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Research Article

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Photocatalytic Behaviour of Copper Doped and Copper-Thiourea Codoped TiO_2 Nanoparticles on Rhodamine B Dye Under Solar Light Irradiation

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ABSTRACT

TiO_2 nanoparticles (TNPs) doped with copper and thiourea was prepared through sol-gel method and characterized using diffuse reflectance UV-vis spectroscopy, FT-IR, XRD and EDX. The photocatalytic activity of the synthesized photocatalysts was tested on the degradation of Rhodamine B (RhB) dye in aqueous medium under solar light radiation. Influence of various operational parameters such as initial concentration, dose of photocatalyst and irradiation time of RhB dye on the photodegradation reaction was investigated to achieve maximum degradation efficiency. The optimum condition for the degradation of the dye has been evaluated. Further, from the results it has been found that doping of TNPs with copper and thiourea plays a vital role for enhancing the removal of RhB dye. A suitable mechanism has been proposed and discussed in order to explain the photocatalytic activity of the synthesized photocatalysts.

Keywords: TNPs; Copper; Thiourea; Photocatalytic activity; RhB dye; Solar light

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INTRODUCTION

Many people around the world don't have accessed to clean drinking water due to water pollution. The water quality is majorly affected by urbanization, growing number of industries and population growth. Dye effluents from textile industries are one of the major pollutants for water pollution. The presence of dyes in natural water bodies is extremely disagreeable and some of which are carcinogenic to human beings [1]. Rhodamine B (RhB) is a synthetic, water soluble, peach-colour and xanthene organic dye. The carcinogenic behavior of RhB dye can irritate the eyes and skin; damage the respiratory, reproductive and nervous system [2,3]. Discharging RhB into aquatic environment makes it a high toxic and low transparent. Moreover, RhB is harmful even at very low concentrations and the later should be removed from wastewater effluent to lessen the effects of environment before discharging [4,5]. The conventional methods like coagulation, filtration and adsorption are ineffective and possess some disadvantages for the complete colour removal and degradation of organics and dyes [6-9]. Titanium dioxide (TiO_2), also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium. Titania exists in three crystallographic forms: rutile, anatase, and brookite. TiO_2, particularly in the anatase form is widely used as the photocatalyst under ultra violet (UV) light. It is used to support the catalytic studies which contain phases of anatase and rutile. For example, Degussa P25 TiO_2 is approximately 85% anatase and 15% rutile [10,11]. TiO_2 has been widely investigated as a heterogeneous photocatalyst for the complete oxidation of toxic contaminants into water and air. The heterogeneous photocatalytic reactions are initiated by absorbing UV photons with concurrent generation of conduction band (CB) electrons and valence band (VB) holes in the TiO_2 lattice. Hydroxyl radicals that are subsequently generated through the reaction of VB holes with water or surface hydroxyl groups mainly account for the strong oxidizing power of the TiO_2 photocatalytic system [12,13]. TiO_2 is an excellent photocatalyst with wider applications in various fields. The main advantages of TiO_2 are its high chemical stability when exposed to acidic and basic compounds, its non-toxicity, low cost and high oxidizing power, which make it a competitive element for photocatalytic applications [14,15]. TiO_2 is used as efficient photocatalysts which have simultaneous potentials of oxidation of organic compounds [16]. In recent years, it was reported that the doping of TiO_2 nanoparticles with transition metal cations is considered to be a good method which enhances through photocatalytic properties and visible light response [17]. The additions of transition metal cations cause the development of a doping energy level between valence band and conduction bands of TiO_2 and translocate the band gap of TiO_2 into the visible region. Further, metal dopant cations can act as a trap for electrons or holes and enhance the photocatalytic activity of TiO_2 under the visible light irradiation [18]. TiO_2 nanoparticles (TNPs) are considered to be an ideal photocatalyst because it is cheap, photostable in solution and nontoxic. The only limitation is that it does not absorb visible light. To overcome this limitation, several approaches including dye sensitization, doping, coupling and capping of TiO_2 have been studied extensively [19-21]. Transition metal ions can provide the additional energy levels within the band gap of a semiconductor [22,23]. Electron transfer from one of these levels to the conduction band requires lower photon energy than in the situation of an unmodified semiconductor. Enhancing the rate of photo reduction by doping a semiconductor with metal ions can produce a photocatalyst with improved trapping to the recombination rate ratio. From a chemical point of view, TiO_2 doping is equivalent to the introduction of defect sites like Ti^{3+} into the semiconductor lattice, where the oxidation of Ti^{3+} species is kinetically fast compared to the oxidation of Ti^{4+} [24]. However the concentration of doping is high and the space-charge region is very narrow, so the penetration depth of light into TiO_2 greatly exceeds the width of space-charge region [25]. Therefore, the rate of recombination of photo generated electron-hole pairs in the semiconductor increases because there is no driving force to separate them. Thus the TiO_2 containing low doping concentrations of metals will enhance the photocatalytic property and high doping reduces the photocatalytic property [26,27]. The aim of this work is to synthesize and characterize undoped TNPs, copper doped (Cu-TNPs) and copper and thiourea codoped TNPs (Cu-TU-TNPs). This study was undertaken to investigate the potential of TNPs as a photocatalyst under solar light radiation for the removal of RhB dye. The effect of three important operational parameters such as effect of initial concentration, effect of dose of the catalyst and effect of irradiation time was explored.

