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Photocatalytic degradation of methyl orange and toluidine blue using advanced oxidation method

Maria Sadia[a], Aminullah Saqib[a], Jehangir Khan[a], Muhammad Zahoor[b,*], Ivar Zekker[c]

[a]*Department of Chemistry, University of Malakand, Chakdara, Lower Dir, Khyber Pakhtunkhwa, Pakistan, emails: mariasadia@gmail.com (M. Sadia), saqib42790@gmail.com (A. Saqib), jehangirchemist@gmail.com (J. Khan)*
[b]*Department of Biochemistry, University of Malakand, Chakdara, Lower Dir, Khyber Pakhtunkhwa, Pakistan, email: mohammadzahoorus@yahoo.com (M. Zahoor)*
[c]*Institute of Chemistry, Faculty of Science, 14 Ravilast, University of Tartu, Estonia, email: ivar.zekker@ut.ee (I. Zekker)*

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ABSTRACT

Dyes being a major pollutant of water worldwide needs special attention to be effectively degraded. The photochemical technique among the applied treatment methods is considered to be the most valuable technique involving oxidative degradation processes. In this study catalytic oxidation of toluidine blue and methyl orange dyes was studied under UV light irradiation using un-doped and metal-doped TiO_2. For doping 1% of Co, Ni and Zn were added to pure titania. Characterization of un-doped and metal-doped TiO_2 catalysts were carried out using energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD). EDX studies show the presence of doped metals in the composition of doped titania. SEM and XRD analysis revealed that titania is in dispersed form as well as also forms agglomerates and exhibits anatase phase, respectively. Initial dye concentrations, pH and time effects were investigated to determine optimum conditions for maximum dye degradation. An increase in degradation was observed with increase in light exposure and catalyst amount. An efficient degradation of methyl orange and toluidine blue dyes up to 96% and 98% took place at pH 2 and 11, respectively with doped titania. In the absence of light source up to 3%, 5%, 7% and 10% of dye solution was adsorbed on simple and Co, Ni and Zn doped titania respectively. The doped titania proved to be an efficient photocatalyst for dye removal from aqueous samples as compared to simple titania.

Keywords: Photodegradation; Toluidine blue; Titanium dioxide; Methyl orange; Photocatalyst; Un-doped titanium dioxide; Metal-doped titanium dioxide

1. Introduction

Synthetic dyes comprise an important part of industrial water effluents that are discharged by most of manufacturing industries. The impact of these dyes on the environment is a major concern because of the potentially carcinogenic properties of the chemicals [1]. Also, among these dyes some dyes can undergo anaerobic decolorization to form potential carcinogens [2]. The wastewater, which is colored due to the presence of the dyes can block both sunlight penetration and oxygen dissolution that are essential for aquatic life. Consequently, there is a considerable need to treat these colored effluents before discharging them into various water bodies. Different approaches to handle and decontaminate such effluents have been reported in the literature [3]. Typical techniques include

* Corresponding author.

classical methods, such as adsorption [4], coagulation [5,6] ion flotation [7] and sedimentation [8]. All these techniques are versatile and useful, but they all end up producing a secondary waste products that need to be processed further. Another set of techniques that are relatively newer, more powerful, and very promising called as "Advanced Oxidation Processes" has been developed and employed to treat dye-contaminated wastewater effluents [9]. Among photocatalyst, TiO_2 is considered a preferable photocatalyst in detoxification of organic pollutants and water treatment due to its properties such as good stability, non-toxicity, low cost, easy preparation and high redox reactivity [10–13]. Metal-doped and un-doped TiO_2 is extensively used to degrade toxic organic compounds [14], reduce metal-ions [15], improve the biodegradability in cellulose effluents [16] and decolorize a great variety of dyes in solution [17] or in solid mixtures [18]. TiO_2 has a band gap of 3.2 eV [19] and upon irradiation of a photon having energy greater than 3.2 eV; electrons and positive holes are generated in the conduction and valance band of TiO_2. The positive holes can either react directly with organic pollutant or generate hydroxyl radicals that oxidize the organic pollutant. Reduction products are also formed by reaction of electrons with organic compounds [20].

