

RESEARCH ARTICLE

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Photocatalytic effect of TiO_2 and the effect of dopants on degradation of brilliant green

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Abstract

Photocatalysis speeds up the photoreaction in the presence of a catalyst. TiO_2 has low toxicity, less resistance and less corrosion and has semiconductor properties. Its strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. Moreover, TiO_2 has been proven to be a tremendous photocatalyst compound by which many organic substrates have been shown to be oxidatively degraded under UV irradiation. In this research the photocatalytic effect of TiO_2 on degradation of Brilliant Green (BG) was studied. In conjunction the effect of dopants such as Zn and Cu on photocatalysis of TiO_2 were also studied. Structural and morphological properties of TiO_2 were characterized by SEM and XRD. From this research the initial concentration of sample, pH of samples, chemical structure of dyes and catalyst loading were most valuable parameters for dye degradation. TiO_2 showed excellent result on degradation of BG compared with doped TiO_2 . 99% degradation was obtained in presence of TiO_2 , followed by TiO_2/Zn for 87% and TiO_2/Cu for 46%. TiO_2 doped with transition metals can increase or decrease photocatalytic degradation of dyes.

Keywords: Dopant, TiO_2 , UV irradiation, Brilliant green, Photocatalysis

Introduction

Environmental pollutant is the major cause for most of health illness. Water is the main source of contamination and pollution which effects health through biomagnification. Water gets polluted by harmful chemicals, dyes, oils etc. All the wastewater that contains harmful chemicals is drained into nearby water bodies. This causes water pollution and will lead to various health problems to flora and fauna. Among the pollutants of water, dyes play a major role. Most of the dyes released from the pharma and textile industries are mutagenic, toxic and teratogenic that can cause serious health hazards to humans and live stock [1]. Dyes released into environment can impart color to water and also decrease or stop capacity of water reoxygenation by blocking sunlight thereby increasing BOD value. Therefore these conditions can prevent or disturb the growth of aquatic plants and animals [2,3]. The color removal from wastewater from industries is the main concern in green chemistry [4]. Removal of dyes from wastewater

has become a tough issue due to their stable character under harsh condition and biodegradation resistance [5]. There have been reports on usage of natural materials like coconut husk, sunflower stalks, barley husk, lemon peels, rice husk to remove dyes [6]. Advanced oxidation process (AOP) of photocatalysis is really efficient in industrial effluent treatment process with more success rates. Many studies reported that TiO_2 nanoparticles are an excellent photocatalysts for decolorization of dyes. TiO_2 microparticles are less toxic, less resistance and less corrosive than other photocatalysts [7,8]. TiO_2 oxidation is also known as a type of "green" or environmental friendly method [9]. TiO_2 nanoparticles are used extensively because of its intensity and very high refractive index. We used dopants such as Zn and Cu to observe the efficiency of TiO_2 microparticles on dye degradation. Doping techniques are used to incorporate metal ions to enhance photocatalytic effects of TiO_2 nanoparticles. Metal ions such as Cobalt, Iron, Nickel, Tungsten, Zinc can be incorporated during preparation [10,11].

BG is also known as Ethanaminium,N-[4-[[4(diethylamino)phenyl] phenylmethylene] -2,5-cyclohexadien-1-ylidene]-N-ethyl-,sulfate. The chemical formula is $\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_4\text{S}$

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and molecular weight is 482.64 g/mol. BG is chiefly used in modern textile industries. They are also used in staining and biological applications such as large intestine staining, skin staining, to color fibers, printed circuit boards, inks and also used in antiseptic preparation which is active against Gram-positive bacteria. BG will cause some degree of hypersensitivity reactions, carcinogenicity, microbial and fish toxicity [12]. TiO_2 nanoparticles has been proven

to be a tremendous photocatalyst by which many organic substrates have been shown to be oxidatively degraded and undergoes complete mineralization to give much safer byproduct Carbon dioxide (CO_2) under UV exposure [13]. Typically TiO_2 nanoparticles are used and studied in the treatment of water such as textile waste water, ground water etc [14]. Numerous studies have been conducted on performance of TiO_2 nanoparticles, as