EXPERIMENTAL SECTION

Materials and Methods

Titanium isopropoxide from Sigma Aldrich, Copper chloride dihydrate, Thiourea and absolute ethanol from Merck, Nitric acid, RhB dye from Himedia were purchased. Ultraviolet-visible spectroscopy (UV-Vis) was analyzed using a JASCO V-670 UV-VIS Spectrophotometer. Formation of TiO_2 nanoparticles was checked using Fourier transform infrared spectroscopy (FTIR) in Perkin-Elmer Spectrum-1 instrument with freshly dried KBr pellets in the range of 4000-400 cm^{-1}. Powder X-ray diffraction (XRD) measurements were recorded with D8 advance Bruker AXS diffractometer using CuKα radiation (λ=1.5406 Å). Alumina was used as a standard to eliminate instrument peak broadening. EDX analysis was used for the elemental analysis and determination of chemical compositions of the sample. EDX were examined by FE-SEM (JSM-6700F, JEOL, Japan) equipped with an in-situ EDX spectrophotometer. The photocatalytic degradation of MG dye was studied in the presence of solar light irradiation. 100 ml borosilicate glass beakers were utilised as reaction vessel throughout the photocatalytic degradation experiment.

Synthesis of Photocatalysts

Synthesis of photocatalysts such as undoped TNPs, Cu-TNPs and Cu-TU-TNPs has been well established during the last decade and their synthetic methods were presented clearly in recent literature [28]. Initially, 8.4 mL titanium (IV) isopropoxide (TiP) was dissolved in 10 mL absolute ethanol (Solution A). Solution B, which consists of 10 mL absolute ethanol, 1 mL concentrated HNO_3 and 1 mL of distilled water, was slowly added to solution A, and then, the mixture was continuously stirred for 18 hours to yield a wet-gel. Further, the wet-gel was left aside for 6 hours and then dried at 110ºC for 15 hours in hot air oven. Finally, TiO_2 nanopowder was calcined at 300ºC for 5 hours. Same synthetic procedure was followed in order to synthesize Cu-TNPs and Cu-TU-TNPs by adding 0.097 grams of $CuCl_2.2H_2O$ (which is equal to 1% of TiO_2 mass) and 0.0432 grams of Thiourea (which is equal to 1% of TiO_2 mass) to solution B respectively along with the TiO_2 precursor.

RESULTS AND DISCUSSION

Absorption Spectra

The UV-Vis DRS spectra of undoped TNPs, Cu-TNPs and Cu-TU-TNPs are depicted in Figures 1 and 2. From the DRS spectra, band gap for all the synthesized samples were calculated using kubelka-munk formulae [29]. The band gap is one among an important tool to reveal the photocatalytic behaviour of the samples [30]. From the previous studies, the band gap of TNPs are found to be 2.85 nm and the doping with metals and non-metals will reduce the value of band gap. The reduction of band gap will enhance the photocatalytic activity of the photocatalyst [31].

