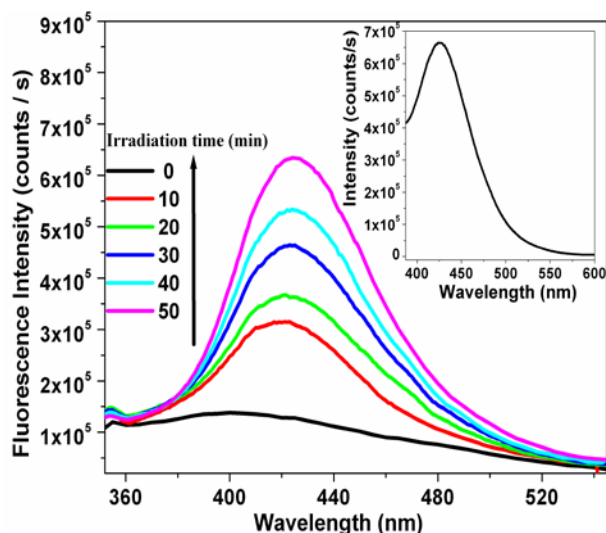
**Figure 7: Representation of Degradation Mechanism of Phenol-Based Pollutants (Sarkar *et al.*, 2015)**

The generation of  $\text{OH}\cdot$  has been recognised by terephthalic acid (TA) photoluminescence analytical systems (Barreto *et al.*, 1994), where TA combined with hydroxyl radicals and formed highly fluorescent 2-hydroxy terephthalic acid (HTA) (Figure 8 inset) as stated by the following equation.



The corresponding photo-luminescence spectral study of NPs/TA system under light irradiation, indicates the increase in luminescence intensity of the solution with irradiation time (Figure 8), which is responsible for formation of more and more HTA and  $\text{OH}\cdot$ .





**Figure 8: Fluorescence Spectro-Metric Variations of Terephthalic Acid (TA) in Presence of  $\gamma$ - $\text{Fe}_2\text{O}_3$  Nano-Catalyst under Light Irradiation. Inset: Fluorescence Spectrum of the Commercial HTA (Sigma-Aldrich) (Dutta, Maji & Adhikary, 2014)**

## Conclusion

In summary, the proposed nano-scaled materials are widely explored as an efficient photo-catalyst for the degradation of various organic pollutants under solar and visible light illumination. They exhibit different catalytic efficiencies based on different size, shape and morphology. The catalytic performances have also been improved by tuning band-gap energy and surface area during the synthesis process. Finally, an environmentally friendly, cost-effective technology has been developed for solar-light-driven photo-catalysis so that most of the solar spectrum and light energies can be utilized for large-scale waste-water treatment processes.

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