Cu(II) Doped TiO$_2$ for Photodegradation of Remazol Black B in Aqueous Solution

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Abstract

In the present investigation, Cu(II) doped TiO$_2$ was prepared by a precipitation method. The precipitate was calcined at 300 ºC for 2 hours. The prepared doped catalyst was characterized by scanning electron microscope (SEM), energy dispersive X-ray (EDX) spectroscopy and X-ray diffractometry (XRD). SEM images revealed that the morphology of the doped catalyst was different from that of TiO$_2$. Elemental analysis was accomplished by EDX that indicated the presence of Cu, Ti and O atoms in the prepared sample. XRD analysis confirmed that TiO$_2$ was present as anatase with almost no distortion in peak position due to the presence of Cu(II) in some interstitial sites. Photodegradation of remazol black B (RBB) was carried out at different experimental conditions under different light sources. The catalytic efficiency of Cu(II) doped TiO$_2$ increased up to a certain dosage then reduced with a further increase in the amount of photocatalyst. The optimum conditions for degradation was found at pH 3.0 under UV light. Under these experimental conditions, Cu(II) doped TiO$_2$ degraded 98.8% of RBB, on the other hand, undoped TiO$_2$ degraded only 80.0% of RBB.

I. Introduction

Recently water pollution has become one of the massive problems worldwide. One of the prime causes of water pollution is the discharge of unused azo dyes into industrial effluents from several industries such as paper, textile, plastics, cosmetics, food, etc[1]. The textile industry is the most potential source of industrial waste that contains mainly azo dyes with -N=N-, –C=C–, –C≡N– groups as chromophore and other groups like –NH$_2$, –OH, –COOH, –SO$_3$H as auxo-chrome. Synthetic azo dyes are toxic, carcinogenic, and unhygienic for the ecosystem. These dyes are not biodegradable under aerobic conditions which can create dissolve oxygen deficiency and inhibit photosynthetic activity by disallowing sunlight penetration through water[2,3]. They have an adverse and serious impact on human health[4]. Therefore, prior treatments are needed to discharge into the aquatic environment. There are different treatment methods which are physical, chemical, and biological methods[5]. Physical and biological methods can only exchange pollutants between two phases without destroying these completely[6,7]. On the other hand, chemical methods can destroy completely the azo dye by breaking of nitrogen double bond to harmless fragments. The advanced oxidation processes (AOPs) are mostly used method for destruction of organic pollutants from water. Strong oxidizing species hydroxyl radicals (˙OH) in AOPs attack dye to convert low molecular weight biodegradable nontoxic, nonharmful components[6,8,9]. Among different AOPs, semiconducting oxide mediated photodegradation is better than other methods because these oxides are cheaper and can be reused several times. TiO$_2$, ZnO, WO$_3$, and other photocatalysts were used for several decades for wastewater treatment. Photoexcited electron of TiO$_2$ under UV light irradiation produces stable, highly efficient, strong oxidative hydroxyl radicals (˙OH) which makes it better than all other photocatalysts[10-12]. The large band gap of TiO$_2$ (~3.2 eV) limits its applicability as photocatalyst[13]. It is, therefore, needed to create an energy level or more energy levels between the valence band and conduction band for the tuning band gap by incorporating transition metal or metal oxide[14,15]. Photogenerated electron-hole pair recombination is another limitation for the photocatalytic activity of TiO$_2$[13,16]. To reduce recombination and ameliorated photocatalytic efficiency of catalyst it must be needed to trap charge on catalyst surface[17]. Several techniques have been reported to modify TiO$_2$ such as doping with elements, deposition with noble metals, dye sensitization, and coupled semiconductor[18-21]. For the creation of energy level between valance band and conduction band, promotion of charge transfer and separation of photogenerated charge, doping is promising technique because dopant can trap charge on the conduction band of catalyst surface and slow down electron hole pair recombination rate[22,23]. Cu (II) is the best than other dopant metal ions due to its availability in the earth's crust and is an economically cheap material[24]. Cu(II) can easily incorporate in the interstitial site of TiO$_2$ because of its lower ionic radius than Ag, Au, Pt ions[25]. It can easily alter the properties of the host particle, electronic structure, and light absorption properties which makes it more effective than an undoped catalyst[26]. The goal of this research is to prepare Cu(II) doped TiO$_2$ photocatalyst by a precipitation method. These materials are then characterized by SEM, EDX and XRD. The catalytic efficiency of the catalyst is investigated by degradation of aqueous solution of remazol black B (RBB, Fig.1) under different light sources.

