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Synthesis, Characterization and Visible Light Photocatalytic Degradation Study of Thiourea modified Nano Titania Composites

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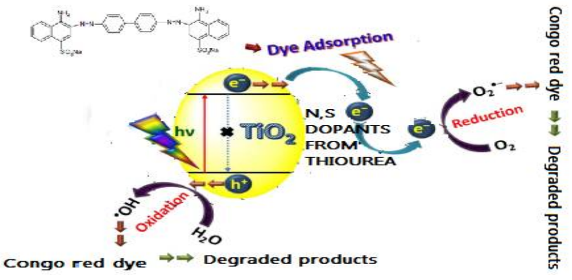
ABSTRACT

In the present work, visible light induced photocatalytic degradation of Congo red dye in aqueous medium was investigated by employing Thiourea modified nanotitania (NT) particles. The composites were synthesized by organic solvent free controlled hydrolysis of titanium tetrachloride followed by dispersing thiourea and the samples were designated as x mole % thiourea titania nanocomposites (where x= 5, 10, 20 mole %). These composites have been characterized by X-Ray Diffraction (XRD), 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 nanotitania particles with increase in the content of Thiourea 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 dispersing Thiourea on the surface of nanotitania particles. With an optimum increase in the Thiourea content, the photocatalytic activity of the composites was improved and a superior photocatalytic activity was observed with 10% Thiourea -nanotitania composite material.

Graphical Abstract



Visible light Photocatalyticdegradation mechanism of synthesized x mole % thiourea- nanotitania composites on Congo red dye

Keywords: Visible Light Photocatalytic degradation, Thiourea modified Nano Titania, 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 untreated 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 of 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 [15-16] among many precursors and in the present work the same material was used to synthesize NT particles followed by exfoliation of thiourea on NT particles. The mole % of thiourea was arranged as 5%, 10% and 20 % respectively in the composite materials and its effectives were investigated for visible light induced photocatalytic degradation of Congo red dye (Figure 1).

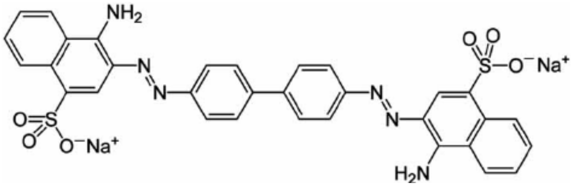


Figure 1. Structure of Congo red dye(C.I. Direct Red 28)

MATERIALS AND METHODS

TitaniumTetrachloride ($TiCl_4$) and Thiourea of AR grade were used for the present work with more than 99% purity. Congo red dye (Qualigens) with chemical formula $C_{32}H_{22}N_6O_6Na_2S_2$ (C.I.Direct Red 28, M.W=696.67 g mol/L) was the azo dye selected for the study. All the chemicals were used as procured without any further purification. De-ionised water was used all throughout the study.

Synthesis of Thiourea modified Nano Titania Composites: 350 mL of De-ionised water is taken into three different beakers. In order to maintaing a 1:50 mL ratio of $TiCl_4/H_2O$, 6.9 mL of $TiCl_4$ was slowly added into each of the three beakers and left for 30 minutes on magnetic stirrers to allow the reaction to proceed. This [Precursor/ Solvent] volume ratio of Titanium Chloride / water produces around 5.0 grams of titania nanoparticles. To the reaction mixture in the three different beakers under constant stirring, stoichiometric quantities of thiourea were added to prepare 5 mole %, 10 mole% and 20 mole % Thiourea – Titania nano composites. The final mixtures were heated at around 100° C to 120° C to vaporise the chloride ions and the gel obtained was dried in an electrical hot air oven at 80° C. The composites obtained were finely ground and sintered at 400° C for 4 hours. The composites were consecutively designated as 5%, 10% and 20% Thiourea-Titania Nano Composites.

Photocatalytic measurements: UV-Visible spectrophotometer (Systronics-105, wavelength range: 340-960nm) was used to study the photocatalytic performance of the synthesized nanocomposites. 10 mg of the each composite material was added to 10 ppm of 100 mL of the dye solution (λ_{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, 5mL 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.

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

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-Kα radiation (λ= 1.54059 A°) 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).

