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Photocatalytic degradation of azo dye Reactive Red 15 over synthesized titanium and zinc oxides photocatalysts: a comparative study

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ABSTRACT

Nanoparticle TiO_2 and ZnO were prepared by facile method. The XRD pattern study shows that there is no obvious difference in crystal composition of various shapes of TiO_2 and ZnO. The photocatalytic degradation of Reactive Red 15, commonly used as a textile dye, using synthesized titanium and zinc oxides was investigated. The effects of influential parameters such as initial pH, catalyst loading, initial dye concentration and addition of hydrogen peroxide were studied. The degradation efficiency was expressed by the removal of color and chemical oxygen demand (COD). The study reveals that: (1) Both catalysts, under corresponding optimal conditions, can be employed as an effective photocatalyst for the elimination of color and COD from dye wastewater. Also, ZnO is more efficient catalyst than TiO_2; (2) Addition of proper amount of hydrogen peroxide improves both the decolorization and the degradation of the dye; (3) The photocatalytic degradation of Reactive Red 15, in the presence of both photocatalysts, obeyed pseudo-first order kinetics. The biodegradability ratio BOD_5/COD increases from original zero up to 0.52 and 0.6 within 90 minutes irradiation time using 1 and 0.75 g/L TiO_2 and ZnO, respectively.

Keywords: Nanoparticle, Photocatalytic oxidation, Titanium dioxide, Zinc oxide, Azo dyes, Reactive Red 15, Biodegradability

1. Introduction

Textile dyeing and finishing industry is one of the major pollutants among industrial sectors. Color in textile effluents is particularly a consequence of dyeing cotton products with reactive dyes; since up to 30% of the used dyestuffs remain in the spent dye-bath after the dyeing process [1]. Synthetic dyes are toxic refractory chemicals, which can generate intensive hazardous color to the environment. About 70% of reactive dyes are of azo type. In the washing process, about 50% of a reactive dye is exhausted in hydrolyzed and unfixed forms [2]. These dyes resist aerobic biodegradation [3,4]. Where, anaerobic treatment has ability for removal of the colors of azo dyes by transforming the azo bond to aromatic amines [4–6]. These amines are carcinogenic and they are more dangerous than the parent dyes. Many technologies including physical,

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chemical and biological methods have been developed to deal with environmental pollution [7–10]. But, the current dye-house wastewater treatment methods are ineffective to completely remove the dye from effluent streams. In recent years a new set of technologies termed advanced oxidation processes (AOPs) for removing treatment of pollutants in from both water and wastewater has become the focus of many researches [11]. Among them, the photocatalytic oxidation process using photocatalysts is a promising alternative for treatment of polluted water [12–14]. This method is based on the illumination of semiconductors such as TiO_2, ZnO, Fe_2O_3, CdS and ZnS which can be induced to the electron–hole pairs due to their electronic structure by photons with a proper energy level. The valence band holes are powerful oxidants (+1.0 to +3.5 V vs. NHE depending on the semiconductor and pH), while the conduction band electrons are good reductants (+0.5 to 1.5 V vs. NHE). These species subsequently either recombine or react with the adsorbed electron donors and acceptors on the surface of the semiconductors [15,16]. Titanium dioxide (TiO_2) in anatase form is the best semiconductor with high stability, more efficiency and low price that is widely used for photocatalytic process. TiO_2 is successfully used as a photocatalyst for the treatment of organic [17–24] and dye pollutants [25–27]. Another photocatalyst that has a similar property of TiO_2 is zinc oxide (ZnO) that has widest application after TiO_2. The photocatalytic degradation mechanism of ZnO is similar to that of TiO_2 [28,29]. In some cases, ZnO was more effective than TiO_2 [30–33]. The aim of this work is to prepare and characterize TiO_2 and ZnO and study the photocatalytic degradation of one of reactive dye using synthesized TiO_2 and ZnO. The effect of important parameters such; pH, catalyst loading, initial concentration of the dye and hydrogen peroxide on the color removal and the degradation of the dye will be investigated.

2. Experimental

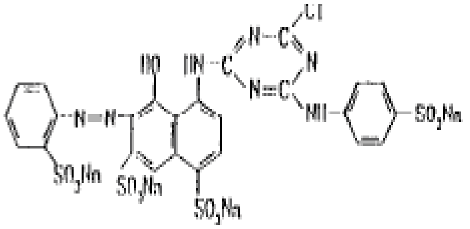
2.1. Chemicals used

Titanium chloride ($TiCl_4$), ethanol, and ammonia were supplied from Sigma–Aldrich (Germany) with any purification. Hydrochloride acid and sodium hydroxide were supplied from Fisher-Scientific (UK). (Reactive Red 15 as one of azo dyes group, provided from Uni–Impex-India, was used as received without any purification. Such type of dye is characterized with its toxicity and its refractory properties to be treated with the traditional wastewater treatment. The chemical structural and the chemical proprieties of the dye are listed in Table 1.