Due to the ability of electron and holes to recombine, often conductive materials are added to photocatalysts to suppress this recombination process. Transmission channels are provided by the conductive material to the photocatalyst surface from the conduction band, which reduce the recombination of electron hole pair and photocatalytic efficiency is enhanced [21]. Doping of TiO_2 with metal or non-metal ions also increase its photocatalytic activity. Metal ions act as a trap for holes or electrons and suppress their recombination. The main drawbacks of using TiO_2 as a photocatalyst is that its band gap lies in the near-UV range of the electromagnetic spectrum: 3.2 eV for the anatase phase. As a result, only UV light can create the electron–hole pairs and initiate the photocatalytic process. However, UV light constitutes only a small fraction (about 3%–5%) of the solar spectrum. So an excessive research is ongoing to shift TiO_2 optical response to the visible light range. So, to enhance the photocatalytic activity of TiO_2 by incorporating an adequate amount of a transition metal oxide such as that of Fe, Zn, Cu, Ni and V essentially lessens the band gap of TiO_2 for the photo-excitation (red shift) and simultaneously reduces the recombination rate of photogenerated electron–hole pairs [22]. In this research, Co, Ni and Zn were used as dopants as wavelength of TiO_2 occurred in visible section, that is, the phenomenon of red shift took place with cobalt. The Co metal acts also as trapper of electron, providing extra duration of time for formation of radicals, used to increase catalyst activity for the process of degradation [23]. The Ni as dopant greatly suppresses process of recombination on the surface of photocatalyst and provide extra duration for holes and electron to produce large amount of OH radicals, and hence increases process of degradation [24]. The conduction band and valence band difference of TiO_2 decreases upon doping with Zn which enhances the photo catalytic activity of TiO_2 and made it active optically. Furthermore, the ionic radii of host Ti^{4+} (0.745 Å) are similar to that of Zn^{2+} (0.74 Å) ions. Hence Zn^{2+} ion can easily substitute Ti^{4+} in titanium lattice without distorting the crystal structure and stabilize the anatase phase over a range of metal ion concentration. The inclusion of Zn^{2+} metal ion as dopants also causes an increase in the number of O^{2-} and OH, radicals on the solid electrical layer of titanium that contributes to effective dye degradation [25].

The aim of the current research work is to study the photocatalytic process using un-doped and copper, nickel, and zinc-doped TiO_2 photocatalysts in the form of powder for the decolorization and mineralization of methyl orange and toluidine blue dyes.

2. Materials and methods

2.1. Required chemicals

Methyl orange (Sigma-Aldrich, Germany), toluidine blue (Alfa Aesar, USA), titanium isopropoxide with 97% purity (Sigma-Aldrich, Germany), cobalt nitrate (Alfa Aesar, USA), nickel nitrate (BDH chemicals), zinc nitrate (Sigma-Aldrich, Germany), and urea (Sigma-Aldrich, Germany) were used as received. Nitric acid, 65% pure (Merck), hydrochloric acid with 37% purity (Merck), sodium hydroxide (Sigma-Aldrich, Germany) and distilled water was used throughout to carry out different experiments salicylic acid (Sigma-Aldrich, Germany), malic acid (Alfa Aesar, USA).

2.2. Instrumentation

The morphological study of simple and Co, Ni and, Zn doped titanium dioxide were analyzed using scanning electron microscopy (JSM 5910, JEOL, Japan). The elemental structure of the synthesized catalysts was examined by energy-dispersive X-rays (INC 200, Oxford, UK). The phase structure of the catalysts was investigated by X-rays diffraction technique using X-ray diffractometer (Rigaku D/MaxII, Cu tube, Japan). The Cu-anode was used as source of Cu-Kα λ = 1.54184 Å doublet radiations with generator setting (E = 40 keV, I = 40 mA). The photodegradation studies of methyl orange and toluidine blue before and after the addition of simple and doped titanium dioxide under UV light irradiation was measured in terms of absorption using UV/Visible spectrophotometer (UV-1800, Shimadzu, Japan) provided with quartz cuvette and 1 cm path length.

2.3. Synthesis of photocatalysts

Titanium isopropoxide (7.4 mL) and distilled water (100 mL) were taken in a beaker and stirred for 1 h at room temperature. After 1 h stirring titanium hydroxide precipitates were formed. The precipitates were carefully washed with distilled water and dried at 105°C in an oven. The precipitates obtained then were dissolved in 1 M nitric acid solution and $[TiO(NO_3)_2]$ clear solution was obtained. Furthermore, unimolar solution of titanyl nitrate and urea were mixed in a beaker and stirred for 60 min. After stirring, the solution was kept in maffle furnace at 673 K. 1% solution by weight of Co, Ni, and, Zn nitrates were prepared and added to $[TiO(NO_3)_2]$ solution. The reaction mixture

was then titrated against urea and stirred for 60 min. After stirring, the mixture was kept in maffle furnace at 673 K. Finally, the prepared Co, Ni and Zn doped TiO_2 were kept in desiccator for further use [26].

2.4. Photocatalytic test

Photodegradation experiments of methyl orange and toluidine blue using doped (1 wt.% Co, Ni, and Zn) and un-doped TiO_2 as photocatalysts were carried out at room temperature. In a typical experiment, 10 mL of dye (20 mg/L) was taken in a beaker and different concentrations (1–10 mg) of catalyst were added to it. The temperature of the reaction mixture was kept constant with the help of hot plate. The aliquot was allowed to stir continuously under UV light (254 nm, 15 W) irradiation for different time interval (2–110 min). When irradiation time was completed, the aliquot was withdrawn and centrifuged at 1,000 rpm for 10 min. For analysis small amount of the test solution was pipetted out into glass cuvettes and their absorption was monitored with the help of UV/Vis spectrophotometer. Using the following formula degradation efficiency was calculated:

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

where C_0 (mg/L) is the original concentration of dye before the addition of simple and doped titanium dioxide and C (mg/L) is the final concentration of dyes after degradation in the presence of simple and doped titanium dioxide.