The band gap is found to be 2.91, 2.89 and 2.85 for undoped TNPs, Cu-TNPs and Cu-TU TNPs respectively. From the band gap values, it has been clearly shown that the doping of metals and thiourea have brought slight changes on their band gap value when compared with undoped TNPs.

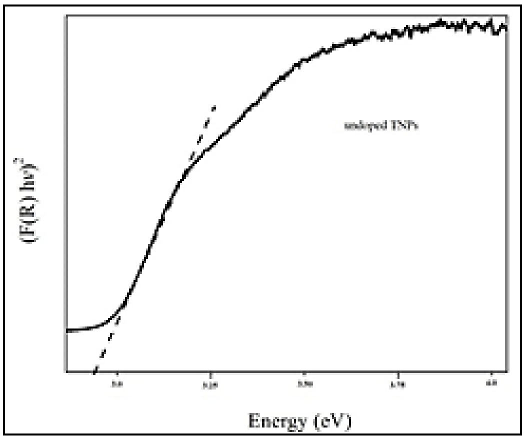

Figure 1: UV-Vis DRS of undoped TNPs (Kubelka-Munk model)

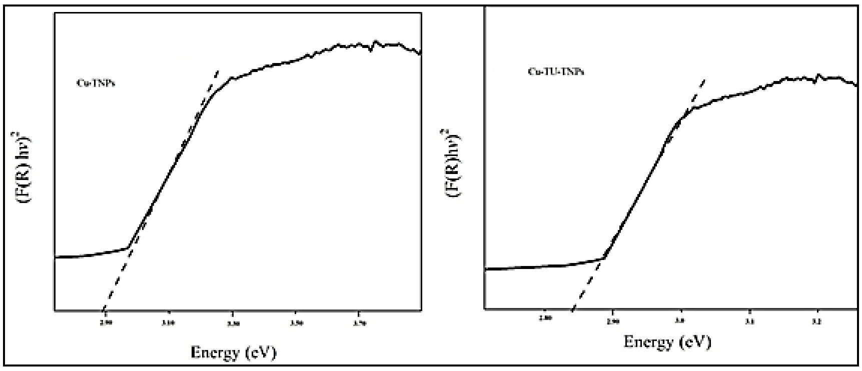

Figure 2: UV-Vis DRS of doped TNPs (Kubelka-Munk model)

FT-IR Spectra

Figure 3 represents the FT-IR spectra of undoped TNPs, Cu-TNPs and Cu-TU-TNPs. The FT-IR spectra of all the samples show peaks near at 3200 cm^{-1} and 1620 cm^{-1}. These two peaks showed the presence of traces of moisture in all the samples. In the FT-IR spectra of undoped TNPs, a broad band at 3248 cm^{-1} and a band at 1620 cm^{-1} were aroused due to moisture. Importantly, the band at 478 cm^{-1} was ascribed to the Ti-O bending mode of TiO_2 which confirmed the formation of TNPs [32,33]. Moreover, the peak was shifted after doping. In the case of Cu-TNPs, the later peak was shifted to 448 cm^{-1}, which might be due to the formation of Cu-O bond [34,35]. In the FT-IR spectra of Cu-TU-TNPs, the peak observed at 1092 cm^{-1} showed the presence of C=S bond [36]. The other peak related to thiourea was not observed. This might be due to the lower percentage of doping.