2.2. Set-up

The photocatalytic oxidation experiments were carried out using a cylindrical photoreactor as shown in Fig. 1. It is of 0.85 L volume, made from quartz, with a coaxial and immersed medium pressure UV mercury lamp was used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100 < \lambda < 280$ nm) range (indication Heraeus), corresponding to photonic flux of 1.32×10^{-5} Einstein s^{-1}. The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater at room temperature. There is one cooling circle for cooling UV lamp. The UV system is placed positioned coaxial inside the reactor vessel. The UV system is made from quartz glass, which is available for the transfer of UV irradiation. The reaction chamber is filled with the wastewater, which is between the reactor walls and UV lamp system. Mixing was accomplished by means of the magnetic stirring.

Table 1
Chemical properties and structure of Reactive Red 15

Name	Structure	BOD_5 (mg/L)	COD (mg/L)	BOD_5/COD
Reactive Red 15		0	72.80	0

COD: chemical oxygen demand.
BOD_5: biological oxygen demand.

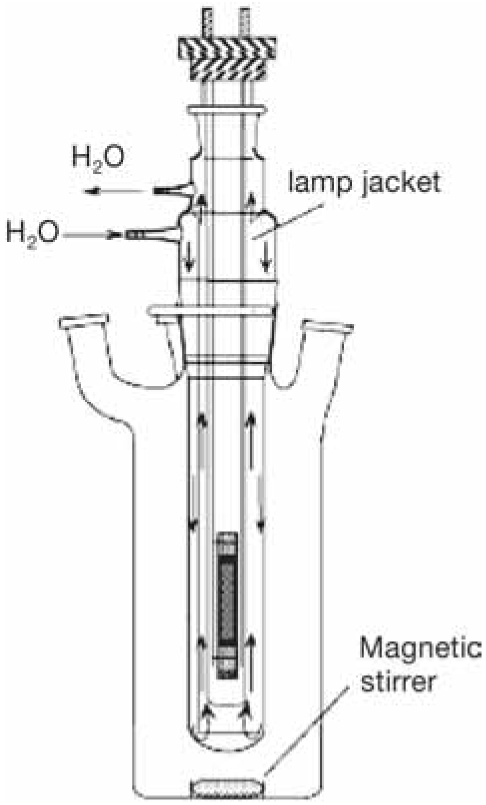


Fig. 1. Batch photoreactor used in the study.

2.3. Procedure

The laboratory photoreactor was filled separately with 0.85 L of the dye solution taken under study. The optimum conditions for UV/TiO_2 and UV/ZnO treatments were investigated. The pH of the solution was adjusted to the desired value with HCl (1 N) or NaOH (1 N), and kept at the same value during the reaction. Then amount of photocatalyst was added into the mixing vessel. The solution was continuously aerated and circulated for 30 min to reach equilibration in the darkness. The lamps were then switched on to initiate the photoreaction. Samples for the analysis of color and COD (5mL) were taken at regular time intervals then centrifuged and catalyst particles were separated. When hydrogen peroxide is added in some experiments, the pH of the phototreated samples was adjusted to 7 to quench the samples and stop the reaction of the peroxide.

2.4. Analytical methods

The percent of color removal of the dye in the reaction mixture at different times was obtained by measuring absorbance at maximum wavelength and computing the concentration from calibration curve. A PD-303 UV spectrophotometer (APEL Type), from Japan was employed for absorbance measurements. Chemical oxygen demand (COD) was carried using dichromate solution as the oxidant in strong acid media, colorimetric method [34].

2.5. Preparation and characterization of photocatalysts

2.5.1. Preparation of TiO_2

Titanium dioxide (TiO_2) powder used in this study was synthesized by the conventional sol–gel process. $TiCl_4$ was first dissolved in an ethanol/water (volume ratio of 4:1) solution, and ammonia was then introduced into the solution until pH reached ca 7.5 to induce precipitation. The resulted gelatinous precipitate was filtered and washed with de-ionized water to reduce [Cl^-] to below 5×10^{-4} M, as determined by titration against standard solution of silver nitrate, and then kept at 80 °C for several hours in air to remove excess ammonia. The resulted powder was then dried and calcined to get the catalyst. The calcination process involved purging the reactor with the gas for 1 h, heating the powder at a rate of 40 °C/h to 450 °C. Finally the powder was calcined at 450 °C for 4 h.

2.5.2 Preparation of ZnO

Zinc oxide was prepared by dissolution of special high grade zinc metal in hydrochloric acid. The resulted solution was cooled to below 15 °C, left at this temperature for 24 h and then filtered. Zinc hydroxide was precipitated by ammonia solution. After holding the resulted mixture for several hours, zinc hydroxide was separated by filtration using water pump and thoroughly washed with de-ionized water to remove remaining chlorides. The produced solid was dried at 60 °C, in stagnant air, using an electric drier. The dried material was then calcined isothermally in an electric furnace at 500 °C for 4 h.