2.5. Degradation of colorless organic compounds

The degradation experiments were also performed for colourless organic compounds like salicylic acid and malic acid has using un-doped and metal-doped titania as photocatalysts under UV light irradiation and the results are given in Table 1.

2.6. Degradation of methyl orange and toluidine blue dyes in the absence of catalysts

The % degradation of subject dyes was also investigated in the absence of simple and doped titania under sun and UV light irradiation. For this purpose time of irradiation was varied in a wide range from 5 to 60 min and the results are given in Table 2.

3. Results and discussion

3.1. Energy-dispersive X-ray spectroscopy characterization

The elemental composition of un-doped and metal-doped TiO_2 was determined by energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum of TiO_2 photocatalyst shows that it consists of titanium and, oxygen only while the EDX spectra of cobalt, nickel, and zinc-doped titania, show the presence of doped metals, that is, cobalt, nickel, and zinc as well in their chemical structure thus, confirming the successful doping of TiO_2 [27].

3.2. Scanning electron microscopy analysis

Characterization morphology of un-doped and metal-doped titanium dioxide via scanning electron microscopy (SEM) analysis shows that titanium dioxide is in dispersed state and also formed agglomerates at some points. Fig. 1a–d represent simple TiO_2, and Co, Ni and, Zn doped TiO_2, respectively. These metals are well deposited on TiO_2 surface and doped titanium dioxide particles are bigger than pure titanium dioxide. The presence of dopant increases the catalyst particle size and causes particles to agglomerate [28].

3.3. X-ray diffraction analysis

X-ray diffraction (XRD) pattern of un-doped and doped titanium dioxide is shown in Fig. 2. Strong diffraction peaks

Table 1
Photocatalytic degradation of colorless organic compounds using un-doped and metal-doped titania as photocatalyst at optimized parameters

Catalyst used	Degradation (%)	
	Salicylic acid	Malic acid
TiO_2	0.6	1
Co/TiO_2	0.9	1.2
Ni/TiO_2	0.8	1.5
Zn/TiO_2	0.9	1.7

Table 2
Dyes degradation in the absence of catalysts under sun and UV light irradiation

Time given (min)	Dyes degradation (%)			
	Sunlight	Sunlight	UV light	UV light
	Methyl orange	Toluidine blue	Methyl orange	Toluidine blue
10	10.11	12.10	9.83	10.98
20	12.50	19.90	12.98	15.19
40	15.30	22.32	13.45	19.90
60	25.29	28.98	18.90	23.20

