



Effect of Graphene Oxide on Nano Titania Particles in Visible Light Induced Photocatalytic Degradation of Congo red

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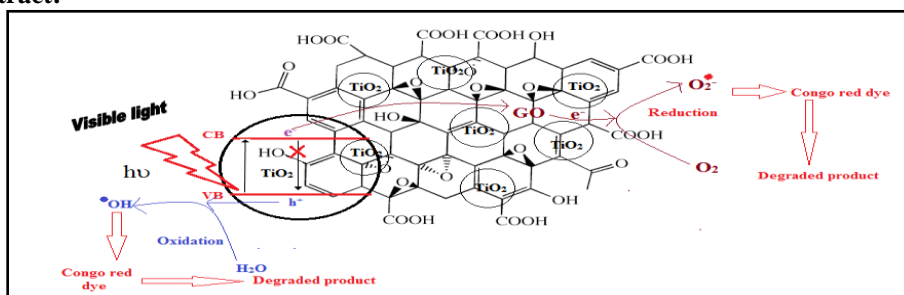
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ABSTRACT

In the present work, visible light induced photocatalytic degradation of Congo red dye in aqueous medium was investigated by employing modified nano titania (NT) particles exfoliated with graphene oxide (GO) particles. The composites were synthesized by organic solvent free controlled hydrolysis of titanium tetrachloride followed by dispersing an aqueous solution of graphene oxide. These composites have been characterized by X-Ray Diffraction (XRD), Fourier Transform Infra-Red Spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FE-SEM), and UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). Efficiency of the composites towards the photocatalytic degradation of Congo red dye was assessed by analyzing the effect of nano titania particles with increase in the content of GO and effect of pH of the dye solution. Photocatalytic degradation of Congo red dye was enhanced by contriving the composites into visible light absorption on grafting GO on the surface of nano titania particles. With an optimum increase in the GO content, the photocatalytic activity of the composites was improved and a superior photocatalytic activity was observed with 10% GO-nano titania composite material.

Graphical Abstract:



Photocatalytic degradation mechanism of synthesized GO-nanotitania composites on Congo red dye under visible light irradiation

Keywords: Photocatalytic degradation, Nano titania, Graphene oxide, Congo red.

INTRODUCTION

Industrial waste waters containing harmful organic dyestuffs with intense color, high toxicity introduced into the aquatic systems has become an exigent task to handle [1]. These non-treated dyes are mostly released from textile industries. Of all the dyes found in the waste waters, aromatic azo dyes were observed to be more complicated in nature due to the presence of carcinogenic azo group (-N=N-) chromophores [2-4]. More than 60% of dyes similar to azo dyes with different chemical structures are used in textile, pharmaceutical, paper, ink industries etc [4]. It is vital to treat the waste waters containing these dyestuffs before released into the water bodies. Over the past few decades, physical and chemical techniques like coagulation, adsorption on activated carbon, reverse osmosis, biodegradation, advanced oxidation processes (AOP) etc are some the established techniques to degrade the organic dyes [5]. Among these techniques, AOP was found to be one of the promising paths to detoxify the organic pollutants in industrial waste waters [6-8]. Photocatalytic degradation using heterogeneous semiconducting materials is one of the routes in AOP and was adopted in many works [9-10]. The most commonly used photocatalysts are TiO_2 , ZnO , Fe_2O_3 , Cu_2O , ZnS and WO_3 . Owing to its low toxicity, high photostability, low cost and high photo efficiency, nanotitania (NT) with anatase phase was reported as one of the familiar and effective photocatalyst [11-13]. However, its large band gap of around 3.2 eV (anatase) and rapid electron/hole (e^-/h^+) recombination confines its usage to UV region [14]. Doping with inorganic metals, modifying titania particles by forming nano composites by introducing carbon materials are few methods to contrive the absorption of the titania particles into visible region. Titanium tetrachloride was reported as one of the discriminating precursor to synthesize photoactive NT particles without impurities [15] among many precursors and in the present work the same material was used to synthesize NT particles followed by exfoliation of graphene oxide (GO) on NT particles. The % of GO was arranged as 1%, 2%, 5%, 10% and 15% respectively in the composite materials and its effectiveness was investigated for visible light induced photocatalytic degradation of Congo red dye (Figure 1).