2.6. Characterization of catalysts

Characterization of the produced oxides was done by using X-ray diffraction analysis (XRD) using Philips diffract meter (40 kV, 30 mA) with nickel filter and copper radiation; the scanning angular range was from 10° to 80°, X-ray fluorescence spectrometry (XRFS) obtained by the analyzer was AXIOS, WD-XRF Sequential Spectrometer-PAN anlytical 2005. The specific surface area, pore size and pore volume of the samples were measured using a Sorptomatic (Model-1990) instrument al 77 K. Prior to the sorptometric experiment, the samples were degassed at 423 K for 12 h.

3. Results and discussion

3.1. Characterization of catalysts

XRD patterns for TiO_2 and ZnO are shown in Fig. 2. The peaks in Fig. 2a X-ray diffraction patterns (XRD) of prepared photoctalysts showed Fig. 5a and b by sol–gel method and further submitted to thermal treatment at 450 °C, the diffraction lines present at 25.2°, 38.7°, 48.1°, and 68.7° in 2θ value, correspond to the anatase phase TiO_2, which represent the indices of (1 0 1), (0 0 4) and (2 0 0) planes, respectively, are confirmed to anatase. Other peaks XRD present at 2θ of 27.6°, 36.2°, 41.1°, 44.2°, 54.4°, 56.8°, 62.9°, 64.2° and 69.2° indicates the formation of rutile phase [36]. Fig. 2b showed XRD patterns of prepared ZnO, that displays the dominant diffraction lines at 2θ values of 36.65°, 39.44° and 41.49° corresponding to (2 0 0) and (2 1 0) planes of cubic phase of ZnO. The broadness of the peaks of XRD lines indicates formation of nanopartices crystalline. In consequence, the well-prepared TiO_2 and ZnO crystal size is calculated from the maximum diffraction peak at Fig. 5a and 5b by Scherrer formula [35], ($d = K\lambda/ß\cos\theta$, where d is the crystallite size, K the Sherrer constant of 0.89, λ is the wavelength of the X-ray radiation (0.15418 nm for Cu Ka), and $ß$ is full width half maximum of diffraction peak measured at 2θ), the average crystalline particle sizes of prepared TiO_2 and ZnO powders are about 41.88 and 49.9 nm, respectively. X-ray fluorescence spectrometry (XRFS) analysis for TiO_2 and ZnO is shown in Tables 2 and 3. These analysis empasized that only TiO_2 and ZnO content in each photocatalyst respresented more 99.75% and 99.56 %, respectively. The surface area of the prepared TiO_2 and ZnO was determined by the BET method is 59 and 40.3 m^2/g, respectively.

3.2. Efficiency of photocatalytic oxidation

3.2.1. Dye degradation

The degradation of Reactive Red 15 dye in terms of COD is shown in Fig. 3. Preliminary runs were performed in presence of photocatalyst without irradiation

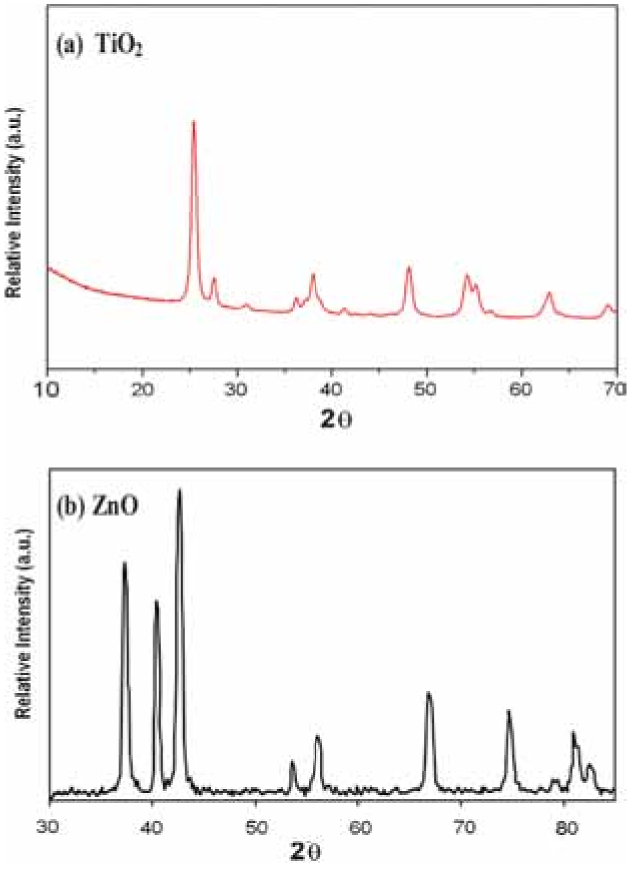


Fig. 2. XRD pattern of the prepared photo catalysts (a) TiO_2, (b) ZnO.