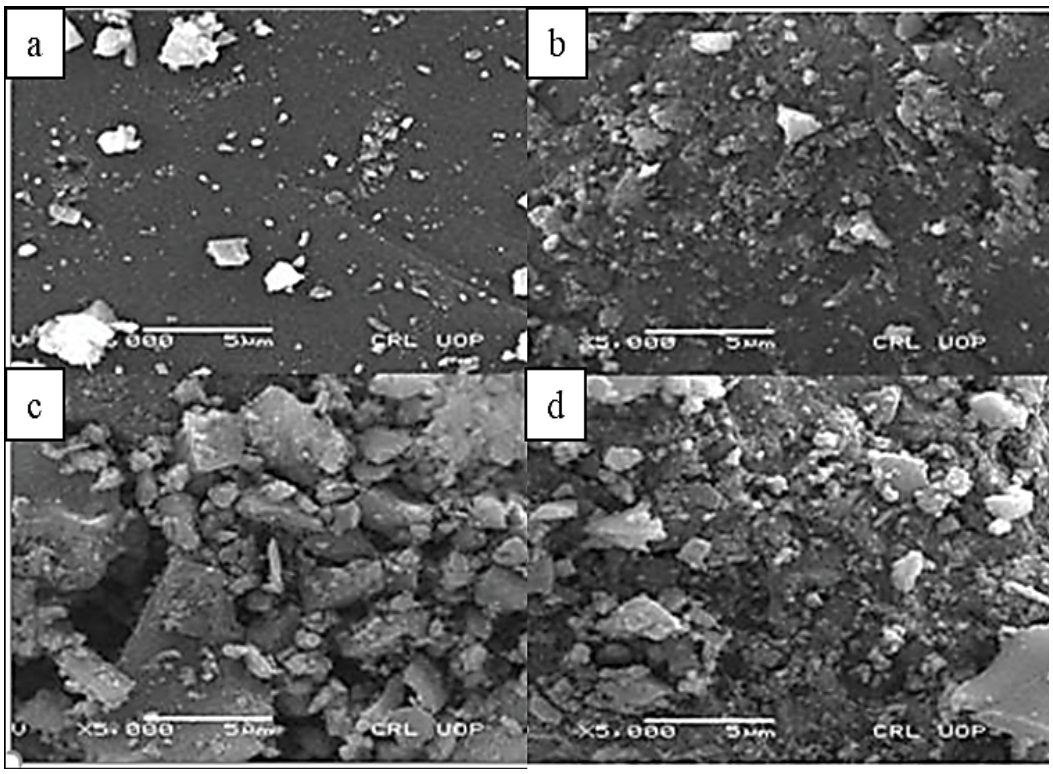

Fig. 1. SEM images of: (a) simple titanium dioxide, (b) cobalt-doped titanium dioxide, (c) nickel-doped titanium dioxide, and (d) zinc-doped titanium dioxide.

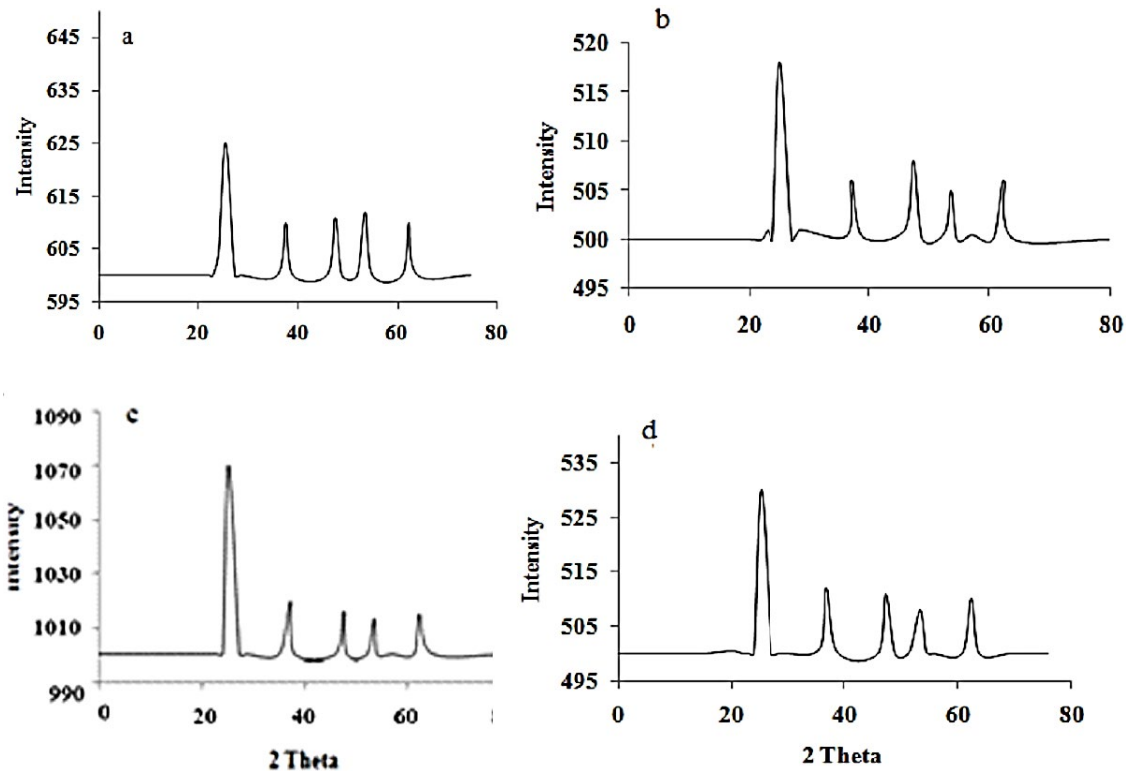

Fig. 2. XRD spectra of: (a) pure titanium dioxide, (b) cobalt-doped-titanium dioxide, (c) nickel-doped titanium dioxide, and (d) zinc-doped titanium dioxide.

at 2θ = 25.3°, 37.2°, 47.4°, 53.3°, and 62.4° are exhibited by titanium dioxide. All the peaks were comparable to the standard spectrum. It is clear from Fig. 2 that all the samples show the anatase phase regardless of the metal content. XRD patterns of metal-doped titanium dioxide samples do not exhibit any diffraction peaks of metals. This is probably due to low metal ions doping contents 1% and also the metals are well dispersed within the titanium crystal phase [29].

No characteristic peaks of doping elements (nickel, cobalt and zinc) were observed thus confirming the synthesis of a single-phase solid solution. It also suggests that in nickel, cobalt and zinc-doped titania, Ti^{4+} (0.6 Å) has been replaced with Ni^{2+} (0.72 Å), Co^{2+} (0.65 Å) and Zn^{2+} (0.74 Å) respectively [30].

