RESEARCH PAPER

Photocatalytic effect of TiO$_2$ and the effect of Nickel, Cobalt and Zinc Doped TiO$_2$ on degradation of Congo red and Bromothimol blue

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Abstract

Doped and undoped TiO$_2$ photocatalysts were prepared by hydrothermal method and characterized by EDX, SEM and XRD analysis, while the photocatalytic activities were tested using Congo red and bromothymol blue as the model compound. The effect of time, catalyst amount, pH and dye concentration were studied. Transition metals (Ni, Co and Zn) doped titania exhibits the highest photocatalytic activity under optimum reaction conditions.

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Introduction

Semiconductor catalyzed photodegradation of organic contaminants both in aqueous medium and air is a promising remediation technology. Among the different semiconductor used, TiO_2 has been perceived as one of the excellent material for its chemical and biological inertness, cost effectiveness, strong oxidizing power and long term stability against chemical and photo corrosion [Erasmai *et al.*, 2006, Fatemeh *et al.*, 2014, Moutusi and Krishna 2014, Muhammad *et al.*, 2009, Muhammad *et al.*, 2015, Qayyum, 2010, Tugba and Isil, 2008] The photocatalytic activity of Titania semiconductor is due to the generation of positive holes in the valance band and excited electrons in the conduction band by the absorption of UV illumination [Xu *et al.*, 2011]. These excited species are mobile and can initiate surface chemical reactions, usually by the generation of highly oxidative superoxide and hydroxyl radicals at the semiconductor interface [Khalid *et al.*, 2015]. However, the band gap of TiO_2 is (3.2 eV), which is large enough and also their electron-hole recombination rate is very high which decreases their photocatalytic efficiency and subsequently reduces their application towards purification of wastewater [Akpan and Hameed 2009, Ali *et al.*, 2014, Balanosky *et al.*, 2000]. Therefore, some strategies were investigated to enhance the photoactivity of Titania through modification [Silvia *et al.*, 2007, Thillai *et al.*, 2011]. Doping with metal or non-metal has been the focus of the attention among these approaches for modification to Titania. To suppress electron holes recombination and also for the onset shift in the band gap absorption doping with transition metal ion into the Titania matrix has been generally reported. Transition metal doped Titania has been found to be very effective for photodegradation of dyes and for remedial of dye contaminated solutions [Akira and Tata, 1997, Alaxander *et al.*, 2013, Kitirote *et al.*, 2012]. Despite the fact that dyes are generally used in industrial applications, limited literature is available on their remediation from industrial effluents using Titania doped with transition metals. Different research articles citing the utilization of the doped semiconductors seems to have no connectivity between them as to concentration of substrates, reaction time and the amount of catalyst. So standardization of reaction conditions is very critical at this point instead of reporting data on different dyes [Nadia *et al.*, 2014, Sajid *et al.*, 2014, Xu *et al.*, 2011].

In this paper we have chosen congo red and bromothymol blue as model pollutants for the photocatalytic degradation test. Therefore, the aim of this work is to evaluate the catalytic efficiency of the doped TiO_2 (Ni, Zn and Co) and undoped TiO_2 toward the degradation of congo red and bromothymol blue in aqueous medium. Moreover, the effects of various parameters such as time, catalyst dose, pH, initial dye concentration were also studied.

Materials and methods

Materials

Congo red, titanium isopropoxide, bromothymol blue, nickel nitrate, zinc nitrate, cobalt nitrate, urea were used as received. Distilled water was used in the synthesis of catalyst and preparation of reagent solution.

Instrumentation

The morphological study of the doped and undoped TiO_2 were analysed using scanning electron microscopy (JSM 5910, Jeol, Japan), The elemental structure of the prepared catalyst was examined by energy dispersive X-rays (INC200, Oxford, UK). The phase structure of the catalysts was measured by X-rays diffraction (X-ray diffractometer Rigaku D/Max-II, Cu tube, Japan). The photodegradation studies of Congo red and bromothymol blue was carried out by using UV/Visible spectrophotometer (UV-1800, Shimadzu, Japan).

Synthesis of Photocatalysts

Titanium isopropoxide (7.4mL) and distilled water (100mL) were taken in a beaker and stirred for 1 hr at room temperature to obtain precipitates of titanium hydroxide. The precipitate was washed several times with distilled water and then dried in oven at 105°C. The dried precipitate was dissolved in 1M nitric acid solution and $[TiO(NO_3)_2]$ clear solution was obtained. Furthermore, equimolar solution of titanyl nitrate

and urea were mixed in a beaker and stirred for one hr. After stirring, the solution was kept in maffle furnace at 673K. The prepared Titania was then kept in desiccators.