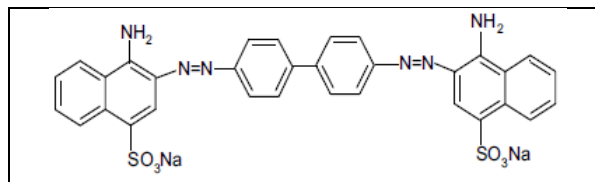


Figure 1. Structure of Congo red (C.I. Direct Red 28)

MATERIALS AND METHODS

Titanium tetrachloride (TiCl_4), graphite powder, potassium permanganate (KMnO_4), phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) of AR grade were used for the present work with more than 99% purity. Congo red dye (Qualigens) with chemical formula $\text{C}_{32}\text{H}_{22}\text{N}_6\text{O}_6\text{Na}_2\text{S}_2$ (C.I. Direct Red 28, $\text{M.W.} = 696.67 \text{ gmol}^{-1}\text{L}^{-1}$) was the azo dye selected for the study. All the chemicals were used as procured without any further purification. The stock solution of the dye was prepared using distilled water.

Synthesis of graphene oxide nano titania composites: Graphene oxide (GO) was prepared by modified Hummers method without any further modification [16], dried and characterized. A standard solution of GO was prepared by dispersing 1 g of GO powder in 100 mL of distilled water and kept under ultrasonication. From this standard solution, 5 mL (0.05 g), 10 mL (0.1 g), 25 mL (0.25 g), 50 mL (0.5 g) and 75 mL (0.75 g) of GO solution was dispersed in five separate beakers each containing 350 mL of distilled water under ultrasonication for a better distribution of the GO particles. In order to maintain 1:50 mL ratio of $\text{TiCl}_4/\text{H}_2\text{O}$, 6.9 mL of TiCl_4 was slowly added to each beaker and left for 30 minutes under ultrasonication to allow the exfoliation of the GO particles on the surface of the nanotitania particles. This

[precursor]/ [solvent] volume ratio of $\text{TiCl}_4/\text{H}_2\text{O}$ produces around 5.0 g of nano titania particles. The final mixtures were heated at around 100 to 120°C to vaporize the chloride ions and the gel obtained was dried in an electrical hot air oven at 80°C. Further, the composite materials were calcined at 400°C for 2 hours. The initial composite material was designated as 1 % GO-NT (0.05 g of GO in 5.0 g of nano titania). Similarly, the other composite materials were designated as 2% GO-NT, 5% GO-NT, 10% GO-NT and 15% GO-NT respectively.

Photocatalytic measurements: UV-Visible spectrophotometer (Systronics-105, wavelength range: 340-960 nm) was used to study the photocatalytic performance of the synthesized nano composites. 10 mg of the each composite material was added to 10 ppm of 100 mL of the dye solution ($\lambda_{\text{max}}=500$ nm) under continuous stirring. After establishing desorption-adsorption equilibrium for 30 minutes in dark conditions, the photocatalytic study was carried out under 400 watts tungsten halide lamp embedded in a wooden breakfront. In pre-determined time intervals, 5 mL of aliquots were drawn, centrifuged and the translucent dye solutions were analyzed using UV-Visible spectrophotometer at 500 nm wavelength. The % degradation of the dye was calculated using equation.1.

$$\text{Photocatalytic degradation \%} = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad \dots (1)$$

where C_0 is initial concentration of the dye and C is the concentration of the dye at a time interval, t .