3.4. Effect of reaction time

Photodegradation of both dyes was studied by varying the reaction time and the results are shown in Fig. 3. The photodegradation of methyl orange and toluidine blue initially increased upon increase in irradiation time up to 50 and 70 min for methyl orange and toluidine blue dyes, respectively, then became constant. The maximum photodegradation of methyl orange and toluidine blue dyes obtained was 75% and 80%, respectively. Further increase in time had no effect as the available active sites on catalyst surface became occupied by dyes, therefore, degradation process became constant.

3.5. Effect of catalyst amount

A series of analysis with different concentration of catalyst has been carried out for determination of the optimal amount of photocatalyst. The concentration of the photocatalyst was varied between 0.001 to 0.01 g and the results are shown in Fig. 4. The photodegradation of methyl orange and toluidine blue dyes increased from 10%–80% and 9%–85% by increasing catalyst amount from 0.001 to 0.004 g and from 0.001 to 0.008 g, respectively, and thereafter remained constant. This may be due to an increase in the number of available active sites responsible for generation of hydroxy radical as a result, the photocatalytic process becomes fast, but at higher concentration the photodegradation process becomes constant as the suspended titanium dioxide blocks the penetration of light in solution after exceeding the optimal amount [31].

3.6. Initial dye concentration effect

Initial dye concentration effect on photocatalytic process of both dyes has been examined. In the photodegradation process, the degradation of methyl orange and toluidine blue decreases by increasing dye concentration from 5–60 mg/L as shown in Fig. 5. Initially, at lower dye concentration the photodegradation was high but was observed to decreases at higher concentration. Photodegradation rate depends upon the numbers of radicals formed on the photocatalyst surface and also on probability of radical's reaction with molecules of dye. At higher dye concentration, the adsorbed dye molecules decrease the generation of reactive radicals by occupying the active sites and also inhibit the interaction of dye molecules with photocatalyst surface. Photocatalytic process also becomes slow due to absorption of light by large number of dye molecules and photons never reach the surface of photocatalyst [32].

3.7. Effect of pH

Reaction solution pH strongly affects the efficiency of photocatalytic activity due to amphoteric behavior of titanium dioxide photocatalyst. By varying solution pH, the surface charge of titanium dioxide changes. Under acidic

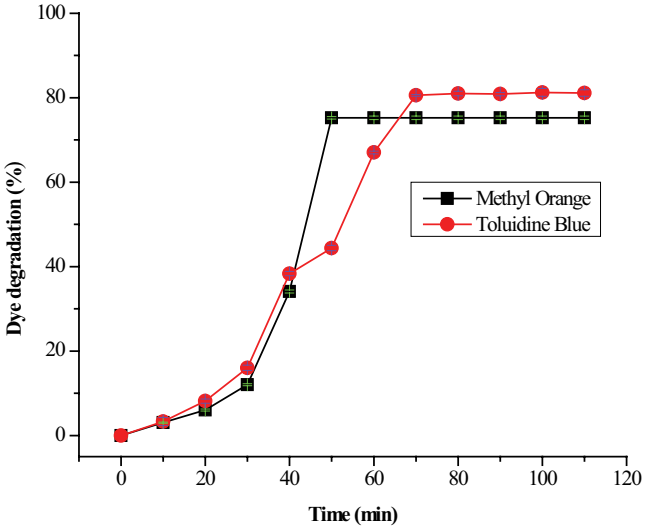

Fig. 3. Effect of time on % degradation of dyes. (Methyl orange: reaction time varied 0–110 min, pH 3, dye concentration 4 mg/L, and catalyst amount 0.008 g. Toluidine blue: time varied 0–110 min, pH 12, dye concentration 4 mg/L, and catalyst amount 0.008 g).

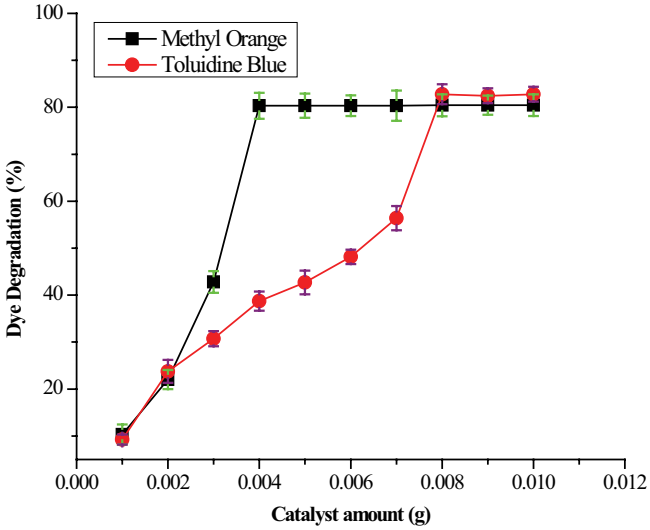

Fig. 4. Effect of amount of catalyst on % dyes degradation. (Methyl orange: reaction time 50 min, pH 3, dye concentration 4 mg/L, and catalyst amount 0.001–0.01 g. Toluidine blue: time 70 min, pH 12, dye concentration 4 mg/L, and catalyst amount 0.001–0.01 g).