1wt.% solution of Ni, Zn and Co nitrates were prepared and added to $[TiO(NO_3)_2]$ solution. The reaction mixture was then titrated against urea and stirred for one hour. After stirring, the mixture was kept in maffle furnace at 673 K. Finally, the prepared metal doped Titania was kept in desiccators.

Photocatalytic Test

Photodegradation experiments of Congo red and Bromothymol blue using doped (1wt% Ni, Zn and Co) and undoped TiO_2 as photocatalysts were carried out at room temperature. In a typical experiment, 10mL of congo red (20mg/L) and bromothymol blue (10mg/L) solution were taken in a beaker and to which added different concentration (1mg to 10mg) of catalyst. The temperature of the reaction mixture was kept constant to a desire value with the help of hot plate. The aliquot was allowed to continuously stir under UV light (254nm, 15W) irradiation for different time (10 to 100 minutes). When irradiation time was completed the aliquot was withdrawn and centrifuged at 1000rpm for 10 minutes. For analysis small amount of the test solution was pipetted out into glass cuvettes and their absorption was monitored with the help of UV/Visible spectrophotometer. Using the following formula percent removal of dyes in aqueous solution was determined as Degradation rate (%) = $\left(\frac{A_0 - A}{A_0}\right) \times 100$

Where A_0 represents initial absorbance and A represents the absorbance of dye after irradiation with UV light.

Result and discussion

SEM and EDX

SEM was used to determine the surface morphology of the undoped and doped Titania. SEM photographs at different magnification were taken and are shown in Fig. 1. As it is illustrated from the fig. that the Titania are in dispersed form and also formed agglomerates at some point. Fig. 1.B-D represent the

photographs of nickel, zinc and cobalt doped titania respectively. These metals are well deposited on the surface of Titania. From the fig. it can be seen that the doped Titania particles are bigger than pure Titania. Hassan *et al.* [Hassan and Sayed, 2016] reported that the presence of dopant increases the catalyst particles size and cause particles to agglomerate.
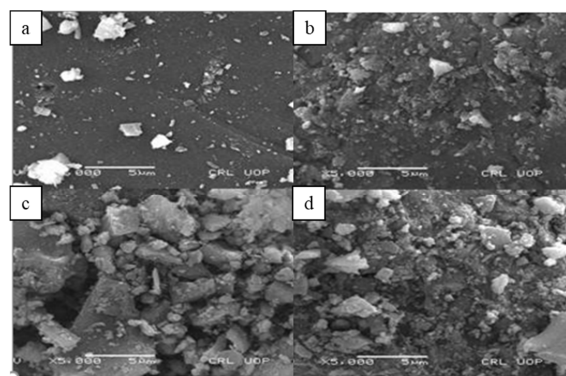

Fig. 1. SEM image of titania photocatalyst, a) Pure TiO_2, b) Co/TiO_2, c) Ni/TiO_2, d) Zn/TiO_2.

For determination of elemental composition of undoped and doped Titania energy dispersive X-rays was used. The EDX spectrum of modified titania photocatalyst can be seen in Fig. 2A which reveals that the photocatalyst only consists of titania and oxygen, while the EDX spectra of cobalt, nickel and zinc doped titania are given in Fig. 2B-D, which represent that the photocatalysts consist of oxygen, titanium, and doped metals i.e. nickel, cobalt and zinc as well in their chemical structure respectively.