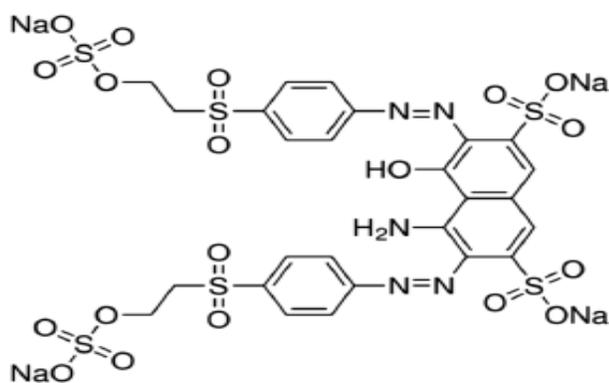_____

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Fig. 1 Structure of RBB.

II. Experimental

Preparation of Cu(II) doped TiO$_2$ composite

Cu(II) doped TiO$_2$ photocatalyst was prepared by the precipitation method[27]. For preparation of 5 wt% Cu(II) doped catalyst, copper nitrate trihydrate and glycerol were added by 1:2 mole ratio in 100 mL deionized water where Cu(II)–glycerol complex was formed. Copper–glycerol complex was precipitated on TiO$_2$ surface at pH 12.0 that was attained by adding 0.5 M NaOH solution with constant stirring. After stirring for an hour, a light blue precipitate (presumably Cu(OH)$_2$/TiO$_2$) was formed and centrifuged to remove from the supernatant solution. The precipitate was washed several times using deionized water to remove the impurities. The separated precipitate was dried in on oven at 78 °C for 5 hours. Finally, Cu(OH)$_2$/TiO$_2$ powder was calcined at 300°C for 2 hours and stored for further use.

Characterization of TiO$_2$ and Cu(II) doped TiO$_2$ composite

TiO$_2$ and copper (II) doped TiO$_2$ composite samples were characterized by SEM, EDX and XRD. SEM (JSM-6490LA, JEOL) was used for the characterization of surface morphology of catalyst. EDX attached with SEM is an analytical technique used for determination of elemental composition of a sample. The purity of composite was also determined by using this instrument. XRD data was recorded (Philip PW-1380 X-ray generator operating at 40 kV-30 mA) to investigate phase structure of the catalysts.

Photodegradation efficiency

Photodegradation efficiency of Cu(II) doped and undoped TiO$_2$ was studied by performing the experiments under irradiation of UV light, artificial visible light and sunlight. The change of concentration of the dye was monitored at wavelength λ_{max} = 597.5 nm under different experimental conditions like different catalyst dosage, different dye concentration, different pH, light sources. A typical experiment was carried out as follows. The catalyst with dye solution was placed on a magnetic stirrer and was exposed to light source. The

suspension was taken at different time intervals and then the catalyst was separated by centrifugation. Absorbance was measured using a UV-visible spectrophotometer and percent degradation was calculated by the equation:

$$\% \text{ Degradation} = \frac{A-B}{A} \times 100\%$$

where A is the absorbance of RBB solution at the λ_{max} at zero time and B is that of RBB solution at any time.