solution titanium dioxide surface is positive charge and in basic solution its surface becomes negatively charged. Therefore, a series of analysis were conducted at different pH values to investigate the pH effect on the decolorization of dyes. The effect of pH was studied in the pH range 1–14. The maximum photodegradation of methyl orange and toluidine blue obtained was pH 2 and 11 respectively, as shown in Fig. 6 and then photodegradation decreased by further increase in pH gradually [33]. Being an anionic dye the adsorption of methyl orange on the positive surface of photocatalyst is higher under acidic condition therefore,

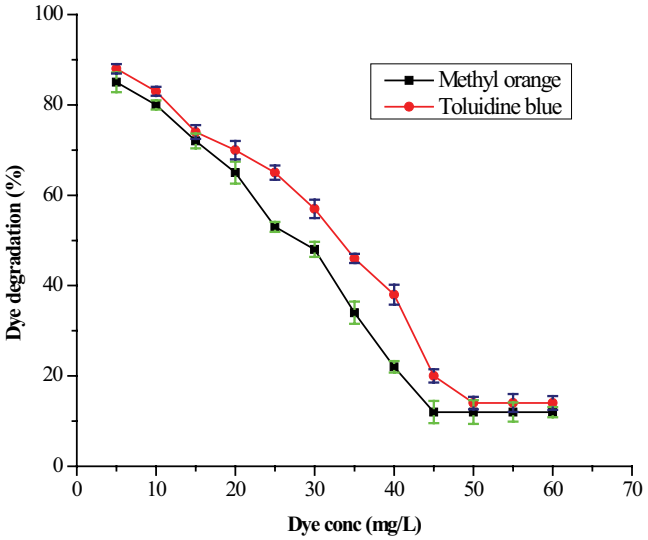

Fig. 5. Dyes degradation (%) under different initial dye concentration (5–60 mg/L). (Methyl orange: reaction time 50 min, pH 3, dye concentration 4 mg/L, and catalyst amount 0.004 g. Toluidine blue: time 70 min, pH 12, dye concentration 4 mg/L, and catalyst amount 0.008 g).

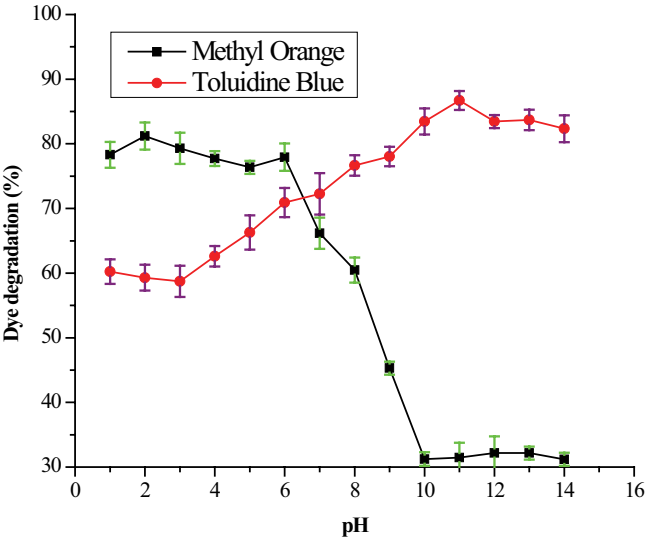

Fig. 6. Effect of pH on % dye degradation. (Methyl orange: reaction time 50 min, pH 1–14, dye concentration 4 mg/L, and catalyst amount 0.004 g. Toluidine blue: time 70 min, pH 1–14, dye concentration 4 mg/L, and catalyst amount 0.008 g).

photodegradation rate increased up to pH 2. But further increase in pH leads to decrease of photodegradation rate due to columbic repulsion between negatively charged photocatalyst surface and adsorbed anionic dye. Toluidine blue is cationic dye and its degradation was higher in basic medium being at pH 11 and then decreases at higher basic pH.

3.8. Photodegradation of subject dyes on un-doped titanium dioxide

When pure titanium dioxide was used in photodegradation of methyl orange and toluidine blue dyes the degradation obtained was 83% and 88%, respectively. The direct relationship between catalyst amount and % degradation was observed, that is, upon an increase in catalyst amount an increase in % degradation occurred, due to the production of more hydroxyl radicals.

3.9. Photodegradation subject dyes on metal-doped titanium dioxide

3.9.1. Photodegradation of cobalt-doped titanium dioxide (1 wt.%)

At the optimized conditions, that is, amount of catalyst, time, pH, dye concentration and, dopants effect on the photocatalytic degradation of subject dyes was studied. About 90% methyl orange and 93% of toluidine blue dyes were photodegraded using cobalt-doped titania (Co/TiO_2).