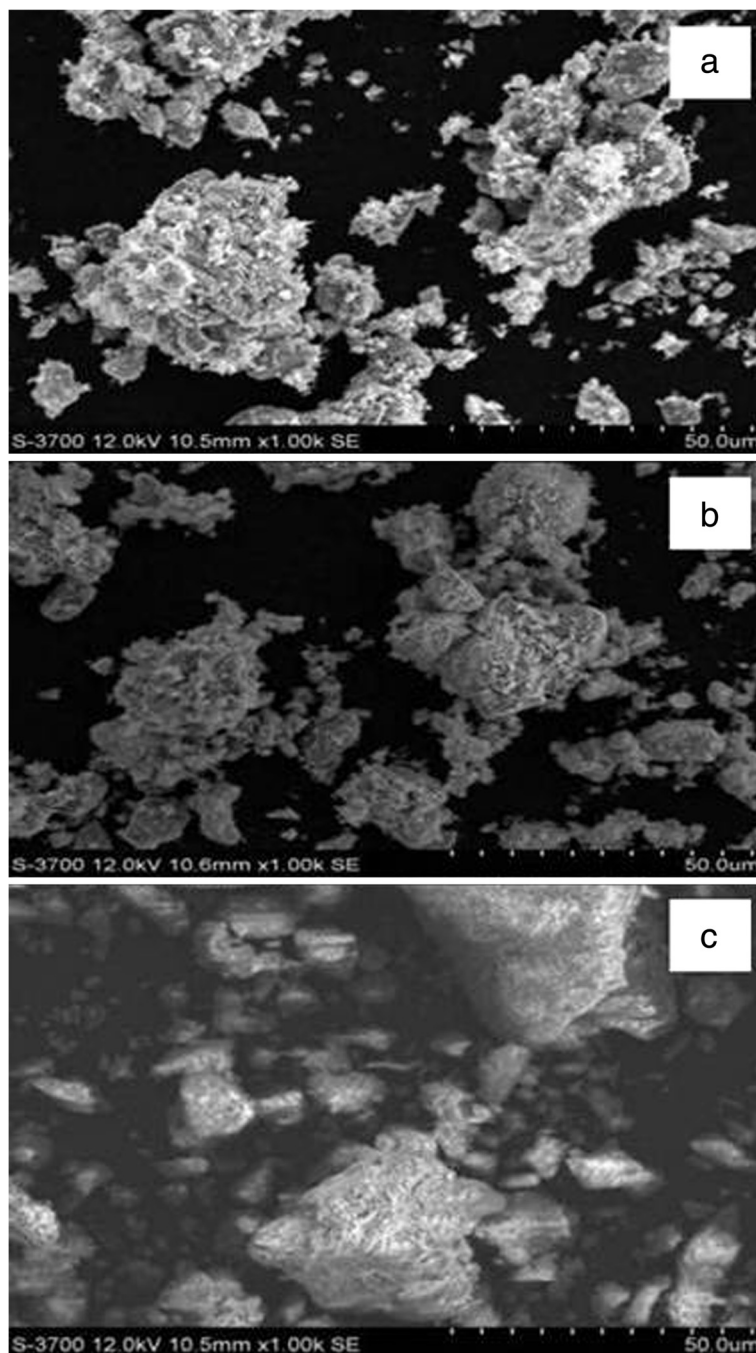


Figure 1 SEM images of (a) TiO_2 , (b) TiO_2/Zn and (c) TiO_2/Cu annealed at 400°C for 3 hours.