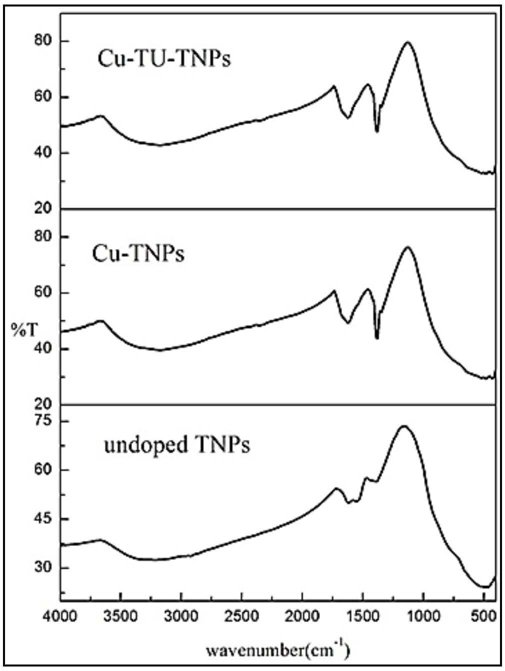

Figure 3: FT-IR spectra for doped and undoped TNPs

XRD Analysis

Figure 4 represents the XRD studies of TiO_2 nanoparticles and the results were well agreed with the previous reports. In the X-ray diffraction pattern of undoped TNPs, a main peak at $2\theta = 25.4°$ attributed to the 1 0 1 planes (JCPDS 21-1272) of anatase phase. There is no observation of peak at 2θ near at 27° indicates the absence of any rutile phase in the synthesised TNPs [37]. $2\theta = 25.3°$ and 25.4° are the major peaks observed for Cu-TNPs and Cu-TU-TNPs respectively. These values clearly indicate that doping of copper did not cause any deviation in the major peaks [38]. The reason for this might be due to the occupation of guest metal ions in the substitutional sites of titanium ions in the host lattice of TNPs. Further in the XRD patterns of Cu-TU-TNPs, thiourea was not observed. This might be due to the lower percentage of doping. The average interplanar distance (d) and the average crystallite size were calculated using Debye-Scherrer equation. The average interplanar distance was found to be 3.53 Å, 3.45 Å and 3.52 Å for undoped TNPs, Cu-TNPs and Cu-TU-TNPs respectively. The average crystallite size was found to be 3.87 nm, 3.15 nm and 4.41 nm for undoped TNPs, Cu-TNPs and Cu-TU-TNPs respectively.

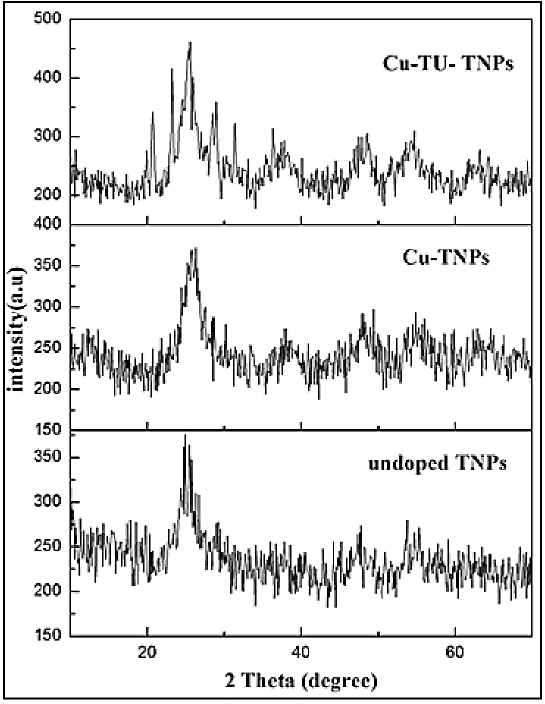

Figure 4: XRD pattern of doped and undoped TNPs

EDX Analysis

Figures 5 and 6 represent the EDX analysis for undoped TNPs and Cu-TNPs, which were used for the elemental analysis and determination of chemicals present in the TNPs. The result clearly shows that the doping of copper in TNPs was proceeded well. Further, the compositional analysis of synthesized Cu-TNPs, the weight percentage ratio of Copper in Cu-TNPs was found to be 1.09.