3.9.2. Photodegradation of nickel-doped titanium dioxide (1 wt.%)

The degradation of methyl orange in case of nickel-doped titania (Ni/TiO_2) was 92% and for toluidine blue 94% was observed. The catalytic efficiency of TiO_2 enhances upon doping with Ni metal.

3.9.3. Photodegradation of subject dyes using zinc-doped titanium dioxide (1 wt.%)

The conduction band and valence band difference of TiO_2 decreases upon doping TiO_2 with Zn which enhances the photo catalytic activity of TiO_2 and made it active optically. The removal of methyl orange achieved with zinc-doped titania (Zn/TiO_2) was 96% and that of toluidine blue was 98% under optimized conditions. The presence of Zn^{2+} as a dopant acts as follows:

$$Zn^{2+} + e^- \rightarrow Zn^+ \quad (2)$$

$$Zn^+ + O_{2(ads)} \rightarrow Zn^{2+} + O_2^{-\bullet} \quad (3)$$

$$Zn^+ + h^+ \rightarrow Zn^{2+} \quad (4)$$

$$Zn^{2+} + h^+ \rightarrow Zn^{3+} \quad (5)$$

$$Zn^{3+} + OH^- \rightarrow Zn^{2+} + OH^{\bullet} \quad (6)$$

$$Zn^{3+} + e^- \rightarrow Zn^{2+} \quad (7)$$

Due an increase in the number of O^{2-} and OH, radicals on the solid electrical layer of titanium dioxide the most effective dye degradation occurred when Zn was used as dopant.

3.10. Comparison between un-doped and metal-doped titanium dioxide

Degradation efficiency of methyl orange with un-doped TiO_2 was 83%, while with Co, Ni and, Zn doped TiO_2 was 90%, 92%, and 96% respectively. The photodegradation of toluidine blue obtained with un-doped TiO_2 was 88%. The dye remediation with Co, Ni and, Zn doped TiO_2 was 92%, 93%, and 98% respectively. These results show that the subject metals doped TiO_2 showed enhance degradation activity as compared to un-doped TiO_2 as given in Fig. 7. The subject metal ions accept electrons from valence band of TiO_2 and allow huge time separation of charge within the materials. Metal ion as dopants reduces band gap energy of TiO_2 and, further enhancement in radical's formation, therefore, increases degradation activity. Among the subject metal ion examined as dopants, excellent photocatalytic activity was observed for zinc ion suggesting the good dispersion of metal ion in the crystalline structure of titanium dioxide [32]. The proposed mechanism of they selected dyes degradation is summarized in Fig. 8.

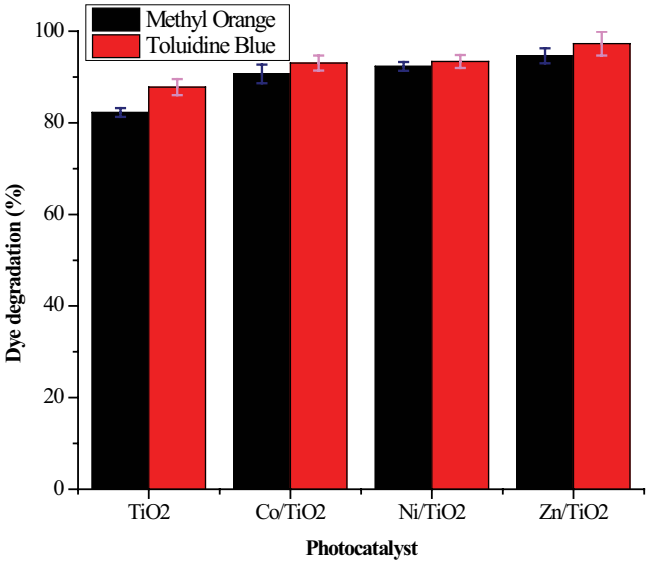

Fig. 7. Photocatalytic degradation of un-doped and metal-doped TiO_2 of methyl orange and toluidine blue dyes. (Methyl orange: reaction time 50 min, pH 2, dye concentration 4 mg/L, and catalyst amount 0.004 g. Toluidine blue: time 70 min, pH 11, dye concentration 4 mg/L, and catalyst amount 0.008 g).

3.11. Degradation of dyes in real water samples

The performances of un-doped and metal-doped TiO_2 photocatalysts under the above-mentioned optimized conditions was examined for degradation of methyl orange and toluidine blue dyes in real wastewater samples. For this purpose, wastewater of a dyeing textile industry using these dyes was collected and the presence of these dyes was first confirmed with the help of spectrophotometer and then their degradation studies were carried out using un-doped and metal-doped titanium dioxide as photocatalysts. The results obtained are given in Table 3. These results suggest that the Zn doped titanium dioxide acts the best photocatalyst for the removal of methyl orange and toluidine blue. A comparison of present adsorbent capacity with those reported in literature is given in Table 4.