III. Results and Discussion

Characterization of prepared Cu(II) doped TiO$_2$ by SEM

Fig. 2 represents the SEM images of TiO$_2$ and Cu(II) doped TiO$_2$ at the same magnification. The morphology of these two catalysts is slightly different. The particles of TiO$_2$ are spherical and aggregated whereas those of Cu(II) doped TiO$_2$ are fibrous and irregular. The particle size of Cu(II) doped TiO$_2$ seems to be smaller than that of pure TiO$_2$. This indicates that the surface area of the doped catalyst is higher than that of undoped catalyst. The decrease of the particle size may be caused due to the hindering of particle growth by introduction of Cu atoms into the TiO$_2$ crystal structure.
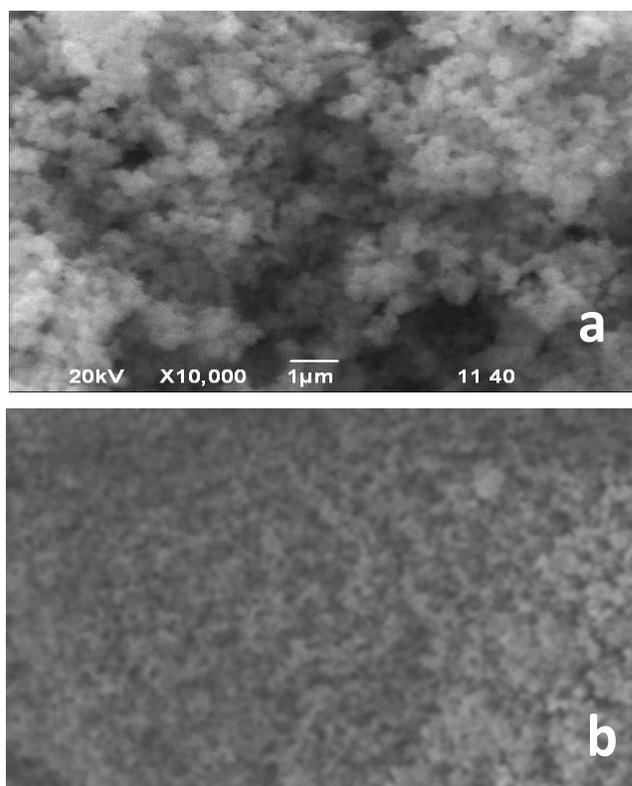

Fig. 2. SEM images of TiO$_2$ (a) and Cu(II) doped TiO$_2$ composite (b).

Characterization of prepared Cu(II) doped TiO$_2$ by EDX

The EDX analysis shows the elemental composition of the doped composite (Fig. 3).
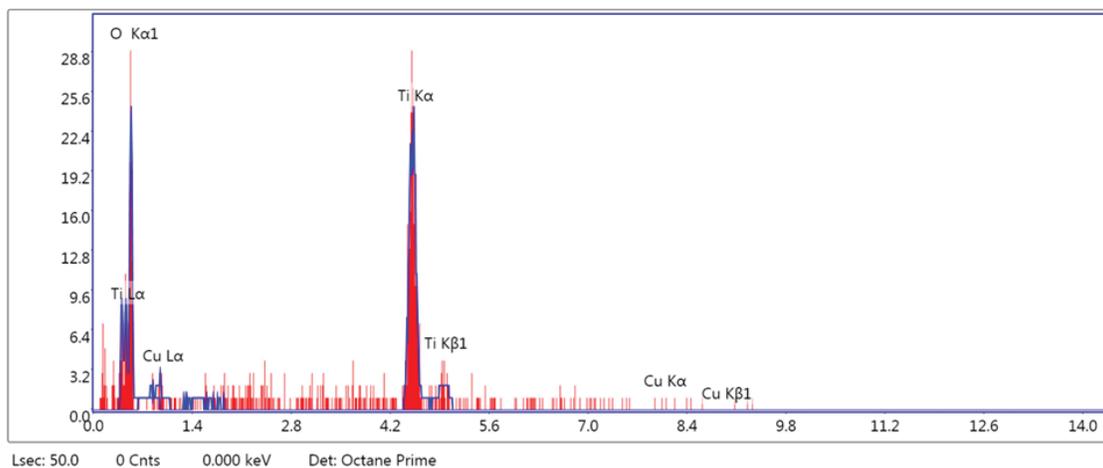
Fig. 3. EDX spectra of Cu(II) doped TiO$_2$ composite.

The spectrum represents the peaks that correspond to Ti, Cu and oxygen atoms. The results represent that the average weight percentage of Cu = 1.18, O = 23.38 and Ti = 75.44 and atomic percentage of Cu = 0.61, O = 47.83 and Ti = 51.56. These results indicate that an interaction between Cu and TiO$_2$ has been taken place at the molecular level. This doped composite catalyst is a chemical mixture of Cu and TiO$_2$.