XRD Study

The crystalline phase of undoped and doped Titania photocatalyst was determined by XRD. In Fig. 3.A-D XRD pattern showed strong diffraction peak at $2\theta = 25.2°$, $37.1°$, $47.5°$, $53.5°$ and $62.3°$ which are exhibited by anatase TiO_2. All the peaks were comparable to the standard spectrum. The peak intensity of diffraction pattern will increase proportionally with increase in particle size. It can be observed that all the samples have anatase formation. No diffraction peaks of metals in the pattern of metal doped Titania samples were observed. This is may be due to low metal ions doping contents 1% and also the metals are well dispersed within the Titania crystal phase [Balaram *et al.*, 2016, Shamalah *et al.*, 2013].
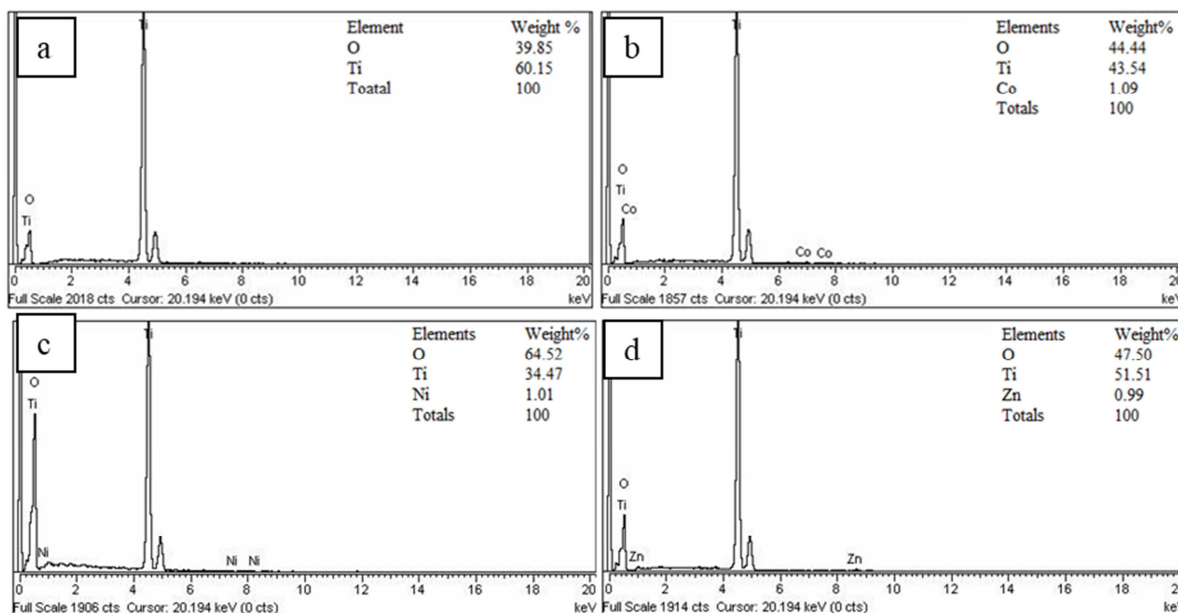
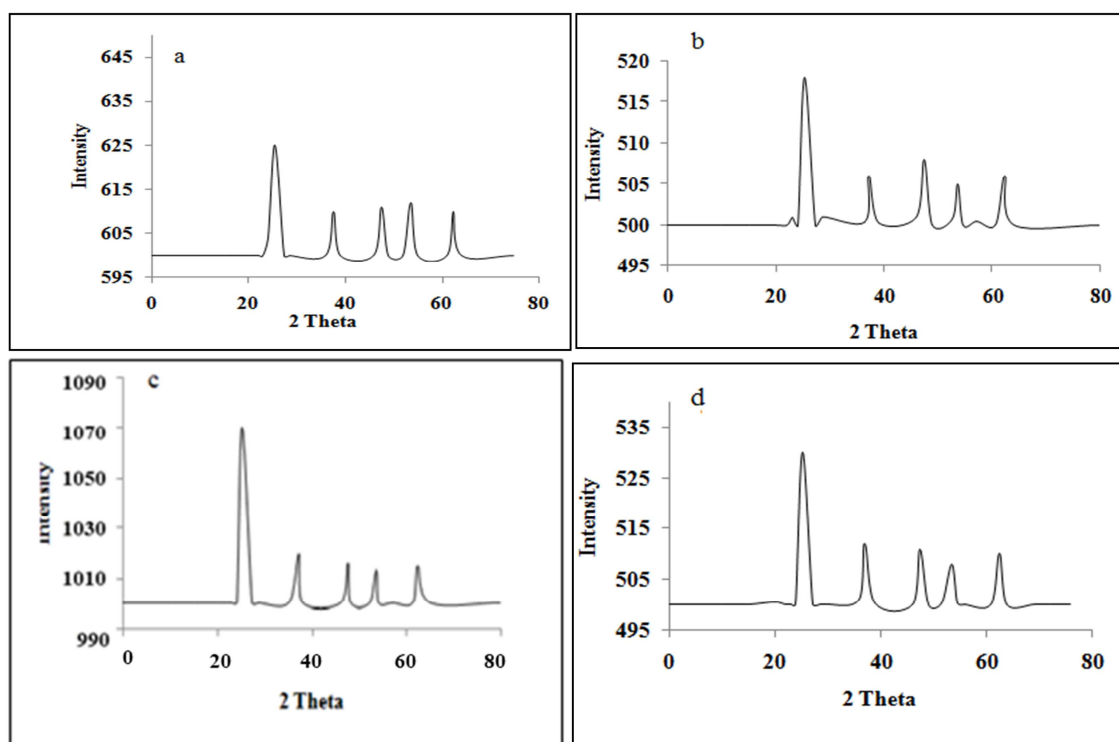**Fig. 2.** EDX spectrum of, A) TiO_2, B) Co/TiO_2, C) Ni/TiO_2, and D) Zn/TiO_2.