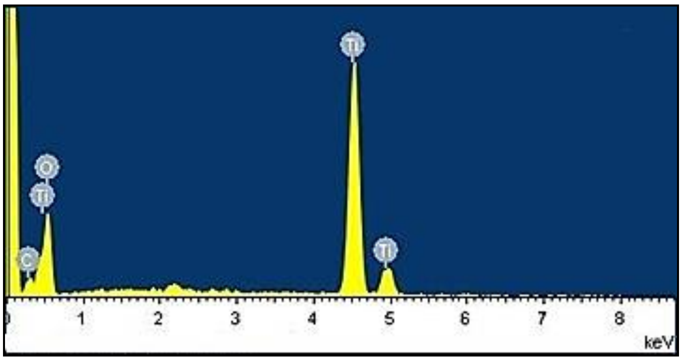

Figure 5: EDX behavior of undoped TNPs

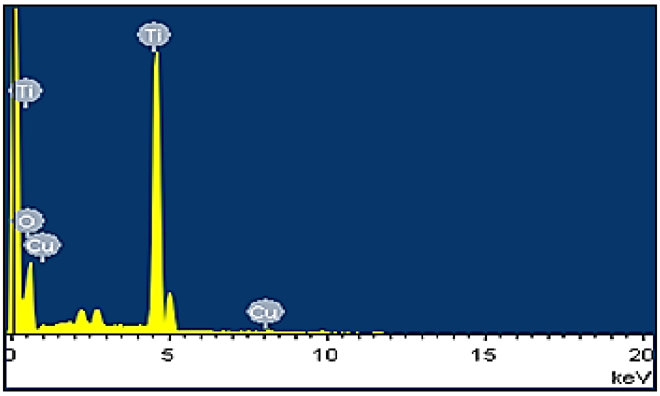

Figure 6: EDX behavior of Cu- TNPs

Effect of Initial Concentration

Photocatalytic degradation of RhB dye was studied at different concentrations ranges from 15 ppm to 75 ppm in the presence of undoped TNPs, Cu-TNPs and Cu-TU TNPs under solar light irradiation. 30 mL of RhB dye solution with different concentrations (15 ppm, 30 ppm, 45 ppm, 60 ppm and 75 ppm) was taken in a 100 mL beaker. About 30 mg of photocatalyst was suspended in each reaction medium. Then the above reaction mixture was continuously stirred for 120 minutes under solar light irradiation. A portion of the mixture was withdrawn before and after irradiation. The mixture was centrifuged immediately and the supernatant was evaluated for the measurement of the residual dye concentration. The absorption maxima for each solution were measured by using UV-Vis spectrophotometer (Table 1).

Through the experiment it was observed that the dye removal was decreased with increase in initial concentration of it. Whenever the concentration of dye solution increases, the photons get interrupted before they can reach the surface of the catalyst and thus decreases the absorption of photons by the photocatalysts. Due to this reason the photocatalytic degradation rate of the dyes with higher concentration gets reduced [39] and more dye molecules were adsorbed on the surface of the photocatalysts by increasing the concentration of dyes, which results the occupation of active sites of the photocatalysts [40-42]. Hence, the photocatalytic degradation rate of dye is linearly related with that of initial concentration of dyes. The optimum concentration of RhB dye is fixed as 45 ppm for further studies (Figure 7).

Table 1: Effect of initial concentration of RhB dye under solar light irradiation

Initial concentration of RhB dye (in ppm)	Percentage removal of RhB dye (%)			Reaction medium conditions
	undoped TNPs	Cu-TNPs	Cu-TU-TNPs	
15	46.92	53.43	63.82	Irradiation time = 120 minutes
30	39.87	45.27	57.91	
45	31.26	34.68	50.96	
60	23.66	28.51	40.73	Catalyst concentration = 30 mg
75	17.53	23.3	34.5	
90	13.28	19.93	26.84	

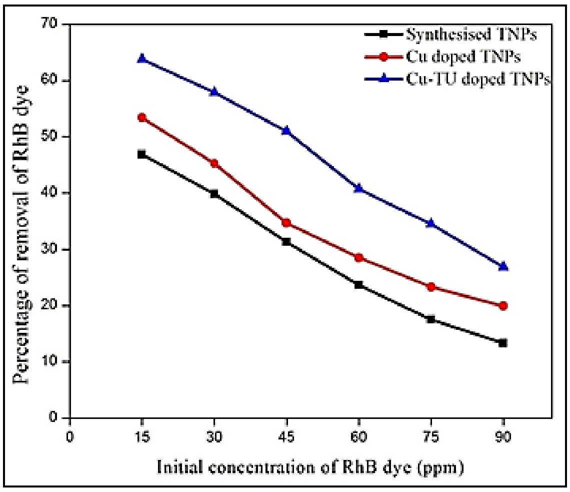

Figure 7: Effect of initial concentration of RhB dye under solar light irradiation