RESULTS AND DISCUSSION

X-Ray Diffraction studies: The XRD patterns of the synthesized composite materials were recorded in the 2θ range of 10-80° at a step interval of 0.02° with the counting time of 5s at each point. Figures .2.a, 2.b, 2.c shows the XRD pattern of the 5 mole %, 10 mole %, 20 mole% Thiourea doped titanium oxide nanocomposites respectively. It was clear from the diffraction patterns that the 2θ values at 27.5°, 36.2°, 39.3°, 54.4°, 62.2°, 64.1°, 69.4°, 76.6° and 82.4° can be perfectly assigned to the crystal planes of the (101), (103), (004), (200), (105), (211), (204), (116), and (303) of the body-centred tetragonal titanium dioxide which were in good agreement with anatase phase of nanotitania particles (JCPDS No. 21-1272). Further, the characteristic peak of thiourea at 2θ= 25.2° corresponding to the C (0 2 0) plane was almost not observed in the composites and it may be due to the well exfoliation of the thiourea particles on the surface of nanotitania [17-18].

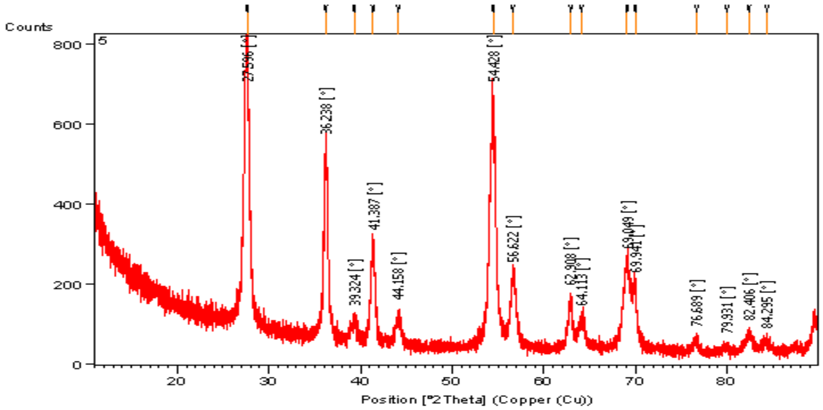


Figure 2.a. XRD Pattern of 5 mole % thiourea-titania nano composite

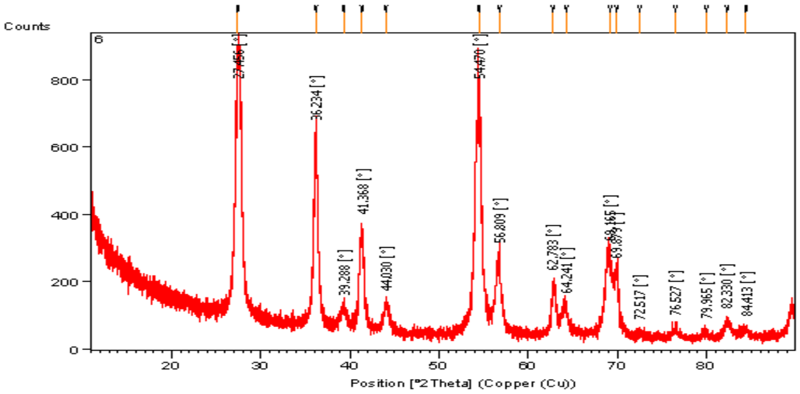


Figure 2.b. XRD Pattern of 10 mole % thiourea-titania nano composite

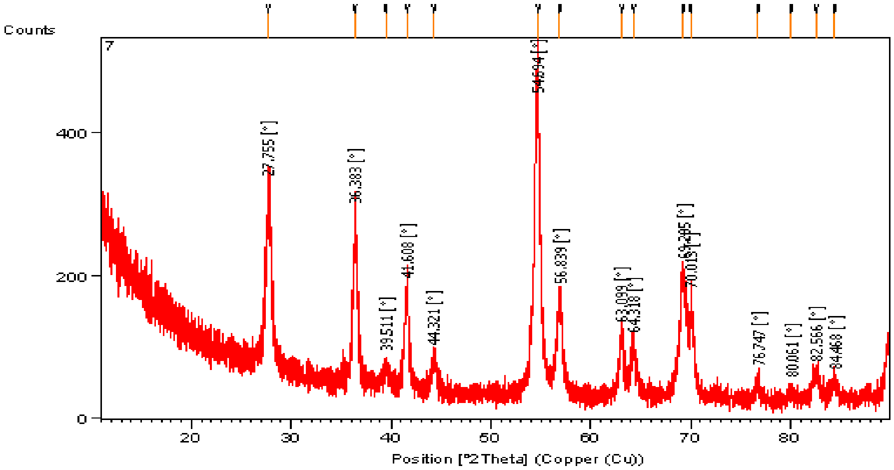


Figure 2.c. XRD Pattern of 20 mole % thiourea-titania nano composite

UV-Diffuse Reflectance (UV-DRS) studies: Figures 3.a, 3.b and 3.c depict the opticalproperties of the Thioureatitania nanocomposites. The nanotitania particles were synthesized bymaintained 1:50 [precursor]/[solvent] volume ratio and also a higher specific surface area was reported in the earlier works [15]. It is observed that with an increase of Thiourea content in the composites, theabsorbance of the composites was increased gradually which may be due to enhanced surface area of the nano composites and active