Table 2
Composition of TiO_2

Constituent	Weight %
TiO_2	99.78
MgO	0.03
Al_2O_3	0.05
CaO	0.04
ZnO	0.02
Na_2O	0.04
SO_3	0.01
Cl	0.03

Table 3
Composition of ZnO

Constituent	Weight %
ZnO	99.546
SiO_2	0.118
Al_2O_3	0.093
F_2O_3	0.086
CaO	0.053
NiO	0.021
SO_3	0.01
Cl	0.071

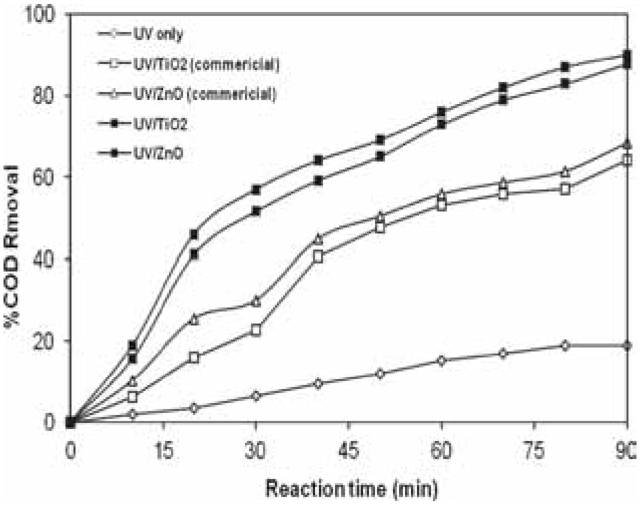


Fig. 3. Effect of UV light and UV with different photocatalyst on degradation of Reactive Red 15 dye (Catalyst loading 1 g/L, pH = 6, initial dye concentration = 100 ppm).

using initial dye concentration of 100 ppm and a catalyst loading of 1 g/L, to investigate the adsorption of this dye on the surfaces of the used catalysts. The results showed that there is no significant removal of COD level even after 180 min. Also, photolysis experiments were performed under UV irradiation and, in the presence of different photocatalysts. Removal of COD was reduced by 19% in the direct photolysis within 90 min. But COD removals were increased by introduction of photocatalyst due to generation of free radicals after irradiation of TiO_2 and ZnO in dye solution. The degradation of the dye reduced by 56%, 58%, 86%, 88 % in presence of ZnO (sigma), TiO_2 (Aldrich), prepared TiO_2 and prepared ZnO, respectively. The results indicated that the observed high decomposition in the UV/photocatalyst process is exclusively attributed to the photocatalytic reaction on the semiconductor particles. It has been investigated that the photocatalytic degradation of dye is initiated by photoexcitation of the semiconductor to electron–hole pairs on the catalysts surfaces [36]. Daneshvar et al. performed the photocatalytic degradation of Diazinon [29] and azo dye Acid Red 14 [32] using TiO_2 and ZnO. They are reported that the adsorption of these contaminants on the photocatalysts surface was not considerable and the removal of these pollutants was related to the photocatalytic oxidation process. From the figures, it is obvious that the photodegradation, represented by COD removal of dye is time-dependent and increases by increasing the irradiation time. This trend was similar for both photocatalysts. Also, prepared ZnO and TiO_2 was more efficient in dye degradation under UV irradiation rather than commercial ones that because they are nanopartices size photocatalyst and thus photocatalytic activity increases with decreasing particle due to the retardation of the electron–hole recombination. Anpo et al. [37] noted that the activity increases with decrease in particle size. According to them, reduction in particle size might result in some electronic modification of TiO_2 and produce an enhancement of the activities of electrons and holes and/or suppression often radiation less transfer of absorbed photon energies. Similar results were reported by Xu et al. [38] from the study on the photocatalytic degradation of methylene blue in aqueous suspensions.

3.2.2. Decolorization

Fig. 4 shows the color removal of the Reactive Red 15 by photocatalytic oxidation using the prepared TiO_2 and ZnO. Complete color removal needed up to 40 min when ZnO was used while 50 min irradiation time were needed when utilizing TiO_2; the complete removals of COD required prolonged irradiation as shown in Fig. 3.

Obviously, decolorization process is easier than the COD removal. COD began to decrease markedly after the complete removal of color. After 50 min irradiation time, the color of the dye was completely disappeared with 66.3% COD removal using TiO_2, while after 40 min irradiation time, the color of the dye was completely disappeared with a corresponding 54.7% COD removal using ZnO, thus ZnO acts as photomediator that enhancing corresponding reaction rate.