Effect of Dose of the Photocatalyst

In order to reduce the amount of photocatalyst for dye degradation, it is custom to determine the effect of dose of the photocatalyst used for the removal of RhB dye. Hence, the effect of modification on the photocatalyst to improve dye degradation properties were evaluated with different concentrated solutions of undoped TNPs, Cu-TNPs and Cu-TU-TNPs. In each experiment, 30 mL of 45 mg/L RhB dye solution was taken in a 100 mL beaker. Then various amounts

(10 mg, 20 mg, 30 mg, 40 mg, 50 mg and 60 mg) of photocatalysts were suspended in each reaction mixture. Then the reaction mixture was continuously stirred for 120 minutes under solar light irradiation. A portion of the mixture was withdrawn before and after irradiation. The mixture was centrifuged immediately and the supernatant was evaluated for the measurement of the residual dye concentration. The absorption maxima for each solution were measured by using UV-vis spectrophotometer. It was observed that the photocatalytic degradation efficiency of catalyst is increased with an increase in catalysts concentration up to 1.333 g/L, and after that the increase of amount of the catalysts does not affect the photocatalytic degradation remarkably. The reason behind the decrement of rate of photocatalytic activity of photocatalysts can be understood from the fact that the decrease in availability of vital active sites and the penetration of solar light into the suspension formed [43,44]. The addition of higher amount of photocatalyst (>1.333 g/L) to the dye solution increases the turbidity of the suspension and there is a decrement of solar light penetration due to increased scattering effect. Moreover, at high photocatalyst loading, it is very tough to retain the suspension homogenous due to particles agglomeration, which decreases the number of vital active sites [45,46]. The optimum dose of the photocatalyst is fixed as 30 mg (Table 2 and Figure 8).

Table 2: Effect of dose of the photocatalyst concentration on RhB dye under solar light irradiation

Dose of the catalysts (in mg)	Percentage removal of RhB dye (%)			Reaction medium conditions
	Undoped TNPs	Cu-TNPs	Cu-TU-TNPs	
10	11.29	15.97	19.85	Irradiation time = 120 minutes
20	16.74	24.73	30.61	
30	30.44	35.52	51.19	
40	39.88	43.84	57.48	RhB dye concentration = 45 ppm
50	42.91	48.73	61.64	
60	45.58	51.61	64.33	

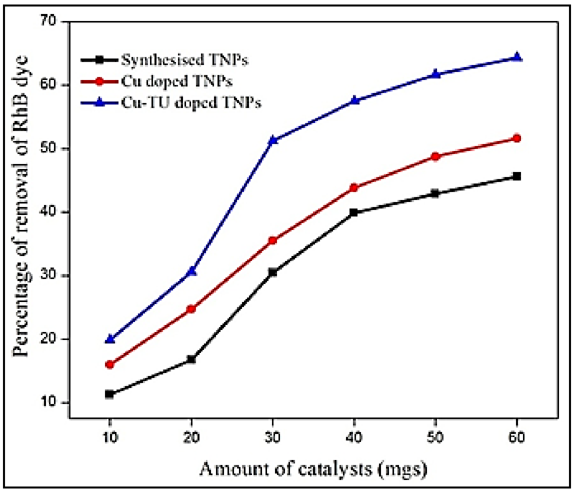

Figure 8: Effect of dose of the photocatalyst concentration on RhB dye under solar light irradiation

Effect of Contact Time

Irradiation time plays a vital role in the decolouration process of the dyes. The irradiation time is varied from 30 minutes to 180 minutes for RhB dye in the presence of undoped TNPs, Cu-TNPs and Cu-TU-TNPs under solar light irradiation. From this experiment it was observed that the dye removal percentage increased with increase of irradiation time. 30 mL of 45 mg/L of RhB dye solution were taken in a 100 mL beaker. About 30 mg of photocatalysts were suspended in each reaction medium. The reaction mixture was continuously stirred for 180 minutes under solar light irradiation. A portion of the mixture was withdrawn before and after irradiation. The mixture was centrifuged immediately and the supernatant was evaluated for the measurement of the residual dye concentration. The absorption maxima for each solution were measured by using UV-vis spectrophotometer. From the previous studies, it was reported that the photodegradation rate is increased with increase of irradiation time [47,48]. This is due to at low light intensity reactions, electron-hole formation which are pivotal and electron-hole recombination is insignificant and considerably negligible [49,50]. Although, when light intensity increases the electron-hole pair separation emulates with recombination and results lower effect on the rate of the reaction [51-53]. The optimum time for RhB dye is fixed as 120 min for further studies (Table 3 and Figure 9).