sites in the photocatalyst. This clearly results that the thiourea particles were perfectly exfoliated on the surface of the nanotitania particles enhancing the visible light absorption capacity of the composites. It also indicates a strong chemical interaction between the titanium ions and the oxygen and nitrogen moieties in thiourea. There was also narrow decrease in the band gap of 10 mole % thiourea titania nanocomposite material and this may be due to a strong diffusion of the nitrogen dopants into the titania moiety and caused a reasonable drop in the band gap. Further increase in the mole % of thiourea in the composites did not bring much difference in the band gap as excess dopant atoms may decrease the number of active sites in the composites and these results were presented in table 1. These findings were in close agreement with the earlier works [19].

Morphology studies: The FESEM images of the synthesized composite materials were presented in figures. 8a, 8b, 8c. From the FESEM micrographs of Thioureatitania nanocomposite material, It was found that there was a significant change in the particle size of the composites which may be due to well exfoliation of Thiourea on nanotitania in the composite materials [20].

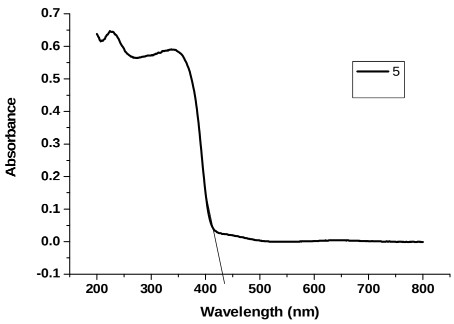


Figure 3.a. UV-DRS spectra of 5 mole % Thiourea-titania nanocomposite

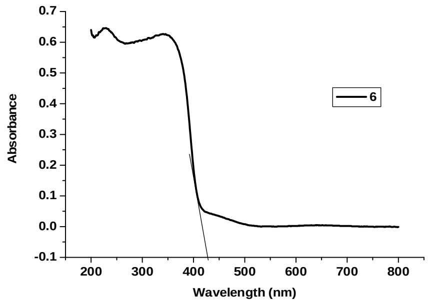


Figure 3.b. UV-DRS spectra of 10 mole % Thiourea-titania nanocomposite

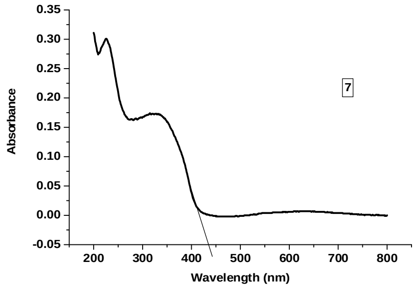


Figure 3.c. UV-DRS spectra of 20 mole % Thiourea-titania nanocomposite

Table 1. Absorption Edges and Band Gap Values of the Samples

SAMPLE	ABSORPTION EDGE (in nm)	Band Gap (eV)
5 Mole % Thiourea modified Titanium Oxide	426.0	2.91
10 Mole % Thiourea modified Titanium Oxide	428.7	2.89
20 Mole % Thiourea modified Titanium Oxide	435.0	2.85