3.3. Effect of the operating conditions

3.3.1. Effect of pH

The influence of initial pH on the photocatalytic process is more complex and the observed effect is

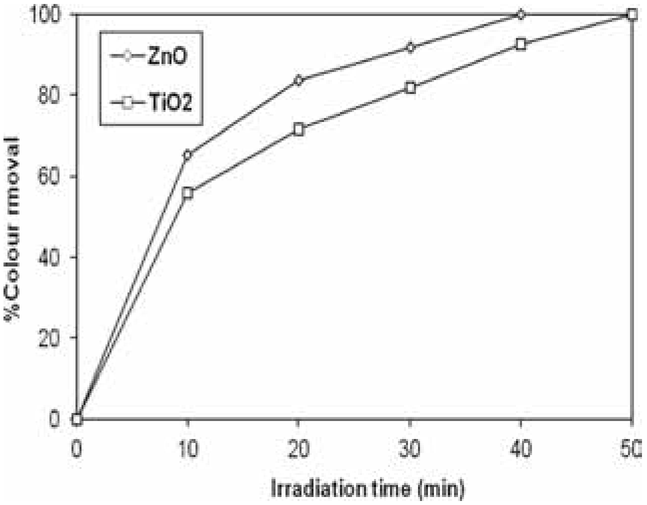


Fig. 4. Color removal with the photocatalytic oxidation of Reactive Red 15 dye with TiO_2 and ZnO. (Catalyst loading 1 g/L, pH = 6 and 9 for TiO_2 and ZnO, respectively, initial dye concentration = 100 ppm).

generally dependent on the type of pollutant and the zero point charge (zpc) of photocatalyst used in the oxidation process [12]. The pH of solution influences the surface charge properties of the photocatalyst since it has significant effects on the electrostatic interaction between the catalyst surface and the pollutant molecules. Therefore, the effect of pH of the initial substrate on the removal of a key parameter must be investigated. Measurement of an overall parameter as COD might be used for choosing the optimum pH, or at least to determine the effect of pH on the behavior of the chosen key parameter. Fig. 5 illustrates the effect of pH values on the % COD removals for the Reactive Red 15 dye by photocatalytic oxidation with TiO_2 and ZnO at the same catalyst loading and irradiation time.

The results indicated that the COD removal rates increased with increasing pH up to 6 and 9 for TiO_2 and ZnO, respectively, and decreased thereafter. It was previously shown that the zero point charge (zpc) of TiO_2 and ZnO are 6.25 and 9.3 [39,40], respectively. Therefore, the best pH of the treated solution should be limited to these two values, when using TiO_2 or ZnO, because the electrostatic interaction among the Reactive Red 15 dye anions and positive surface of catalyst is enhanced [29,30]. At pH above the pH_{zpc}, the number of negatively charged sites on the photocatalyst surface increased. A negatively charged surface site is not favored due to the increased electrostatic repulsion. Thus, pH values of 6 and 9 are the best initial pH values for TiO_2 and ZnO, respectively in the photocatalytic decomposition of dye. The effect of pH on the photocatalytic degradation of various organic pollutants was studied by other researchers and the similar results were observed [31,33,40].

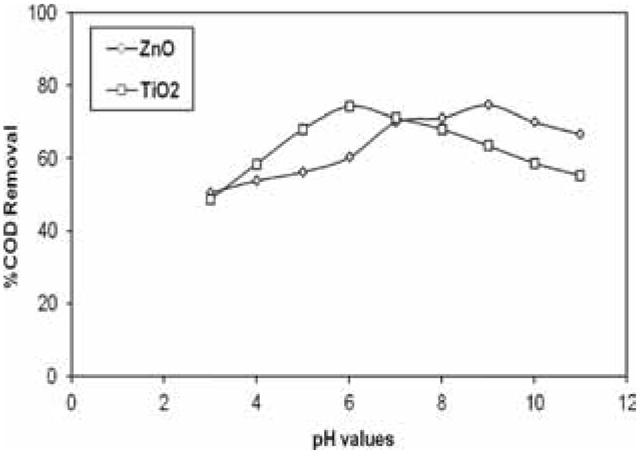


Fig. 5. Effect of pH values on photocatalytic oxidation of Reactive Red 15 with TiO_2 and ZnO. (catalyst loading 1 g/L, irradiation time 60 min, initial dye concentration=100 ppm).

3.3.2. *Effect of catalyst loading*

The effect of catalyst loading on degradation of the dye is shown in Fig. 6 for TiO_2 and ZnO. The catalyst loading changed from 0.25 to 1.25 g/L on 0.25 intervals. The figure shows that the % COD removal was enhanced, for both of photocatalysts, when the amount of catalyst in the reactor increased up 1 and 0.75 g/L for TiO_2 and ZnO, respectively and then decreased. It should be pointed out that, the catalyst loading affects both the number of active sites on photocatalysts and the penetration of UV light through the suspension. With increasing catalyst loading the number of active sites increases, but the penetration of UV light decreases due to shielding effect [41]. The catalyst loading increases, the number of active sites increases but the penetration of UV light decreases due to shielding effect [41]. Photocatalytic degradation rate, which is influenced by both the number of active sites and the penetration of UV light, therefore pass through a maximum at the optimum catalyst loading. Similar results were observed previously by others for instance the optimum value of catalyst loading was reported to be 2 g/L TiO_2 for photocatalytic degradation of monocrotophos [40], 1.66 g/L TiO_2 for photocatalytic removal of phenol [45], 4 g/L ZnO and 4 g/L TiO_2 for photocatalytic degradation of azo dyes Acid Red 18 and Reactive Orange 4, respectively [28,42].