4. Conclusion

Photocatalytic degradation of methyl orange and toluidine blue dyes employing metal-doped TiO_2 was found very effective for the degradation of the subject dyes-contaminated samples as compared to un-doped titania. Co, Ni and Zn metals were used as dopants and it was found that Zn doped TiO_2 are best catalysts for photodegradation of methyl orange and toluidine blue dyes in an aqueous medium as compared to Co and Ni doped and un-doped titania. Different characterization techniques confirmed the successful doping of titania with Ni, Co and Zn. The effect of increasing pH, irradiation time, catalyst dosage, and initial dye concentration was investigated. The rate of degradation decreased with increasing the initial dye concentration and a linear relationship was found with catalyst amount at pH 2 and 11.

Author contributions

A.S. carried out the main experimental work, M.S.; Encouraged, supervised the findings of the work and took

Table 3
Comparison of un-doped and metal-doped titanium dioxide catalysts for subject dyes degradation from textile water sample at optimized conditions of pH, time and catalyst amount

Type of catalyst	Initial dye present in water sample (mg/L)	Dye degradation %	Dye degradation %
		Methyl orange	Toluidine blue
TiO_2	5	82	84
Co/TiO_2	5	89	91
Ni/TiO_2	5	92	95
Zn/TiO_2	5	93	96

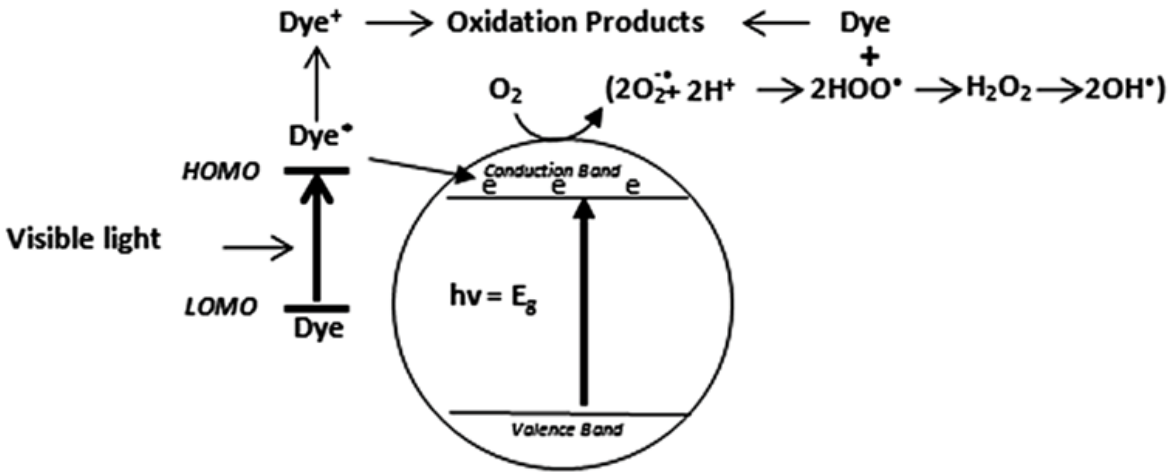

Fig. 8. Proposed mechanism of methyl orange and toluidine blue dyes degradation using metal-doped titania as photocatalyst.

Table 4
Comparison of current work with reported work

Catalysts	Degradation %		Reference
	Methyl orange	Toluidine blue	
TiO_2	70	NA	[34]
TiO_2	74	NA	[35]
TiO_2	NA	68	[36]
TiO_2	NA	72	[37]
TiO_2	82	84	Current work
Co/TiO_2	73	NA	[38]
Co/TiO_2	76	NA	[39]
Co/TiO_2	NA	74	[40]
Co/TiO_2	NA	77	[41]
Co/TiO_2	89	91	Current work
Ni/TiO_2	81	NA	[42]
Ni/TiO_2	83	NA	[43]
Ni/TiO_2	NA	82	[44]
Ni/TiO_2	NA	84	[45]
Ni/TiO_2	92	95	Current work
Zn/TiO_2	83	NA	[46]
Zn/TiO_2	82	NA	[47]
Zn/TiO_2	NA	83	[48]
Zn/TiO_2	NA	85	[49]
Zn/TiO_2	93	96	Current work

the lead in writing the manuscript. J.K.: helped in writing the manuscript. I.Z., and M.Z.; Contributed to the interpretation of the results and writing the original and revised version of the paper. All authors provided critical feedback and helped, shape the research, analysis and manuscript.

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Conflicts of interest

The authors declare that they have no conflicts of interest.

Data availability

All the data associated with this research has been presented in this paper.

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Symbols

C_0	—	Original concentration of dye, mg/L
C	—	Final concentration of dyes, mg/L
Co/TiO_2	—	Cobalt-doped titania
Ni/TiO_2	—	Nickel-doped titania
Zn/TiO_2	—	Zinc-doped titania

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