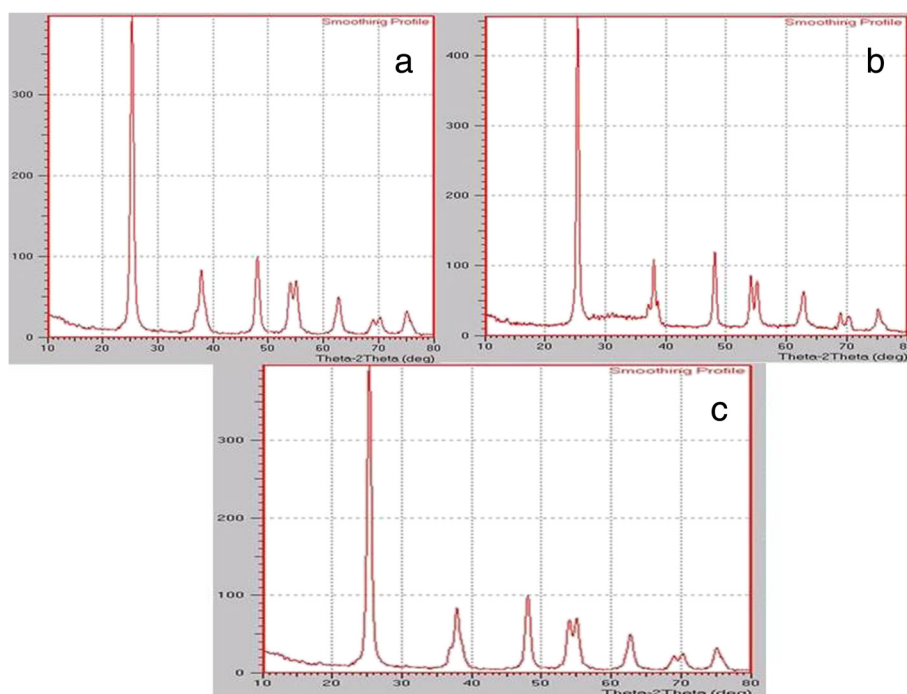


Figure 2 XRD patterns of (a) TiO_2 , (b) TiO_2/Zn and (c) TiO_2/Cu annealed at 400°C for 3 hours.

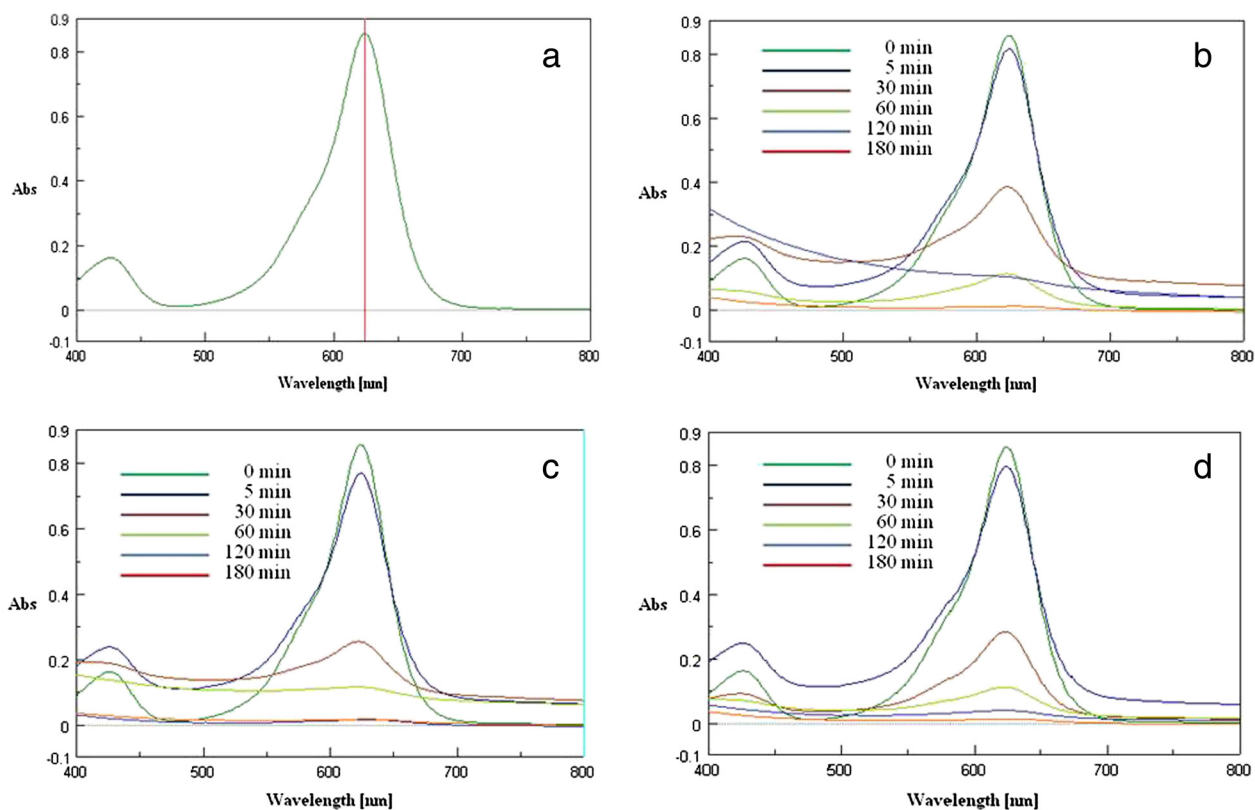
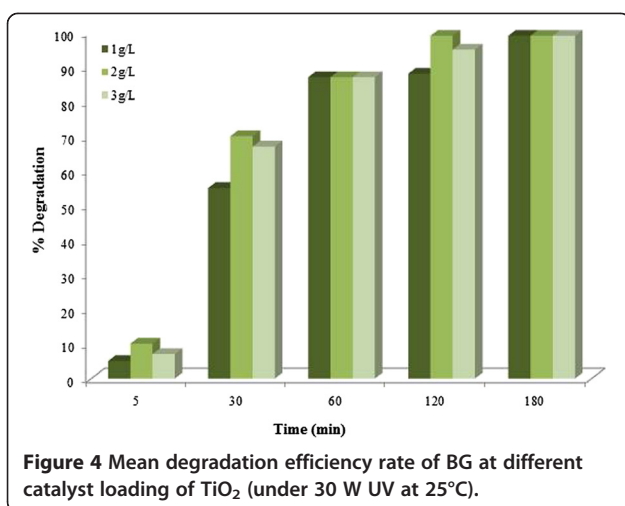