Fig. 3. XRD pattern of, A) TiO_2, B) Co/TiO_2, C) Ni/TiO_2, D) Zn/TiO_2.

Preliminary studies to measure the effect of UV light

The results of preliminary study carried out to measure the effect of UV light on the photodegradation process is shown in Fig. 4. First experiment was performed with dye solution mixed with titania and exposed to UV light, second experiment was carried out without UV light and the third experiment was carried out by exposing dye solution to UV light in the absence of titania. The extent of degradation, though not very efficient, when the degradation experiments were performed with UV light alone. The degradation level was observed to enhance when the same experiment was carried out with titania in the absence of UV light.

This suggests that the extent of degradation observed could have resulted from adsorption of dye molecules onto the surface of titania particles. The degradation efficiency was significantly enhanced when titania was used in the presence of UV light. Zahra *et al.* [Zahraa *et al.*, 2006] investigated that the activity of the photocatalyst in the presence of UV light has to do with the activation of the active sites on the catalyst surface. The electron- hole pairs generated onto the surface of catalyst are responsible for the photodegradation of dye
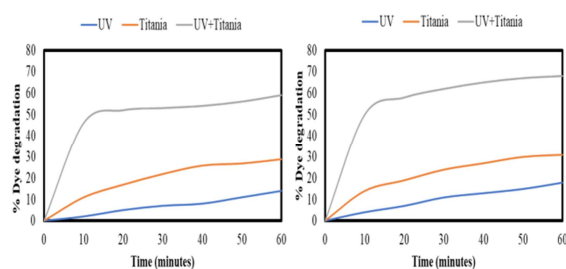

Fig. 4. Results of preliminary studies to measure the effect of UV light on the degradation of (A) congo red: (B) bromothymol blue.

Photodegradation of dye

The absorption of UV light on the surface of Titania produces photogenerated electrons and holes. The positive holes react with water and result in the formation of hydroxyl radicals. These hydroxyl radicals are reacting with organic dye and degrade the dye molecules. The electrons in the conduction band can reduce molecular oxygen to superoxide radicals. The superoxide radical form hydrogen peroxide and subsequently form hydroxyl radical which take part in the degradation of organic dyes as shown in Fig. 5 [Rauf *et al.*, 2011].
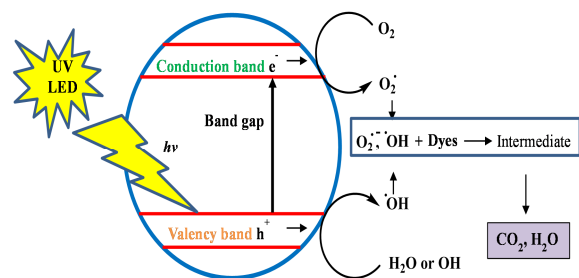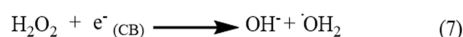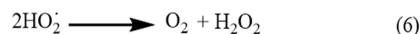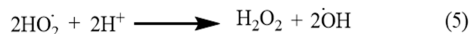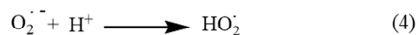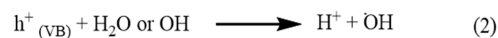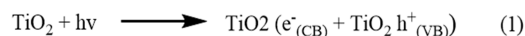

Fig. 5. Mechanism of photodegradation of dyes.