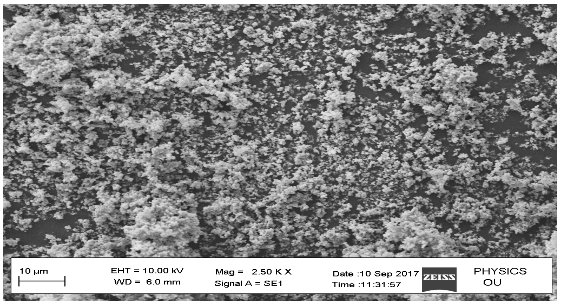


Figure 4.a. FESEM of 5 mole % Thiourea-titania nanocomposite

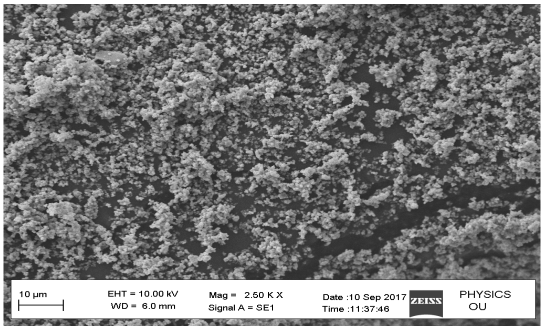


Figure 4.b. FESEM of 10mole % Thiourea-titania nanocomposite

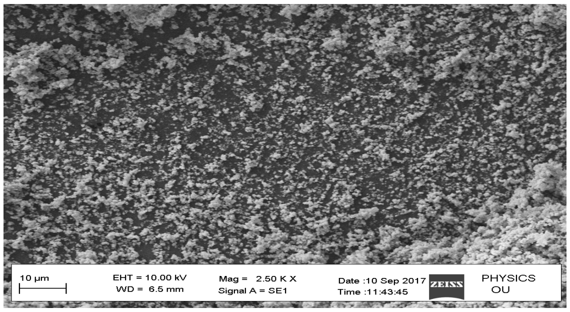


Figure 4.c. FESEM of 20mole % Thiourea-titania nanocomposite

Photocatalytic studies: The photocatalytic activity of the synthesized nanocomposite materials was examined for the visible light degradation of Congo red dye solution. 10 mg of the each composite material was dispersed separately in three 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.5 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 mole % of thiourea in the composites. It was also clear that the irradiation time was reduced from 180 minutes to 60 minutes by 10 mole % thiourea titania nano composite material for the Congo red dye degradation. This may be attributed to the significant change in the band gap (2.89 eV) of the material compared to nanotitania (3.2 eV). On comparison with this material, almost similar degradation was observed with 20 mole % thiourea titania nanocomposite material as its band gap was around 2.85 eV.

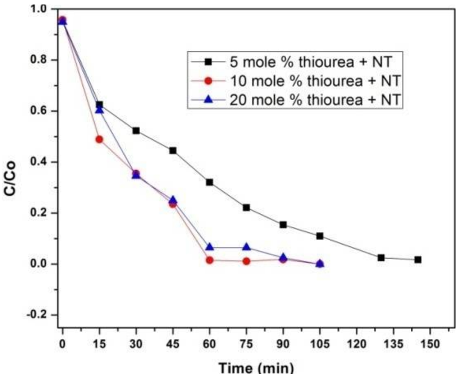


Figure 5. Photocatalytic degradation of Congo red dye in the presence of x mole % thiourea titania nanocomposites under visible light irradiation. [Dye]= 10 ppm, Catalyst load = 10 mg/ 100 mL

Effect of mole % of thiourea on photocatalytic degradation: We have performed the photocatalytic degradation of Congo red dye with x% thiourea titania nanocomposite under visible light. Figure.6 shows the efficiency of mole % of thiourea 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 thiourea content in the composites from 5 % to 20 % and a superior degradation efficiency (100 %) was achieved with 10 mole% thiourea titania composite material. This can be attributed to high capability of nitrogen and sulphur dopants in the lattice sites of titania which can store electrons and shuttles the electrons. The presence of N and S-atoms in the form of thiourea 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 mole % of thiourea in the composite did not show any appreciable change in the degradation efficiency. This may be due to agglomeration of the thiourea particles to form large particles thereby decreasing the specific surface areas of the nano titania composites [18].