It should also be noted that the optimum value of catalyst loading is strongly dependent on the type and initial concentration of the pollutant and the operating conditions of the photoreactor [13]. In present study,

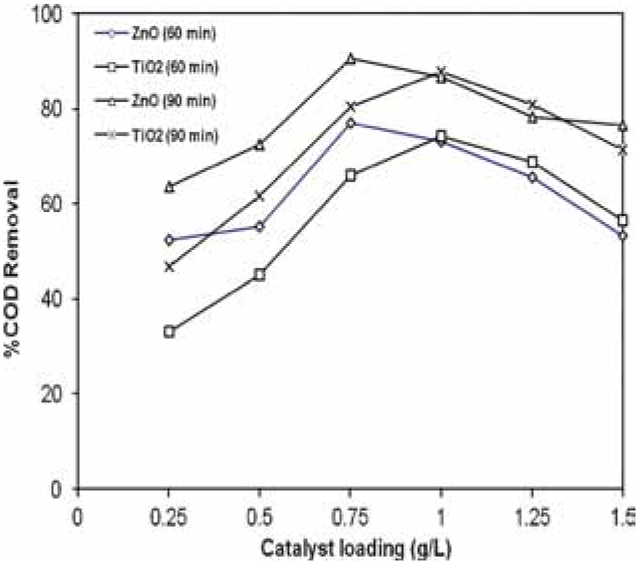


Fig. 6. Effect of catalyst loading on photocatalytic oxidation of Reactive Red 15 with ZnO and TiO_2. [pH = 6 and 9 for TiO_2 and ZnO, respectively, irradiation time 60 and 90 min, initial dye concentration = 100 ppm].

the optimum catalyst loading for TiO_2 was 1 g/L with corresponding 74.1% and 87.8% COD removals after 60 and 90 min. irradiation time, respectively, and pH value of 6. Whereas, the optimum catalyst loading for ZnO was 0.75 g/L with corresponding 76.9% and 90.5% COD removals after 60 and 90 min. irradiation time, respectively, and pH equals 9.

3.3.3. Effect of initial dye concentration

Figs. 7 and 8 show the plot of $\ln(COD_0/COD)$ vs. time at different initial concentrations of Reactive Red 15 dye at the optimum operating conditions (TiO_2: catalyst loading 1 g/L, pH = 6; ZnO: catalyst loading 0.75 g/L, pH = 9). As can be seen from these plots, the photocatalytic degradation of the dye containing TiO_2 and ZnO follows pseudo-first-order kinetics at low initial dye concentration.

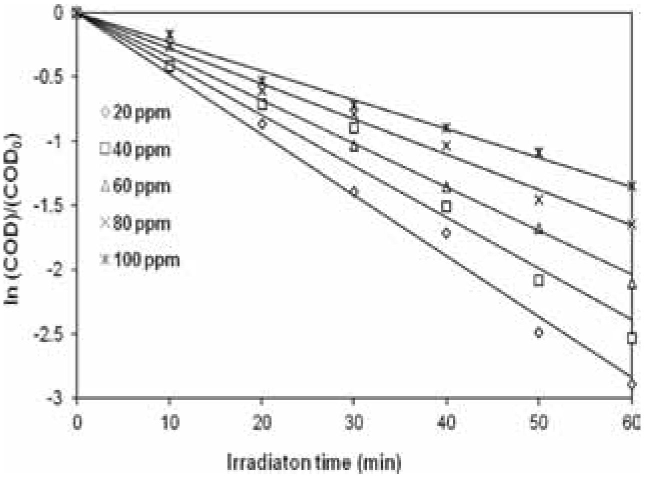


Fig. 7. Pseudo-first-order kinetic representation for the photocatalytic oxidation of Reactive Red 15 dye with TiO_2. [TiO_2: catalyst loading 1 g/L, pH = 6].

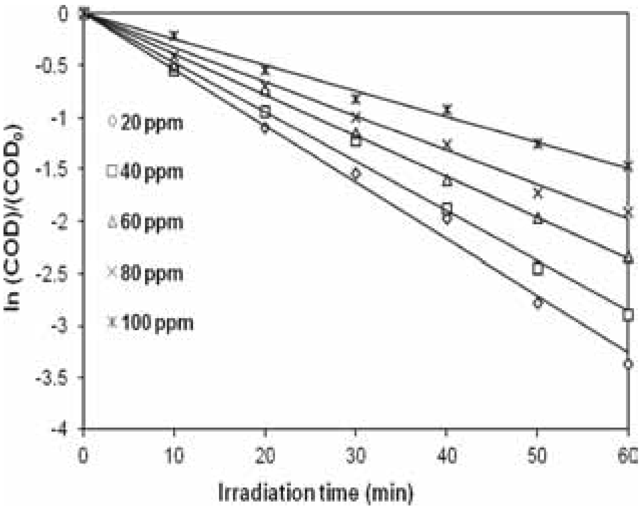


Fig. 8. Pseudo-first-order kinetic representation for the photocatalytic oxidation of Reactive Red 15 dye with ZnO. [ZnO: catalyst loading 0.75 g/L, pH = 9].