The following is the reaction sequence of Titania semiconductor, activated by UV light in aqueous media.

$$TiO_2 + h\nu \longrightarrow TiO2\ (e^-_{(CB)} + TiO_2\ h^+_{(VB)}) \quad (1)$$

$$h^+_{(VB)} + H_2O \text{ or } OH \longrightarrow H^+ + \dot{O}H \quad (2)$$

$$e^-_{(CB)} + O_2 \longrightarrow \dot{O}_2^{-} \quad (3)$$

$$\dot{O}_2^{-} + H^+ \longrightarrow H\dot{O}_2 \quad (4)$$

$$2H\dot{O}_2 + 2H^+ \longrightarrow H_2O_2 + 2\dot{O}H \quad (5)$$

$$2H\dot{O}_2 \longrightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 + e^-_{(CB)} \longrightarrow OH^- + \dot{O}H_2 \quad (7)$$

The radical species that are most active during photodegradation are $O_2^{\bullet-}$, $HO_2^\bullet$ and $\cdot OH$, employing photocatalysis for complete oxidation.

Effect of irradiation time

The Titania photocatalysts showed that the degradation of congo red and bromothymol blue initially increases rapidly with irradiation time and then almost level off. The Titania photocatalysts degradated about 55% of congo red within 10 minutes, while the degradation of bromothymol blue obtained as 62% within 10 minutes by using same catalyst. On catalyst surface the adsorption of hydroxyl radicals increases with increase in time and hence photodegradation is also increased. After coverage of active sites by hydroxyl radicals, the photodegradation becomes constant [Azarmidokht *et al.*, 2010].

Effect of catalyst dosage

The amount of catalyst is one of the important factors that affects the rate of photocatalytic degradation as the optimum amount of catalyst ensures proper penetration of light onto the surface of catalyst and also avoids undo scattering of radiations. So the amount of TiO_2 was varied from 0.1mg/L to 10mg/L to measure the effect of catalyst dosage in dye removal. Catalyst dosage of 10mg/L exhibited the most degradation for bromothymol blue and congo red and then the degradation remained constant upto 11mg/L. The increase of catalyst amount beyond 10mg/L for congo red and bromothymol blue might resulted in the agglomerates of catalyst particles, hence the portion of the titania surface became inaccessible for photon absorption and hence the photodegradation rate remained constant.

Effect of pH

The effect of pH on the photodegradation was determined at different pH value such as 2, 4, 6, 8 and 10. The desired pH of the solution was achieved by adding NaOH and HCl solution. The results showed that neutral pH is favourable for the maximum degradation of congo red, while for bromothimol blue, acidic pH is favoured in aqueous medium. Photodegradation of cogo red reaches maximum value at neutral pH. At higher pH the titania surface is negatively charged and repels the R-SO$_3^-$ ions of congo red. Furthermore congo red dye at highly acidic pH tends to aggregate and forms tautomerism. About 90.5% of bromothimol degradated at pH 2. Titania surface becomes positive in acidic medium. The negative charge species (O and OH) of bromothimol blue got adsorbed readily on the positive active sites and consequently increased the degradation efficiency [Azarmidokht *et al.*, 2010, Silke *et al.*, 2001].

The effect of initial dye concentration

The effect of initial concentration of dyes solution on the photodegradation is essential aspect of the study. The initial concentration of both dyes was chosen in the range of 2-70mg/L at optimum conditions of pH, catalyst dose and irradiation time. The percent degradation decreases as initial concentration of dye solution increases. As the concentration of dye increases, more and more dye molecules are adsorbed on the surface of Titania; thus, the production of hydroxyl radicals is decreased. Consequently the absorption of photons by titania decreases and the percent degradation hence thus reduced. [Faisal *et al.*, 2007].

Photocatalytic activity of metal doped titania at optimum conditions

Nickel doped titania (1 wt.%)

At the optimised conditions of time, pH, catalyst amount and initial dye concentration, the effect of dopants on photocatlytic degradation of congo red and bromothymol blue was studied. Percent degradation of congo red and bromothimol blue increased from 84 and 76 to 98 and 96 respectively under UV light irradiation. The effect of nickel as dopant increased the efficiency of Titania as the nickel dopant inhibited the particles digestion as well

as slowed down the recombination process, thus large amount of photon absorbed on nickel doped Titania surface and produced maximum number of hydroxyl radicals [Ban and Ekram, 2016].

Zinc doped titania (1 wt.%)

TiO$_2$/Zn (10mg/L) photocatalyst was added to congo red (20mg/L) and bromothimol blue (10mg/L) solution to determine TiO$_2$/Zn photocatalyst efficiency in decolorization/degradation. About 91% congo red and 90% bromothimol blue degradation was observed. The addition of zinc as dopant increased the photocatalytic activity of Titania. This increase is due to the addition of zinc as dopant as it slowed down the recombination process inside Titania semiconductor and therefore produced large number of hydroxyl radicals and positive holes [Pooja *et al.*, 2014].