Figure 3 (a) Absorbance of brilliant Green 4 ppm (b) Absorbance of BG with catalyst loading of 1 g/L TiO_2 (c) 2 g/L TiO_2 (d) 3 g/L TiO_2 (under 30 W UV at 25°C).



they showed that relatively high surface area of catalyst per unit of reactor volume [15]. In aqueous environment, TiO₂ generates hydroxyl radicals, which endorse the oxidation of organics under UV irradiation [16]. This has been successfully engaged in the mineralization of several hazardous chemicals such as dyes, phenols, haloaromatics, halogenated biphenyls and more. In this research for the first time TiO₂ microparticles alone and TiO₂ along with dopants

such as Zn and Cu microparticles are used to check the photocatalytic activity for degradation of BG under UV radiation. This photocatalytic reaction takes place at room temperature and the intermediate products are less non-toxic because they are completely mineralized to CO₂. Morphological and structural properties are evaluated using SEM and XRD respectively.

Materials and methods

Preparation of Titanium dioxide microparticles

15 ml of titanium isopropoxide was transferred into 250 ml beaker and added with 30 ml of distilled water (DW). The contents were stirred for 20 minutes till the contents were clear. 2.2 g of CTAB was transferred into a 100 ml clean beaker and 20 ml of DW was added to it and the contents were stirred for 5 minutes till the solution was clear. The dissolved CTAB was added to the beaker containing titanium isopropoxide. Then, required quantity of NH₄OH was transferred dropwise by means of burette into the beaker containing titanium isopropoxide and CTAB. The contents were continuously stirred with the help of magnetic stirrer for 2 hours after addition of NH₄OH. After 2 hours, the contents were filtered using Wattman filter paper and precipitate was washed with DW for 10 to 15 times. After sufficient