Characterization of prepared Cu doped TiO$_2$ by XRD

The XRD spectra of TiO$_2$ and Cu(II) doped TiO$_2$ are presented in Fig. 4. The peaks were observed at 2θ = 25.34˚, 36.94˚, 37.80˚, 38.62˚, 48.05˚, 53.92˚, 55.09˚, 62.72˚ and 68.85˚, which correspond to (101), (103), (004), (112) and (200), (105), (211), (204) and (116) planes of anatase phase respectively. The obtained results closely matched with anatase (JCPDS card no. 78-2486)[27,29]. The intensity of peaks of copper (II) doped TiO$_2$ is higher than that of pure TiO$_2$. EDX analysis showed the presence of Cu but no extra peak was observed which indicates that dopant ions may occupy the interstitial sites of Ti^{4+} without distortion of the host lattice[16]. Moreover, it should be noted that the Cu(II) doped sample exhibits a typical structure of TiO$_2$ crystal without any detectable peak of the dopant. This result may be due to the fact that the copper might be introduced into the interstitial positions of the TiO$_2$ crystal structure[21].
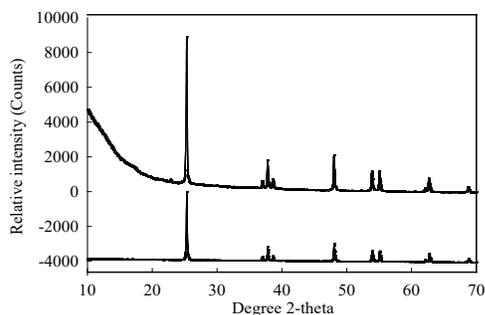
Effect of the doped catalyst dose on photodegradation of RBB

The effect of catalyst dosage on the photodegradation of RBB has been investigated by varying the amount of prepared catalyst from 0.1 g to 0.6 g/100.0 mL in 5.0×10^{-5} M aqueous solution. The percentage of photodegradation of RBB increases with the increase in the amount of the composite photocatalyst loading up to a maximum value and then decreases with a further increase in the catalyst loading (Fig. 5). The degradation of RBB increases from 64.0% to 96.5% with increasing the catalyst loading from 0.10 g to 0.50 g. A further increment in the catalyst loading causes a decrease in the degradation of 90.4% at a catalyst loading of 0.60 g. The reason behind this is that the increase in the catalyst loading leads to enhanced number of active sites on the catalyst surface. As a result, more photons can be absorbed on the active site, producing more electron-hole pairs which lead to more production of OH˙ radical in the illumination area[30-32]. At the latter stage, the photodegradation decreases because of the reaction medium becomes opaque which reduces the light photons entering into the reaction vessel[30].
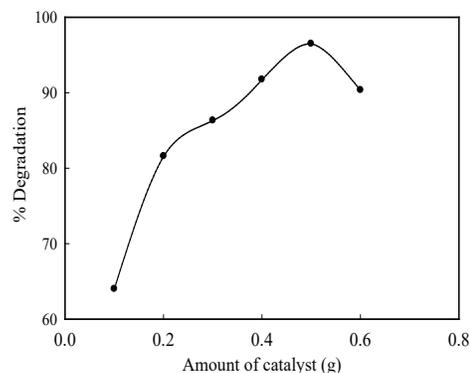

Fig. 5. Effect of amounts of Cu(II) doped TiO$_2$ catalyst on degradation of RBB, [RBB]$_0$ = 5.0×10^{-5} M.

Fig. 4. Comparison of XRD pattern of Cu(II) doped TiO$_2$ composite (top) and TiO$_2$(bottom).

Effect of concentrations of RBB on photodegradation

The effect of different initial concentrations of RBB on the photodegradation has been investigated by variation of the initial dye concentrations from 3.0×10^{-5} M to 7.0×10^{-5} M with a fixed amount of catalyst 0.2 g in 100 mL solution (Fig. 6). The results indicate that the percent of photodegradation increases with a decrease in the initial dye concentration. The maximum degradation is found at a dye concentration of 3.0×10^{-5} M. More concentrated dye solution reduces the penetration of the light to the catalyst surface which reduces the production of electron-hole pairs and the rate of formation of hydroxyl radicals and super oxide ions (O^{2-}). These lead to a decrease in the percentage of the degradation[30,33]. As the catalyst surface area is fixed, a fixed number of dye molecules can be adsorbed on the catalyst surface although the initial concentration of dye is higher. The unadsorbed dye molecules could not be degraded due to a smaller number of reactive oxidant species present[34]. So, the degradation decreases at higher dye concentration.
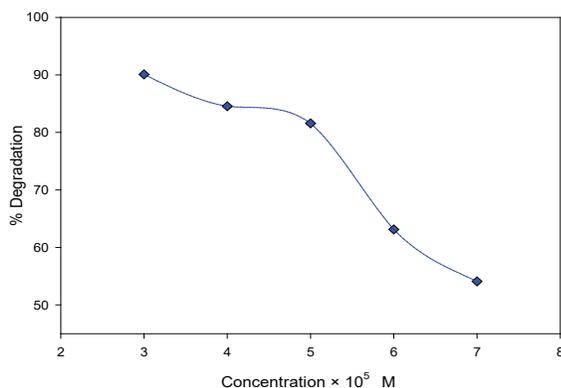

Fig. 6. Effect of concentrations of RBB on photodegradation using the composite, amount of doped catalyst = 0.20 g.