Cobalt doped titania (1 wt.%)

Addition of cobalt as dopant also increased the degradation of both dyes as the divalent cobalt ions also acted as electron trapper and decreased the recombination rate as a result the activity of catalyst increased [Muhammad *et al.*, 2015].

Comparison between TiO$_2$, TiO$_2$/Ni, TiO$_2$/Zn and TiO$_2$/Co

Metals (Co, Ni, Zn) doped Titania showed excellent result on photodegradation of congo red and bromothymol blue compared to pure titania and a comparison with already reported results are shown in Table 2 and 3. Respectively. The photodegradation of congo red obtained with pure titania was 76% while in the presence of doped metals like TiO$_2$/Ni, TiO$_2$/Co and TiO$_2$/Zn, the photodegardation efficiency increased to 98%, 94% and 90% respectively. Similarly, an enhancement in the photodegradation of bromothymol blue was also observed from 84% with simple titania to 90%, 91% and 96% using TiO$_2$/Ni, TiO$_2$/Zn and TiO$_2$/Co respectively. The whole comparison is summarised in Table 1. Titania doping with metals can have effect in both the ways as either doping can decrease or increase photodegradation rate of dyes as compared to simple titania. In the current study, an increase in the photodegradation

efficiency of both dyes is observed and it might be due to shortly trapping of electron in the conduction band of semiconductor, which slows the electron-hole recombination rate resulting an increase in the photo catalytic activity of catalysts and thus increasing the photodegradation efficiency. Among the three dopants used, the highest photocatlytic activity was observed for nickel towards photodegradation of both dyes. This different behaviour of nickel doped titania might be due to the well dispersion of nickel metal on the crystalline structure of titania [Abdelkahhar *et al.*, 2005, Muhammad *et al.*, 2015, Pooja *et al.*, 2014].

Table 1. Comparison of simple and doped titania photocatalysts.

Types of dye	Photodegradation using different photocatalysts			
	TiO_2	TiO_2/Zn	TiO_2/Co	TiO_2/Ni
Congo red	76%	91%	94%	98%
Bromothymol blue	84%	90%	91%	96%

Table 2. Comparison of present work for Photodegradation of congo red using different photocatalysts already reported in literature.

Type of catalyst	Catalyst Dosage (gL^{-1})	Dye concentration (mgL^{-1})	Degradation Efficiency (%)	Time (minutes)	References
$Ni_{0.6}Co_{0.4}Fe_2O_4$	3.0	10	66%	120	[33]
$FeSO_4$	0.1	1	80%	120	[34]
TiO_2	0.4	1	70%	120	[34]
ZrO_2	0.7	10	95%	125	[35]
ZnO	0.4	25	50%	180	[36]
Zn-Pd	0.4	25	96%	180	[36]
$Ni-TiO_2$	0.01	20	98%	10	
$Zn-TiO_2$	0.01	20	94%	10	This work
$Co-TiO_2$	0.01	20	91%	10	

Table 3. Comparison of present work for Photodegradation of Bromothymol blue using different photocatalysts already reported in literature.

Type of catalyst	Catalyst dosage (gL^{-1})	Dye concentration (mgL^{-1})	Degradation Efficiency	Time (minutes)	References
ZnO	0.4	2	79%	120	[37]
TiO_2	0.4	2	86%	120	[37]
In_2O_3	0.2	40	44%	15	[38]
HPA	0.2	40	23%	15	[38]
$HPA-In_2O_3$	0.2	40	50%	5	[38]
$Ni-TiO_2$	0.01	10	96%	10	
$Co-TiO_2$	0.01	10	91%	10	This work
$Zn-TiO_2$	0.01	10	90%	10	

Congo red
time: 10 minutes, dye concentration: 20mg/L, pH: 7, catalyst amount: 10mg.

Bromothymol blue
time: 10 minutes, dye concentration: 20mg/L, pH: 2, catalyst amount: 10mg.

Conclusion
The present study shows a comparison of simple and doped titania with Ni, Co and Zn for the photodegradation of two common pollutants i.e. congo red and bromothymol blue. The results suggest that doped titania are better photocatalysts as compared to simple titania at optimised conditions of pH, time, catalyst dosage and initial dye concentration. Thus the doped titania are found to be promising photocatalysts for the photodegradation of congo red and bromothymol blue in respect of high degradation rate with maximum degradation efficiency and least photocatalyst dosage.

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