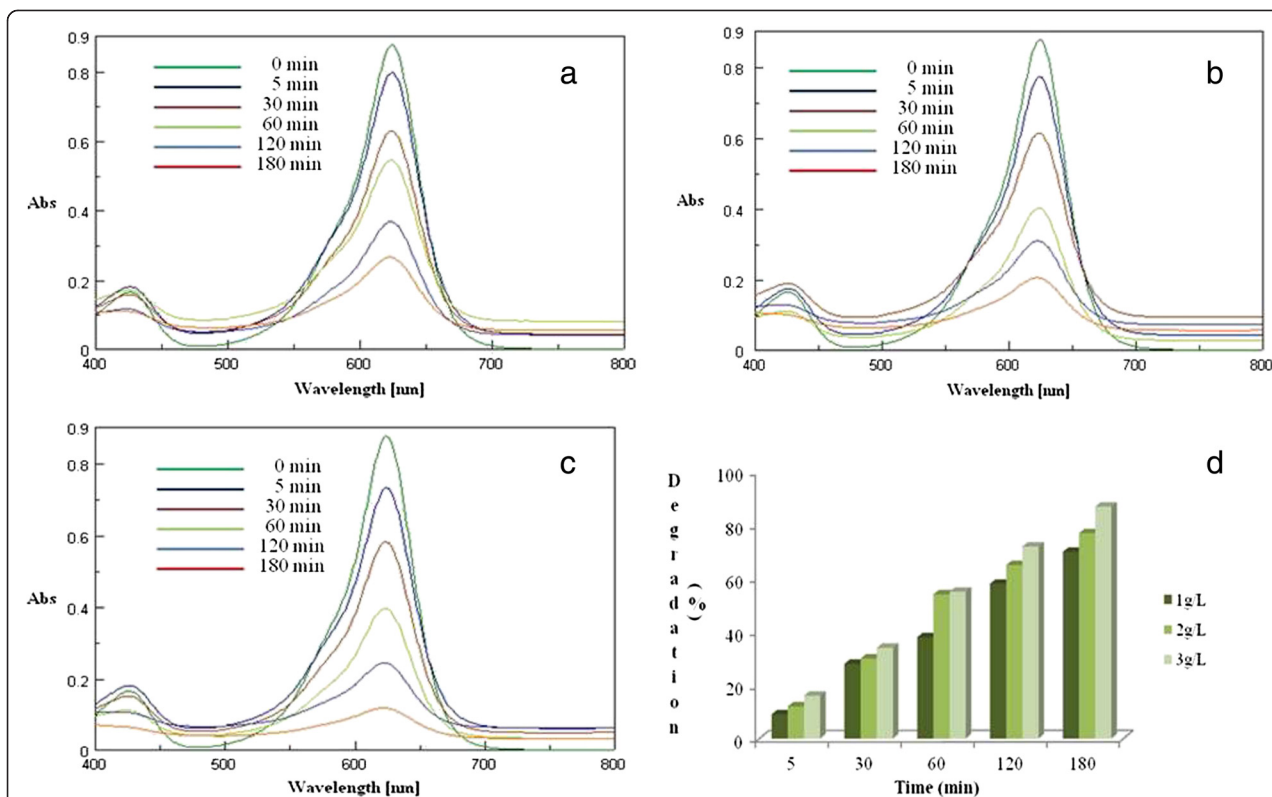


Figure 5 (a) Absorbance of BG with catalyst loading of 1 g/L TiO₂/Zn (b) 2 g/L TiO₂/Zn (c) 3 g/L TiO₂/Zn (d) Mean degradation efficiency rate of BG at different catalyst loading of TiO₂/Zn (under 30 W UV at 25°C).

washing, the precipitate was dried in hot air oven for 5 hours at 90°C. The dried powder was annealed at 400°C for 3 hours in a furnace.

Titanium dioxide doped with 1 wt.% Zn microparticles and 1 wt.% Cu microparticles

The preparation was similar to that of TiO₂ except that 1wt. % Zn and 1wt. % Cu were dissolved in DW and added to the mixture before adding NH₄OH.

Preparation of dye sample and photocatalyst loading

4 ppm of BG was prepared by using DW as solvent. Absorption maximum of BG was determined at 624 nm by using UV-vis double beam spectroscopy (JAS.CO, V-630 model and having power AC100V-240 V, 50/60 Hz, Class 1 protect and made in Japan). 3 aliquots of 4 ppm BG were taken in beakers and in each aliquot 100 mg, 200 mg and 300 mg of TiO₂ nanoparticles were suspended (similar procedure for TiO₂/Zn and TiO₂/Cu nanoparticles). Each aliquot is then subjected to continuous stirring. The reaction is carried out in presence of UV light (30 W). A small portion of sample is withdrawn from each aliquot and centrifuged (Hettich Zentrifugen – EBA 20) at 4000 rpm for 30 minutes. The supernatant solution was used for measuring the absorbance. Absorbance of each sample is

measured at a time interval of 5 min, 30 min, 60 min, 120 min and 180 min.

Results and discussion

Characterization of TiO₂, TiO₂/Zn and TiO₂/Cu microparticles by using SEM

Figure 1 shows surface morphology of microparticles with high-resolution images of the sample. These images gave irregular and angular shape with the grain size and diameter of about 20–50 µm. TiO₂ doped with Cu gave more porous structure than TiO₂ alone this may be attributed to prevention of TiO₂ agglomeration. TiO₂ doped with Zn is almost similar to the structure of pure TiO₂.