Instrumentation: The composite materials were characterized by using X-Ray Diffractometer (PANalytical-X' Pert PRO, Japan) at room temperature using Nickel Filter Cu-K α radiation ($\lambda = 1.54059$ Å) over wide range of $10^\circ \leq 2\theta \leq 80^\circ$ with a scanning speed of 2 min^{-1} . UV-Visible diffuse reflectance spectra were recorded using Single Monochromator UV-2600 (optional ISR-2600Plus, λ up to 1400nm). The morphology of the synthesized composites was studied by Field Emission Scanning Electron Microscopy (FE-SEM, LEO1550). Fourier Transform Infra-Red spectral (FT-IR) data was recorded from BRUKER ALPHA FT-IR with Opus 6.1 version using KBr pellets at 400-4500 cm^{-1} region.

RESULTS AND DISCUSSION

X-Ray Diffraction studies: The XRD patterns of the synthesized composite materials were recorded in the 2θ range of $10\text{-}80^\circ$ at a step interval of 0.02° with the counting time of 5s at each point. Figure .2 shows the XRD pattern of the GO particles and a typical diffraction peak at $2\theta = 10.2^\circ$ corresponding to C(002) plane representing the hexagonal graphite structure and it was almost close to the reported results [17]. The XRD patterns of the NT particles and GO-NT composites were reported in figure.3. It was clear from the diffraction patterns that the 2θ values at 24.8° , 35.7° , 37.5° , 47.4° , 53.7° , 54.4° , 62.2° , 68.5° , 69.4° , 74.8° and 82.3° can be perfectly assigned to the crystal planes of the (101), (103), (004), (200), (105), (211), (204), (116), (220), (215) and (303) of the body-centered tetragonal titanium dioxide which were in good agreement with anatase phase of nanotitania particles (JCPDS 21-1272). There were no significant peaks for other phases of titania like rutile or brookite. Typical diffraction peaks of GO were not observed in the GO-NT composites and it may be due to well exfoliation of the GO particles on the surface of the titania particles or its low diffraction intensity. Peak broadening was observed in the XRD peaks of NT particles which may be attributed to the large particle size and high crystalline nature [15].