The rate expression is, therefore, represented by the following equation:

$$r_A = -\mathrm{dCOD}/\mathrm{d}t = k * \mathrm{COD} \qquad (1)$$

where, r_A, COD and k are the rate of photocatalytic degradation reaction, the chemical oxygen demand and the pseudo-first-order rate constant, respectively. Integration of Eq. 1 gives:

$$\ln(\mathrm{COD}/\mathrm{COD}_0) = -kt \qquad (2)$$

where COD_0 is the initial chemical oxygen demand of the dye and COD is chemical oxygen demand at time t.

The pseudo-first-order rate constant k can be determined by fitting the experimental data with this model. The rate constants and correlation coefficients (R^2) for all experiments are shown in Table 4. The high values of R^2 in the modeling of all cases confirm that the photocatalytic degradation of Reactive Red 15 dye using TiO_2 and ZnO obey pseudo-first-order kinetics.

The results in Table 4 reveal that the pseudo-first-order kinetic constant (k) decreases with increasing the initial concentration of the dye. This can be related to the decrease in the number of active sites on the catalyst surface, which is proportional to the initial concentration of the dye. Thus, the rate of hydroxyl radical generation on the catalyst surface, accordingly, will decrease. Similar results have been reported by other researcher for the photocatalytic oxidation of pollutants [30,42–48].

Table 4
The values of k and R^2 for the photocatalytic degradation of Reactive Red 15 dye with TiO_2 and ZnO at the optimum conditions

Initial dye concentration (mg/L)	TiO_2		ZnO	
	k (min^{-1})	R^2	k (min^{-1})	R^2
20	0.0473	0.991	0.0543	0.992
40	0.0398	0.973	0.0476	0.992
60	0.0340	0.990	0.0393	0.996
80	0.0276	0.992	0.0330	0.993
100	0.0226	0.991	0.0248	0.991

3.3.4. Effect of addition of hydrogen peroxide

The photocatalytic degradation of dye was studied at different hydrogen peroxide concentrations from 1 to 4 ml/L. The obtained data are represented in Fig. 9. The % COD removal increased with adding the H_2O_2 under the UV irradiation with using TiO_2 and ZnO. In addition, the optimum concentration of H_2O_2 was investigated in the experiment series. The results indicated that increasing H_2O_2 concentration to 2 ml/L had a positive effect on the % COD removals. H_2O_2 is a powerful oxidant and electron acceptor so it can trap the electron of the electron–hole pair photogenerated in the reaction (H_2O_2 + e–$OH^\bullet$ + OH^-); therefore, inhibits the electron–hole recombination. Also, hydrogen peroxide under UV irradiation is split and produces hydroxyl radicals (H_2O_2 + *hv*–$2OH^\bullet$). So the number of hydroxyl radicals generated in the photoreaction is directly proportional to the hydrogen peroxide concentration [49,50]. As can be seen from the results when the hydrogen peroxide concentration increased behind 2 ml/L, the % COD removals decreased. This can be explained that H_2O_2 can act as a radical scavenger. When the hydroxyl radicals are formed in the reaction, additional hydrogen peroxide usually recombines with the dissociated hydroxyl radicals and decreasing the photocatalytic oxidation efficiency [11,32].

3.4. Biodegradability

A ratio of BOD_5/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD_5/COD is more than 0.3, the wastewater has a better biodegradability. Whenever the ratio is less than 0.3, the wastewater is difficult to be biodegraded [51,52]. In our study the initial BOD_5/COD for Reactive Red 15 dye before any treatment equals zero, which means, the dye is non-biodegradable and it is difficult to be biologically treated; since it inhibits the respiratory activity of bacterial seed due to its toxicity. To investigate the biodegradability of the dye solution after photocatalytic treated with TiO_2 and ZnO, the ratio of BOD_5/COD were measured at the optimum operating conditions for either photocatalyst and also at the time when the color of the dye was disappeared. As shown in Fig. 10, the results indicate that ratio of BOD_5/COD increased after treatment of the dye with the both tested photocatalysts. As noticed also in Fig. 10, the % COD removal decreased during photocatalytic oxidation. The increase of BOD_5/COD may imply that biodegradability can be enhanced by the photocatalytic oxidation converting nonbiodegradable organics in the dye to biodegradable forms. At optimum operating conditions of the photocatalytic oxidation with TiO_2 (catalyst loading 1 g/L, pH = 6) and ZnO (catalyst loading 0.75 g/L, pH = 9), the ratio of BOD_5/COD reached 0.52 and 0.6 using TiO_2 and ZnO, respectively, within 90 min irradiation time. Fig. 10 also indicates that BOD_5/COD reached 0.3 and 0.35 for TiO_2 and ZnO, respectively, within 50 and 40 min irradiation time; these are the times when the color of the dye completely disappeared. This indicates that initial dye is not biodegradable; however, the biodegradability increased as indicated by the increase of BOD_5/COD of dye solution when the color was completely disappeared. The