XRD

Figure 2 shows the XRD patterns of (a)TiO₂, (b)TiO₂/Zn and (c) TiO₂/Cu annealed at 400°C for 3 hours. In Figure 2a,b and c XRD patterns exhibited strong diffraction peaks at 25.2°, 37.8°, 47.9°,54.0° and 62.6° confirming the anatase TiO₂. All the peaks were similar with the standard spectrum. If there is increase in particle size then the peak intensity of diffraction pattern will increase proportionally. It can be seen that all samples have the anatase structure. Both Zn²⁺ and Cu²⁺ doping in the sol-gel method did not alter the crystal form of TiO₂.

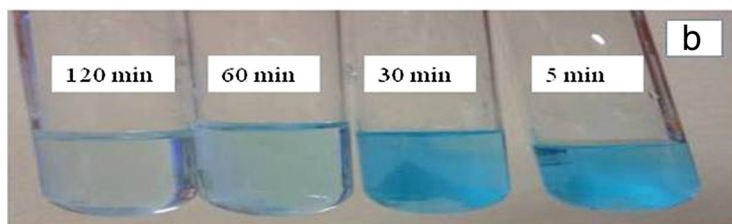
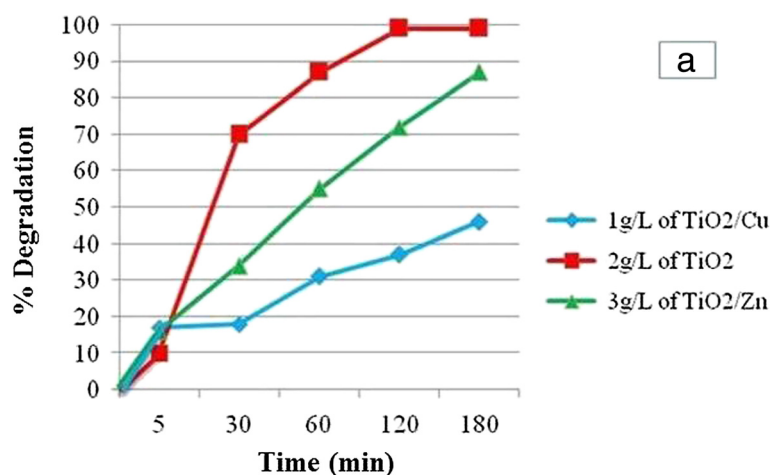


Figure 6 (a) Degradation efficiency rate of BG using 2 g/L of TiO₂, 3 g/L of TiO₂/Zn and 1 g/L of TiO₂/Cu (b) Degradation of BG at 5 min 30 min, 60 min and 120 min with TiO₂ at catalyst loading of 2 g/L.

The absorbance maximum of BG was determined using UV–vis double beam spectroscopy (JAS.CO V-630). The lambda max of a solution of concentration 4 ppm was found to be 624 nm Figure 3(a).