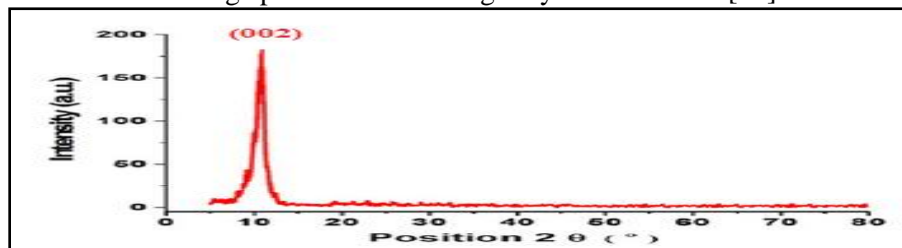


Figure 2. XRD of GO particles

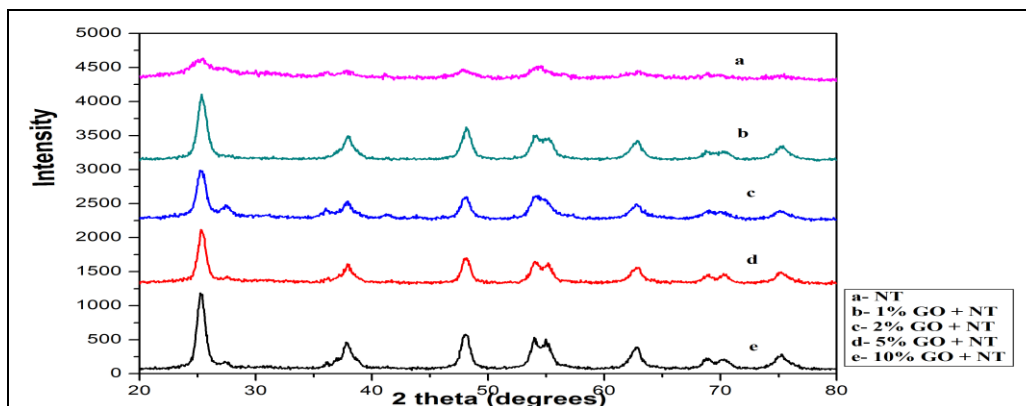


Figure 3. XRD peaks of NT & x %GO-NT composites

UV-Diffuse Reflectance Studies (UV-DRS) studies: Figure 4 depicts the optical properties of the NT particles and GO-nano titania composites. The nano titania particles were synthesized by maintained 1:50 [precursor]/[solvent] volume ratio and also a higher specific surface area was reported in the earlier works [15]. It was observed that with an increase of GO content in the composites, the absorbance of the composites was increased gradually which may be due to enhanced surface area of the nano composites and active sites in the graphene oxide sheets. This clearly results that the GO particles were perfectly exfoliated on the surface of the nano titania particles enhancing the visible light absorption capacity of the composites. It also indicates a strong chemical interaction between the titanium ions and the oxygen moieties in GO. These findings were in close agreement with the similar studies of Graphene oxide-nano titania composites [18, 19].

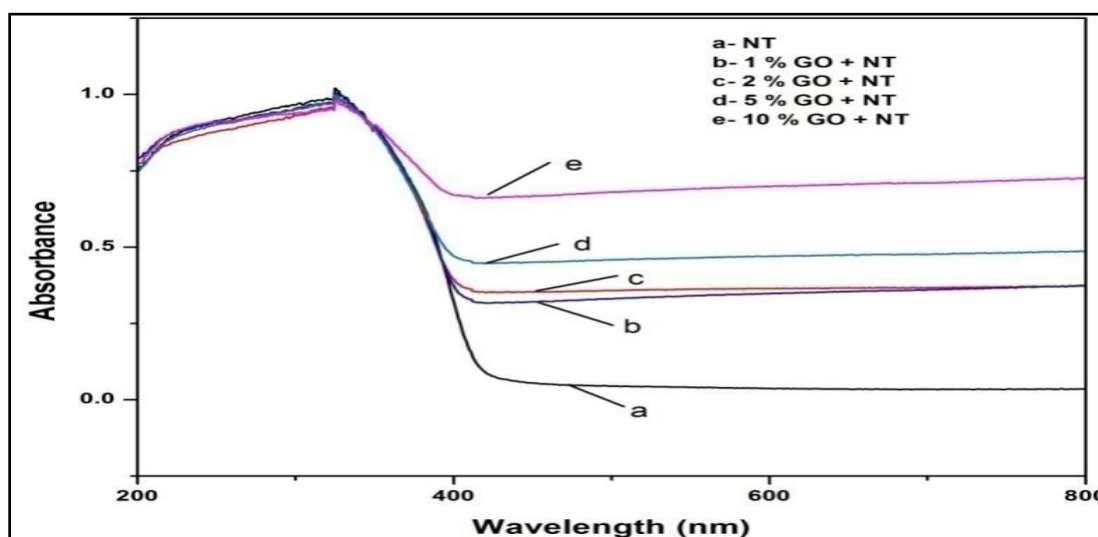


Figure 4. UV-Vis DRS study of composites

(a) NT (b) 1% GO+NT (c) 2% GO+NT (d) 5% GO+NT (e) 10% GO+NT

Morphology studies: The FE-SEM images of the synthesized composite materials were presented in figures. 5a, 5b, 5c. Figure.5a represents that particles were in irregular shapes with formation of aggregates. The FE-SEM micrographs of GO-nano titania composite materials were presented in figures. 5b, 5c. It was found that there was a significant change in the particle size of the composites which may be due to well exfoliation of GO on nano titania in the composite materials [20].