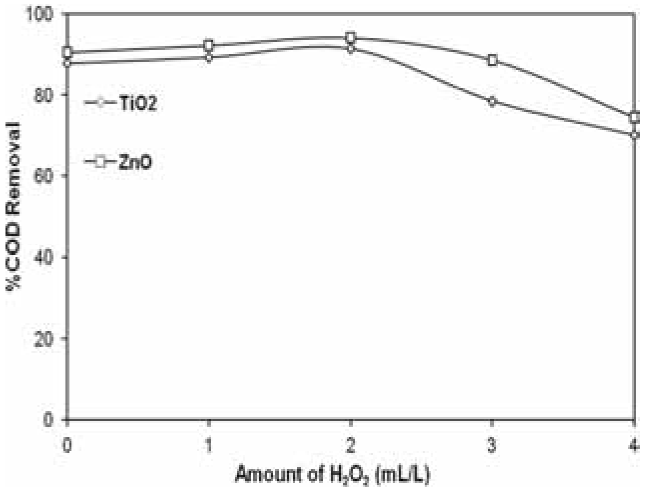


Fig. 9. Effect of addition of H_2O_2 on the photocatalytic oxidation of Reactive Red 15 dye with TiO_2 and ZnO. (Irradiation 60 min; initial dye concentration = 100 ppm, TiO_2: catalyst loading 1 g/L, pH = 6; ZnO: catalyst loading 0.75 g/L, pH = 9].

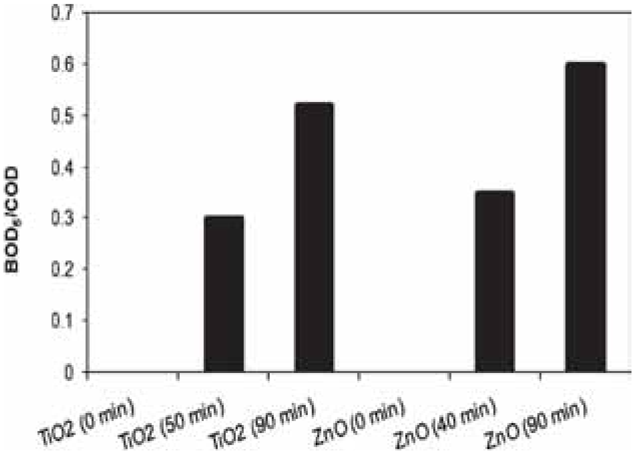


Fig. 10. Ratios of BOD_5/COD of Reactive Red 15 dye after photocatalytic oxidation using TiO_2 and ZnO. (TiO_2: pH = 6, catalyst loading 1 g/L, irradiation time 50 and 90 min; ZnO: pH = 9, catalyst loading 0.75 g/L, irradiation time 40 and 90 min; initial dye concentration=100 ppm).

byproducts arising from decolorization reaction can be biodegraded by biological processes for the tested dye solution. These results confirm the interactive relationship between decolorization and biodegradability in which both the complete decolorization and the improved the biodegradability of the dye solution were achieved at the same time. Therefore reasonable irradiation time may be the period for complete decolorization if mineralization is not the final target by the single photocatalysis. The result implies that photocatalytic oxidation enhanced the biodegradability of the dye–solution and therefore relationship between decolorization and biodegradability exists. When the color disappeared completely, the water containing the dye biodegraded normally and could be discharged for further treatment. The experimental results demonstrate that it is possible to combine photocatalysis with conventional biological treatment for the remedy of wastewater containing generally non-biodegradable azo dyes using the both prepared photocatalyts in this study.

4. Conclusion

This work concludes that:

1. Nanosized TiO_2 and ZnO was prepared with crystalline 41.88 and 49.9 nm, respectively.
2. Photodegradation of Reactive Red 15 dye in presence of UV light alone is very slow process. The addition of TiO_2 and ZnO remarkably accelerated this process.
3. Photocatalytic oxidation efficiency increased with irradiation time, catalyst loading up to 1 and 0.75 g/L using TiO_2 and ZnO, respectively, and also by addition of small amounts of H_2O_2.
4. Initial pH values of 6 and 9 were found to be the optimal pHs for the utilization of TiO_2 and ZnO as photocatalysts, respectively.
5. The photocatalytic oxidation of Reactive Red 15 dye followed a pseudo-first-order kinetic model.
6. At optimum operating conditions the COD removals were 87.8% and 90.5% using TiO_2 and ZnO, respectively. Zinc oxide was a more efficient catalyst than TiO_2 under corresponding optimum conditions.
7. The ratio BOD_5/COD increases with increasing irradiation time; this indicates that the biodegradability of the wastewater can be enhanced by photocatalytic oxidation. The BOD_5/COD of the dye solution reached 0.3 and 0.35 after the photocatalytic oxidation of the dye with TiO_2 and ZnO, respectively.
8. The photocatalytic process can be an alternative for decolorization and further COD removal of the dye from wastewater as a pre-treatment step of conventional biological process.

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