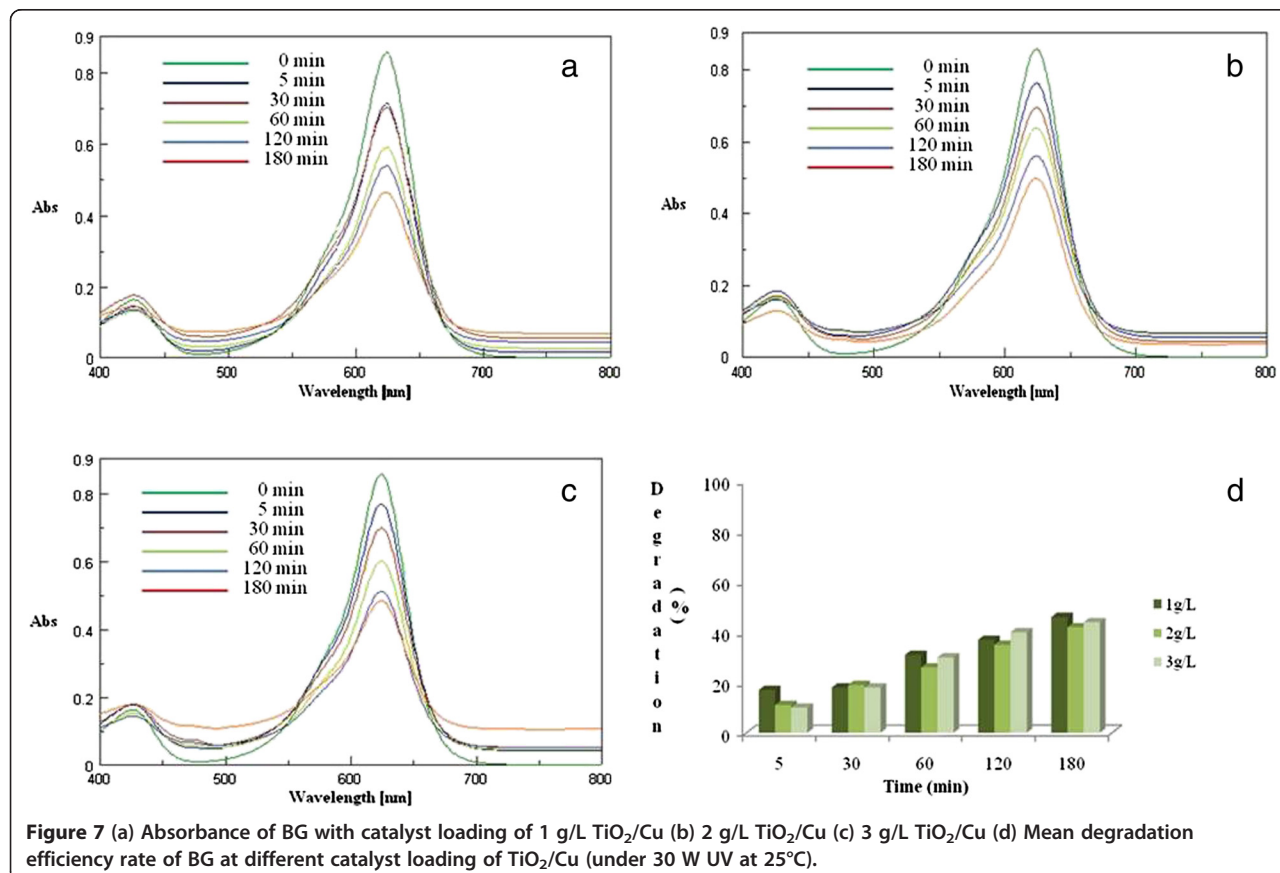
Photocatalysis of TiO₂ on Brilliant Green

1 g/L to 3 g/L of TiO₂ microparticles were added to an aliquot of 4 ppm BG to determine TiO₂ nanoparticles efficiency in decolorization. Catalyst loading of 2 g/L showed better degradation rate than 1 g/L and 3 g/L. About 87% degradation was obtained within 1 hour for all concentrations of catalyst. However, 99% degradation was obtained for catalyst loading of 2 g/L at 2 hours and 1 g/L and 3 g/L at 3 hours (Figure 4). Increase in the concentration of catalyst shows an increase in dye degradation for the first few minutes. This is due to the fact that number of dye molecules adsorbed and photon absorbed increases with increase in catalyst loading. The increase in degradation was probably due to an increase in availability of catalytic sites and adsorption sites.

Initially, the degradation of BG was fast, mostly between 30 min and 60 min. However, the increase of catalyst loading beyond the optimum may result in the agglomeration of catalyst particles, hence the part of the

catalyst surface become unavailable for photon absorption and degradation rate decrease. Consequently, at certain minutes 3 g/L catalyst loading shows a slight decrease in further degradation. This may be due to the blockage of UV penetration in sample that lead to decrease in degradation rate. Optimum concentration is essential for efficient decolorization and degradation.

BG is a triphenylmethane dye which is having 3 phenyl rings. TiO₂ showed excellent degradation of 99% of catalyst loading, whereas TiO₂/Zn (Figure 5) showed degradation of 87% and TiO₂/Cu (Figure 6) showed degradation of 46%. Almost 99% of dye decolorization and degradation occurred at 2nd hour in presence of 2 g/L of TiO₂ (Figure 3). At 3rd hour 1 g/L and 3 g/L also showed 99% of BG degradation. Therefore, TiO₂ is a good photocatalyst among other catalyst on BG degradation. This may be attributed to the nature of BG. The pH of 4 ppm solution of BG is 5.5 The pH can influence adsorption of dye molecule on the photocatalyst to stimulate photooxidation to take place [17]. Few studies stated that TiO₂ particles tend to agglomerate and surface for dye adsorption and photon absorption will be reduced in acidic conditions. Whereas, some journal stated that hydroxyl radicals are easier to be generated by oxidizing, more hydroxide ions available and process is enhanced in



alkaline medium [18]. So the effect of unmodified TiO₂ on BG can be credited to weakly basic p^H of BG.