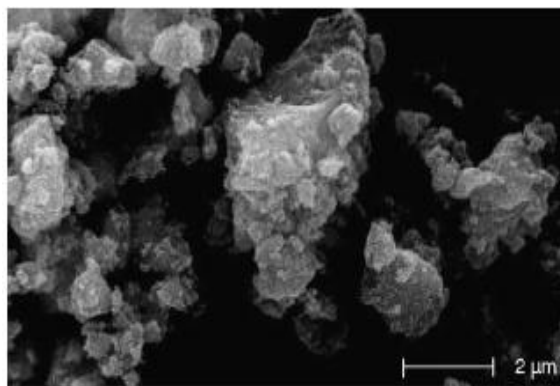


Figure.5a. FESEM image of Nanotitania particles

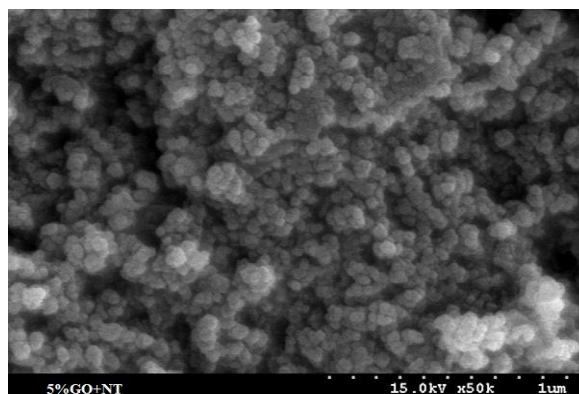


Figure.5b. FESEM image of 5%GO+NT

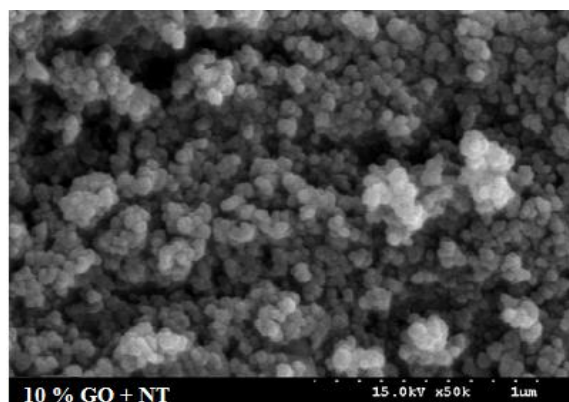


Figure.5c FESEM image of 10%GO+NT

Fourier-Transform Infrared Spectra (FT-IR) analysis: Figure.6 shows the FT-IR spectra of GO-NT composite materials. A transmission peak at 3360cm^{-1} represents the $-\text{OH}$ stretching vibration of GO particles. An absorption peak at 1084cm^{-1} for C-O stretching mode of hydroxyl groups in Graphene oxide was absent in GO-NT peaks. The absorption peaks in the range of $400\text{-}1000\text{ cm}^{-1}$ corresponding to Ti-O-Ti bonds shifted to lower wavelengths (below 1700 cm^{-1}) on introducing Graphene oxide. This can be attributed to the presence of both Ti-O-Ti and Ti-O-C bonds in the composites indicating a strong chemical interaction between surface hydroxyl groups of titania and oxygen functional groups of Graphene oxide. These results were almost in close agreement with the earlier reports [14].