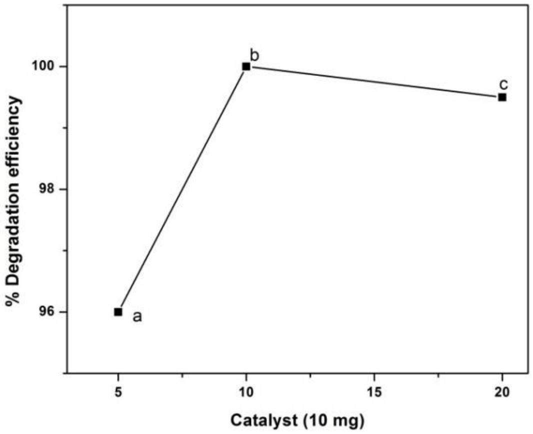


Figure 6. Effect of mole % of thiourea on titania nano composites in % degradation of Congo red dye From the graph, a,b,c= 5,10,20 mole % thiourea titania nanocomposites respectively, Catalyst load= 10 mg 100 mL^{-1}

Effect of pH on degradation of dye solution: The effect of pH of the dye solution in photocatalytic degradation was studied with 10 mole% thiourea titania nanocomposites material by varying the concentrations of HNO_3 and NaOH solution and was shown in table 2. These effects were studied by varying the pH of the dye solution from 5.0-12.0. A steady increase of photocatalytic degradation was observed from pH 5.0-7.0 and reached maximum degradation effect in the pH range of 8.0-9.0. However, the degradation efficiency was slowly decreased from pH 10 and it clearly shows the dye solution has maximum degradation in the pH range of 8.0-9.0.The pH affects the surface properties of

Table 2. Effect of pH on degradation of the dye solution. [Dye]= 10 ppm

pH of the dye solution	**% Degradation of the dye with 10 mg of 10% thiourea-titania nanocomposite material**
5.0	85
6.0	91
7.0	96
8.0	100
9.0	98
10.0	93
11.0	85
12.0	81

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].

Plausible mechanism of photocatalytic degradation: The schematic illustration of the visible light induced photocatalytic degradation of Congo red dye in the presence of thiourea nanotitania composites was shown in figure.7. On visible light irradiation, the electrons (e^-) present in the valence band (VB) of the nanotitania particles get 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 thiourea, these e^-/h^+ pairs combine vigorously and results in a very low photoactivity. On doping with N and S atoms present in thiourea, this e^-/h^+ recombination can be arrested and shifts the electrons for the photocatalytic degradation [23]. 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.

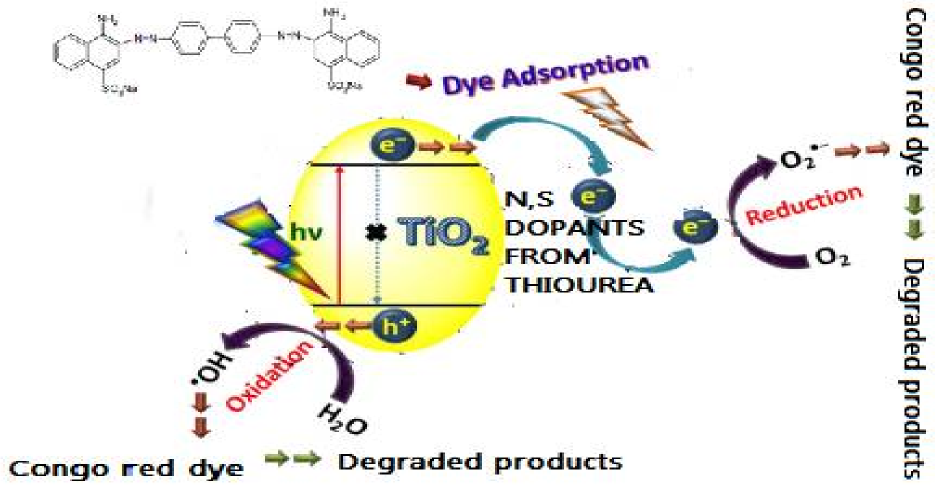


Figure 7. Photocatalytic degradation of Congo red dye in the presence of x mole % thiourea titania nanocompositesunder visible light irradiation

APPLICATIONS

The present study is applicable in the photocatalytic degradation of many other organic dyes like Rhodamine B, Alizarin Red S, Eriochrome black-T etc under visible light irradiation. Further, maximum degradation may be achieved with a low dosage of the x mole % thiourea titania nanocomposites.

CONCLUSIONS

A one step synthesis of organic solvent free controlled hydrolysis of $TiCl_4$ followed by addition of thiourea under magnetic stirring ultrasonication was performed. The as-prepared nano composite materials were characterized by XRD, FESEM, 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 60 minutes, 100 % of the dye solution was degraded with 10 mole% thiourea titania nano composite material for 10 mg dosage of catalyst and 100 ppm dye concentration.

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