Photocatalysis of TiO₂/Zn on Brilliant Green

1 g/L to 3 g/L of TiO₂/Zn microparticles were added to 4 ppm BG to determine TiO₂/Zn microparticles efficiency in degradation. Catalyst loading of 3 g/L showed better degradation rate than 1 g/L and 2 g/L. In this case, higher the catalyst loading higher the degradation rate. At 3 hours, under UV irradiation sample degradation of 70%, 77% and 87% was observed for 1 to 3 g/L respectively. The effect of Zn as dopant decreased the effect of TiO₂ by 13%. The retardation effect of Zn on photodecomposition rate may be attributed to suppression of hydroxyl radicals due to entrapment of conduction band electrons by the adsorbed metal ions.

The presence of metal ions such as Cu²⁺ and Zn²⁺, decreased the rate of BG degradation. TiO₂ showed an excellent degradation of 99% on BG at 2 hours for a catalyst loading of 2 g/L. whereas, TiO₂/Zn showed only 87% with 3 g/L of catalyst loading and TiO₂/Cu showed only 46% with catalyst loading of 1 g/L.

Photocatalysis of TiO₂/Cu on Brilliant Green

1 g to 3 g/L of TiO₂/Cu nanoparticles are added to an aliquot of 4 ppm BG to determine TiO₂/Cu nanoparticles efficiency in decolorization and degradation. Catalyst loading of 1 g/L showed better degradation rate than 2 g and 3 g/L. About 46%, 42% and 44% degradation are observed at 3 hours respectively under UV exposure (Figure 7). Dopants may not have the same effect on trapping electrons and/or holes on the surface or during interface charge transfer because of the different positions of the dopant in the host lattice. Consequently, the photocatalytic efficiency would be different for different types of dopants [19,20].

Comparison between TiO₂, TiO₂/Zn and TiO₂/Cu

TiO₂ showed excellent result on degradation of BG compared with doped TiO₂. 99% degradation was obtained in presence of TiO₂, followed by TiO₂/Zn for 87% and TiO₂/Cu for 46%. TiO₂ doped with transition metals can increase or decrease photocatalytic degradation of dyes. The percentage of dopant is necessary to be determined and the optimum % of dopant is between 0.06 and 1.0 for wastewater degradation [21]. In this study TiO₂ was doped with 1 wt.% of Zn and Cu. The effect of Zn as dopant decreased the effect of TiO₂ by 13%. The retardation effect of Zn on photodecomposition rate may be attributed to suppression of hydroxyl radicals due to entrapment of conduction band electrons by the adsorbed metal ions. The presence of metal ions such as Cu²⁺ and Zn²⁺, decreased the rate of BG degradation these results are in accordance with Chiang et al., [22]. Several reasons

may be attributed for the effect of decreased activity in presence of dopant which includes nature of dye, pH, sample concentration, concentration of dopant etc.

Conclusion

In this research, a study has been carried out on photocatalytic activity of TiO₂, TiO₂/Zn and TiO₂/Cu microparticles on BG their physical and chemical characterization was done by SEM and XRD. The obtained results comply with that of standard. Photocatalytic effect of unmodified and modified TiO₂ nanoparticles were successfully studied in this work. Unmodified TiO₂ is a good choice for cationic dye such as BG. The nature and structure of dyes were important parameter to choose a suitable photocatalyst. On other hand, catalyst loading should also be considered as a parameter. For different dyes different catalyst loading is needed. The degradation efficiency of unmodified TiO₂ is 99% for BG at 2 g/L of catalyst loading during a period of 120 min under UV exposure.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

In this research SM conducted experiments on photocatalytic degradation. RA who is corresponding author for this manuscript supervised, evaluated the progress of the study and prepared manuscript. RP designed experimental procedures and prepared the manuscript. All authors read and approved the final manuscript.

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