Effect of initial pH of the suspension medium on photodegradation of RBB

The effect of pH on degradation efficiency was carried out at pH 2.0 to pH 8.0 under 70 minute irradiation using 0.20 g composite and 3.0×10^{-5} M dye solution (Fig. 7). It has been observed that maximum degradation of 98.8% is found at pH 3.0. Above and below this pH, the percent degradation decreases. The degradation efficiency depends on the pHzpc of the photocatalyst which is 6.5 for Cu(II) doped TiO$_2$. The pH below this pHzpc, catalyst surface is positively charged.[35] As RBB is an anionic dye, it strongly interacts with positively charged particles and is strongly absorbed on the catalyst surface. Hence, the degradation efficiency is the highest at pH 3.0. At lower pH, the degradation efficiency decreases due to coagulation of the TiO$_2$ particles[34]. In the pH range between 3.0 to 6.5, the degradation decreases slowly. However, at a pH above 8.0, the photodegradation decreases sharply to a value of 46.8% at pH 8.0. This is due to the repulsion of negatively charged surface of the catalyst with the negative anionic dye.
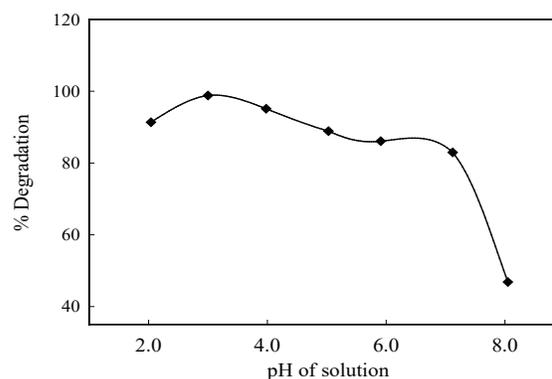

Fig.7. Effect of initial pH of suspension medium on photodegradation of RBB under 70 minutes of irradiation, amount of doped catalyst = 0.20 g, [RBB]$_0$ = 3.0×10^{-5} M.

Effect of different light sources on photodegradation of RBB

The light source has an impact on the photodegradation of dye. The UV light is the most effective light source giving about 98.8 % degradation by 70 minute irradiation (Fig. 8). On the other hand, the artificial visible light is the least effective producing only 54.8% degradation under the same conditions. The sun light shows effectiveness in between the two sources. It can be explained by the fact that UV light has the highest energy photons among the three sources because UV light has the shorter wavelength photons than visible light. Highly energized photons of UV light can strike on the catalyst surface producing a higher number of electron-hole pairs which leads to a higher percent of degradation. On the other hand, photons of visible have lower energy and produce a fewer number of electron and hole pairs than UV light. The sunlight contains mainly visible light photons of higher intensity causing more degradation than the artificial visible light.
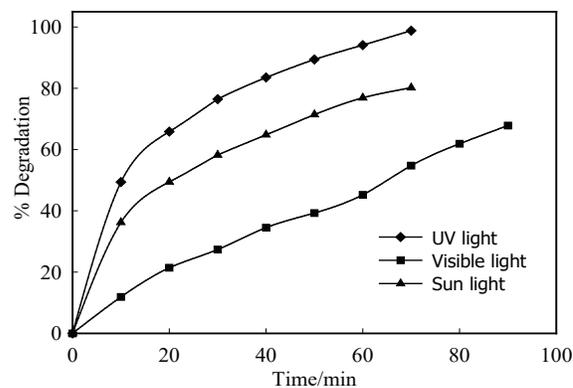

Fig. 8. Degradation of RBB using the composite for different light sources, amount of Cu doped TiO$_2$ catalyst = 0.20 g, [RBB]$_0$ = 3.0×10^{-5} M, pH=3.0.