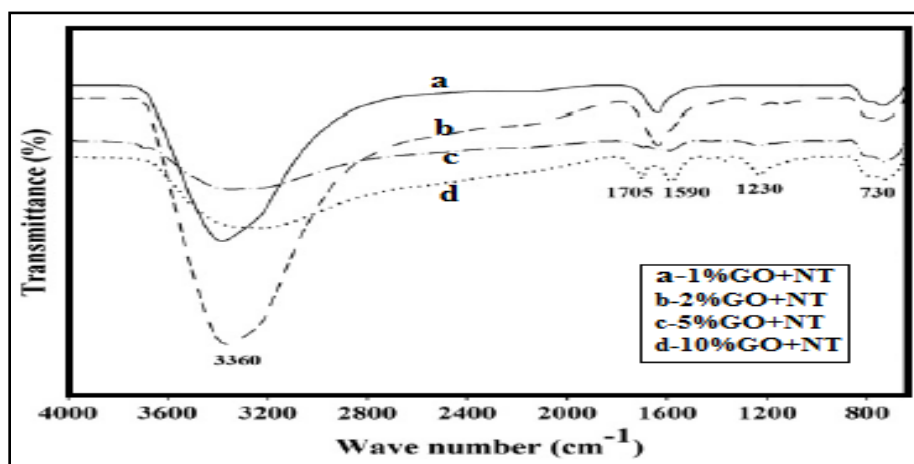


Figure 6. FT-IR spectra of GO-NT composites
(a) 1%GO+NT (b) 2%GO+NT (c) 5%GO+NT (d)10%GO+NT

Photocatalytic studies: The photocatalytic activity of the synthesized composite materials was examined for the visible light degradation of Congo red dye solution. 10 mg of the each composite material was dispersed separately in six different sets of 100 ppm concentrated dye solutions and kept under magnetic stirring in dark for 30 minutes to establish desorption/adsorption equilibrium. Then the mixtures were kept under visible lamp and 5 mL of aliquots were collected for every 15 minutes of time interval. These aliquots were analyzed by using UV-Vis spectrophotometer. Figure.7 shows the decrease in absorbance of the dye solution in the presence of nano titania and the composite materials. It was clear that the absorbance was gradually decreased with increase in % of GO in the composites. It was also clear that the irradiation time was reduced from 150 minutes to 30 minutes by 10% GO-NT composite material for the Congo red dye degradation.

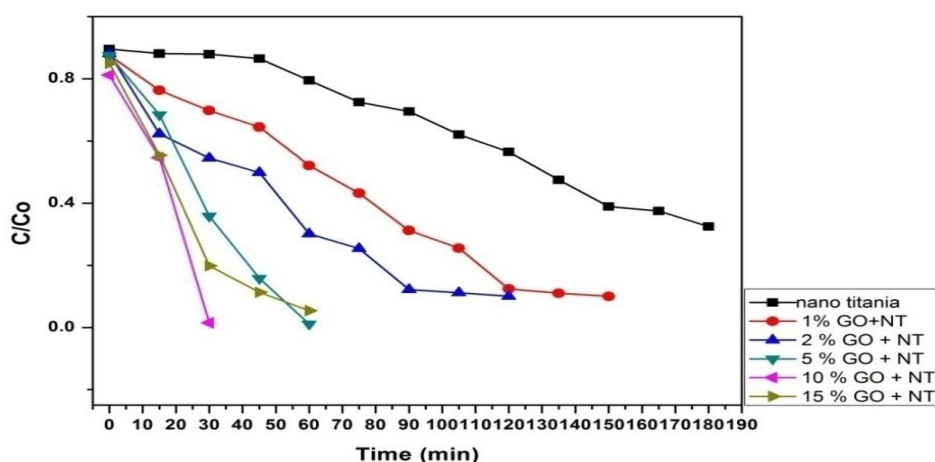


Figure.7. Degradation of CR dye with nano composites
Catalyst load= 10 mg, Concentration of dye solution = 100 ppm