Table 3: Effect of contact time on RhB dye under solar light irradiation

Irradiation time(in min)	Percentage removal of RhB dye (%)			Reaction medium conditions
	undoped TNPs	Cu-TNPs	Cu-TU-TNPs	
30	8.49	13.31	15.06	Catalyst concentration = 30 mg
60	12.09	18.64	23.09	
90	19.62	23.59	36.37	
120	30.44	35.52	51.19	RhB dye concentration = 45 ppm
150	38.65	43.76	58.59	
180	45.71	50.18	63.66	

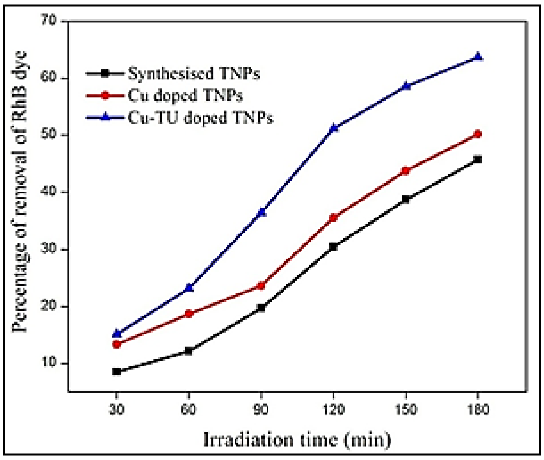

Figure 9: Effect of contact time on RhB dye under solar light irradiation

Mechanism of Photocatalytic Degradation of RhB Dye

On the basis of the previous studies [54-57], a speculative mechanism for photocatalytic degradation of RhB dye may be proposed as follows.

$$\mathrm{RhB} + h\nu \dashrightarrow \mathrm{RhB}^1 \qquad \text{------ (1)}$$

$$\mathrm{RhB}^1 \xrightarrow{\text{ISC}} \mathrm{RhB}^3 \qquad \text{------ (2)}$$

$$\mathrm{M} + h\nu \dashrightarrow e^- (\mathrm{CB}) + h^+ (\mathrm{VB}) \qquad \text{------ (3)}$$

$$e^- + O_2 \dashrightarrow O_2^{\bullet -} \qquad \text{------ (4)}$$

$$O_2^{\bullet -} + \mathrm{RhB}^3 \dashrightarrow \text{Degraded products} \qquad \text{------ (5)}$$

Under solar light irradiation, RhB dye molecule absorbs radiation and jumps first to singlet state (1) and then through inter system crossing (ISC) to triplet state (2) which transfers an electron from its HOMO to the conduction band. Meanwhile, the undoped TNPs and metal doped TNPs (M) absorb the incident light energy which excites the electron of them from HOMO level to conduction band (3). The electrons present at the conduction band of both dye and TNPs and the surface adsorbed oxygen are responsible for the photocatalytic degradation of RhB dye (4,5) and results harmless degraded product.

CONCLUSION

In this study, undoped TNPs, Cu-TNPs and Cu-TU-TNPs were successfully synthesized by sol-gel method and characterized by UV-vis, FT-IR, XRD and EDX. From the photocatalytic degradation studies, photocatalyst efficiency was found to decrease with increase of RhB dye concentration, at the same time, increase with increase in dose of photocatalyst and increase with solar light intensity. Above all, the prepared Cu-TU-TNPs can act as a promising photocatalyst for the removal of RhB dye, and also it was confirmed that doping with metal and non-metal at low level (lower percentage of doping) would enhance the photocatalytic behaviour.

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