Effect of intensity of light on photodegradation

The effect of intensity of UV light was studied at optimum experimental conditions of 0.2 g catalyst, 3.0×10^{-5} M RBB at pH 3.0. A total number of ten tube lights were used in the experimental setup when the intensity was the highest (3.31×10^{-9} Ein cm^{-3}s^{-1}).
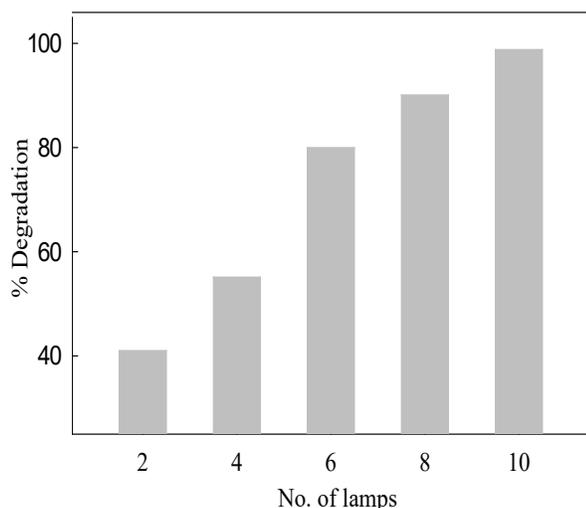

Fig. 9. Effect of different intensities of UV light on photodegradation of RBB under 70 minutes of irradiation, amount of doped catalyst = 0.20 g, [RBB]$_0$ = 3.0×10^{-5} M, pH=3.0.

The intensity was decreased by putting off two tube lights each time. Fig. 9 shows that the percent degradation of the dye decreases with a decrease in the light intensity. This result is in agreement with the previous results (Fig. 8) that the percent degradation decreases due to the lower production electron-hole pairs.

Comparison between doped and undoped photocatalysts

Cu(II) doped TiO$_2$ shows higher degradation efficiency than undoped TiO$_2$ (Fig. 10). Copper has a positive effect on TiO$_2$ that reduces the recombination of photogenerated electron-hole pairs. This, in turn, enhances the degradation efficiency[36]. The conduction band energy difference between TiO$_2$ and Cu(II) suggested that electron transfer was feasible from TiO$_2$ to Cu(II). This could provide enough driving force for charge separation. That's why more OH$^.$ radicals and O^{2-} ions are produced which acts as a strong oxidizing agent for dye degradation and the degradation efficiency is increased. On the other hand, undoped TiO$_2$ can't inhibit the recombination of electron and hole. They produce a lower amount of OH$^.$ radicals and O^{2-} ions.
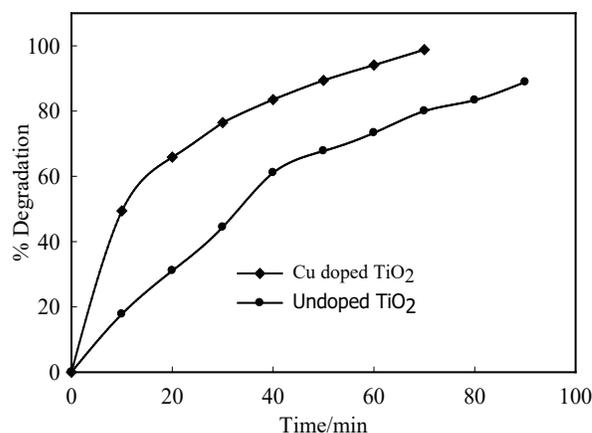

Fig. 10. Degradation of RBB using Cu(II) doped TiO$_2$ and TiO$_2$, amount of catalyst amount = 0.20 g, [RBB]$_0$ = 3.0×10^{-5} M, pH=3.0.

IV. Conclusion

The industrial effluents containing textile dyes can be removed using this photodegradation technique that is one of the most prominent methods of advanced oxidation processes (AOPs). The maximum degradation of the dye has been found at 3.0×10^{-5} M RBB solution with 0.20 g catalyst at pH 3.0. UV light was more efficient for degradation than the sunlight due to its higher energized photons. Increasing the intensity of UV light enhances the degradation of RBB in aqueous solution. Photodegradation study shows that Cu(II) doped TiO$_2$ is more efficient in degradation than pure TiO$_2$. The incorporation of Cu(II) in TiO$_2$ enhances the degradation efficiency by retarding the electron-hole pair recombination. It can be concluded that doping semiconductor metal oxides with other metals like copper can improve the photocatalytic efficiency of the photocatalyst to a considerable extent.

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