Effect of GO composition on photocatalytic degradation: Photocatalytic degradation of anthropogenic dyes using TiO₂-GO composites in the presence of UV light was reported as one of the method for detoxification of organic dyestuffs [20]. As visible light photocatalysis is more pronounced, we have performed the photocatalytic degradation of Congo red dye with x% GO-NT composites under visible light. Figure.8 shows the efficiency of GO composition in the composites for degradation of the dye. It has been clearly observed that the % of degradation of the dye solution was enhanced with increased of GO content in the composites from 1 % to 10 % and a superior degradation efficiency (100 %) was achieved

with 10% GO-NT composite material. This can have attributed to high capability of SP² hybridized carbon atoms in GO which can store electrons and shuttles the electrons. GO particles also controls the rapid recombination of e⁻/h⁺ pairs in the NT particles and thus provides a medium for the photochemical oxidation of the organic dyes[21]. Further increase in the % of GO in 15% GO-nanotitania composite did not show any appreciable change in the degradation efficiency. This may be due to agglomeration of the GO particles to form large particles thereby decreasing the specific surface areas of the Graphene oxide nano titania composites [18].

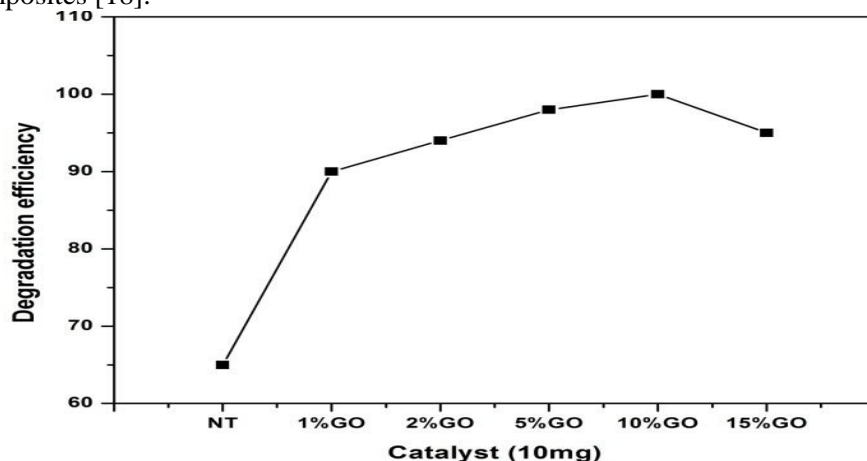


Figure.8. Degradation efficiency of nano composites
Catalyst load= 10 mg, Concentration of dye solution = 100 ppm

Effect of pH on degradation of dye solution: The effect of pH of the dye solution in photocatalytic degradation was studied with 10 %GO-NT nano composite material by varying the concentrations of HNO₃ and NaOH solution and was shown in table.1. These effects were studied by varying the pH of the dye solution from 5.2-12.5. A study increase of photocatalytic degradation was observed from pH 5.5-9.5 and reached maximum degradation effect in the pH range of 7.5-9.5. However, the degradation efficiency was slowly decreased around pH 10 and it clearly shows the dye solution has maximum degradation in the pH range of 7.5-9.5. The pH affects the surface properties of the catalysts and also dissociates the dye molecules by formation of hydroxyl radicals. This can be due to agglomeration of the nano titania particles at low pH which makes the degradation efficiency less. At low pH conditions, the azo groups in CR dye (-N=N-) are susceptible to electrophilic attack and the high concentration of H⁺ ions decreases the electron densities in the azo group [22].

Table.1. Effect of pH on degradation of the dye solution

pH of the dye solution	% Degradation of the dye with 10 mg of 10% GO+NT composite material
5.5	80
6.5	83
7.5	95
8.5	96
9.5	97
10.5	92
11.5	89
12.5	85

Plausible mechanism of photocatalytic degradation: The schematic illustration of the visible light induced photocatalytic degradation of Congo red dye in the presence of Graphene oxide nano titania

composites was shown in Figure.9. On visible light irradiation, the electrons (e^-) present in the valence band (VB) of the nano titania particles gets excited to the conduction band (CB). This stage is referred to as the semiconductor's photo-excitation stage creating a negative-electron (e^-) and positive-hole (h^+) pair. In the absence of GO, these e^-/h^+ pairs combine vigorously and results in a very low photoactivity. The d-orbital (CB) of the nano titania and π -orbital of the graphene oxide interact and forms a d- π overlap [23]. The nano titania particles absorbs the visible light and transports the excited state electron from its CB into the π -orbital of the GO and the excited electrons can be shuttled easily along the conducting network of the GO surface thereby decreasing the e^-/h^+ recombination in the nano titania particles. This negative electron subsequently transfers to the surface of the composite material to react with water and oxygen and yields hydroxyl radicals and super oxide ions respectively. These hydroxyl radicals and super oxide ions would oxidize the Congo red dye. The major reaction steps, the routes of formation of these radicals and the photocatalytic degradation of Congo red dye was described in scheme 1.

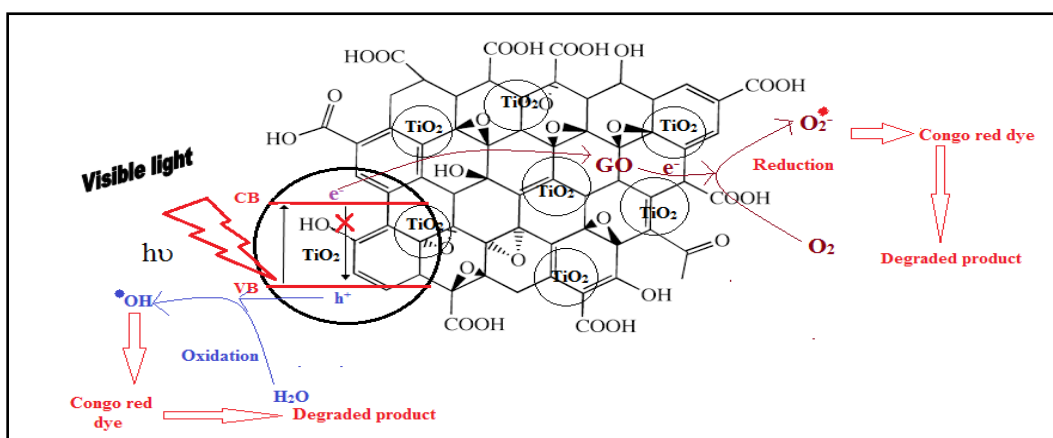
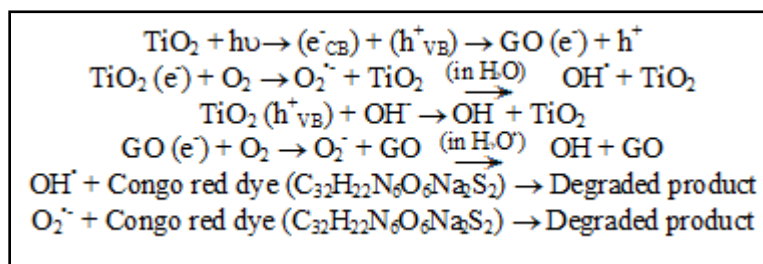


Figure 9. Photocatalytic degradation mechanism of synthesized GO-nano titania composites on Congo red dye under visible light irradiation



Scheme.1. Visible light induced photocatalytic degradation reactions of Congo red dye in the presence of GO-nanotitania composites

APPLICATIONS

The results indicate that this method is useful for high photocatalytic degradation of dye in presence of small dose of nano-titania catalyst and visible light.

CONCLUSIONS

Present work reports a one-step synthesis of organic solvent free controlled hydrolysis of TiCl_4 followed by dispersing an aqueous solution of Graphene oxide under ultrasonication. The as-prepared nano composite materials were characterized by XRD, FE-SEM, FT-IR and UV-Vis DRS techniques and their efficiency was analyzed for photocatalytic degradation of Congo red dye under visible light irradiation. It

was observed that in 30 min, 100 % of the dye solution was degraded with 10% GO-NT composite material for 10 mg dosage of catalyst and 100 ppm dye concentration. High photo catalytic degradation was observed in the pH range of 7.5-9.5.

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