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Methyl red degradation under UV illumination and catalytic action of commercial ZnO: a parametric study

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ABSTRACT

Photocatalytic efficiency of commercially available low-cost ZnO material was evaluated for methyl red (MR) degradation under UV illumination. Photocatalytic reaction system was optimized in terms of dose of catalyst, pH, removal of chemical oxygen demand (COD), intensity/wavelength of UV source. MR degradation followed first-order rate equation, and under optimum conditions 70–99% decolorization was achieved in the concentration range of 10–50 mg/L. About 42% COD removal was achieved for MR solution having concentration 30 mg/L with 1 h illumination and 4.0 g/L ZnO dose. Role of different radical scavengers was also investigated to gain an insight of role of many reactive oxygen species (ROS) in degradation process. These studies revealed that singlet oxygen and the superoxide ions were the main ROS taking part in MR degradation. The present method was compared with other UV-induced photocatalytic processes using other photocatalysts. The recycle ability of the ZnO and the turnover frequency of the process was evaluated. Finally, a comparative account relative to the solar light-induced process of MR degradation using the same ZnO catalyst was revealed.

Keywords: Methyl red degradation; Commercial ZnO; UV light; ROS; Decolorization

1. Introduction

Textile and dying industries discharge huge amount of colored wastewater in surface water bodies, which contains toxic and non-biodegradable compounds like dyes and pigments [1]. Among the coloring materials, azo compounds constitute the largest group. Methyl red (MR) belongs to this group and has its wide applications in textile dying and paper printing industries. This particular dye is harmful causing irritation in eyes, skin, and digestive tract if inhaled or swallowed. It is a mutagen, mitotic poison, and a suspected carcinogen [2,3]. Thus, it is a great concern to remove MR from wastewater in an efficient and cost-effective way before its release to the environment.

Many processes, such as incineration, biological treatment, ozonation, and solid phase adsorption, have extensively been used for the treatment of dye-bearing wastewater. However, these processes have their own limitations. The incineration can generate toxic volatile compounds; the biological treatment requires long time and, in many cases, leads to foul odor. Moreover, in many cases, the process becomes unsuitable due to the resistance of the dye to biological degradation. Ozonation deals with ozone instability, and solid-phase adsorption results in toxic sludge.

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Recently, advanced oxidation processes (AOPs), which include chemical oxidation (O_3/H_2O_2), Fenton and photo-Fenton reagents (Fe^{2+}/H_2O_2, $Fe^{2+}/H_2O_2/UV$), UV-based reactants (UV/O_3, UV/H_2O_2, $UV/O_3/H_2O_2$), photocatalytic redox processes (semiconductor/UV), super critical water oxidation under high temperature and pressure, sonolysis, and γ-beam irradiation have shown great promise for dye degradation [4,5]. The AOPs with heterogeneous photocatalysis [6–9] have shown a great potential towards the destruction of organic dyes leading to total mineralization. Among all the catalysts, titanium dioxide (TiO_2) and zinc oxide (ZnO) are found to be the most efficient and well documented in literature for photocatalytic degradation of pollutants because of faster electron transfer to molecular oxygen [10]. On illumination with the light of energy higher or equal to their band gap energy ($h\nu \geq E_g = 3.2$ eV, where E_g = band gap energy), the catalyst particle is excited and an electron moves from valence band to conduction band thus forming a positively charged hole in the valence band. The conduction band electrons and the valence band holes then migrate to the oxide surface and react with chemisorbed O_2 and/or OH^-/H_2O molecules to generate reactive oxygen species (ROS), such as superoxide ($O_2^{\bullet -}$), hydroperoxide ($^{\cdot}OOH$), singlet oxygen ($^1O_2$), and hydroxyl radicals ($^{\cdot}OH$), which attack the dye molecules leading to their oxidative degradation. The other mechanisms involve the electron in the conduction band to react with the adsorbed dye molecules to form dye radical anion, which, on further reaction, can lead to the destruction of the dye molecules. On the other hand, the adsorbed dye molecules may be directly oxidized by the valence band holes to form dye radical cations, which finally degrade.

Both TiO_2 and ZnO either in the commercially available form or as engineered nanomaterials are popular photocatalysts [11–18]. However, the fate of these modified nanomaterials in the environment and within the microbial population is one of the biggest concerns today. Recent research has been directed towards the potential toxicity of ZnO and other metal oxide nanomaterials. Although significant amount of literature is now available on engineered nanomaterial oxides, we are still in the dark due to their fate in water and wastewater treatment. Moreover nanomaterials are prone to aggregate unless otherwise stabilized by some ways. Due to these reported problems, commercial forms are preferable due to their easy availability and low cost. One problem, we faced with commercial TiO_2 application for photocatalytic applications, is the poor separability from the reaction mixture [19,20]. To overcome this problem, the commercial TiO_2 was modified either by silver impregnation [19,20] or by heating [20]. This type of problem does not occur for commercial ZnO. One more advantage of ZnO is that it has strong luminescence properties, and, as compared to TiO_2, it can absorb larger fraction of visible light. It has already been reported that nano as well as commercial forms of ZnO and TiO_2 can be effectively used for the degradation of azo dyes such as acid red 18, MR, and methyl orange [21–24]. Very recently, we explored the possibility of MR degradation under solar illumination using commercial ZnO (Merck) [25].

The quantum efficiency of ZnO powder is higher compared to that of TiO_2 [26–29]. In the photocatalytic reactions, the semiconductor is activated by ultraviolet (UV) or visible radiation, establishing a redox environment in the aqueous solution, thus acting as a sensitizer for light-induced redox processes [30].

To date, various researchers proposed different mechanisms for dye degradation, which involve different ROS. As reported by many authors, the hydroxyl radical, among the various ROS, plays the major role in destroying the chromophores. Probable mechanism may be presented by a series of reactions (1–9) shown below, finally leading to mineralization [31–34].

1. Absorption of efficient photons and production of holes and electrons:

$$ZnO + h\nu \rightarrow ZnO^* \tag{1}$$

where $h\nu \geq E_g = 3.17$ eV, where E_g = band gap energy:

$$ZnO^* \rightarrow e^-_{cb} + h^+_{vb} \tag{2}$$

2. Formation of singlet oxygen and superoxide ion:

$$(O_2)_{ads} + e^-_{cb} \rightarrow O_2^{\bullet -} \tag{3}$$

$$O_2^{\bullet} + h^+_{vb} \rightarrow ^1 O_2 \tag{4}$$

3. Neutralization of OH^- and H^+ groups into $^{\cdot}OH$ radical:

$$(H_2O \rightarrow H^+ + OH^-)_{ads} + h^+_{vb} \rightarrow H^+ + {}^{\cdot}OH \tag{5}$$

$$O_2^{\bullet -} + 2H^+ + e^-_{cb} \rightarrow H_2O_2 \tag{6}$$

$$H_2O_2 + H^+ + e^-_{cb} \rightarrow {}^{\cdot}OH + H_2O \tag{7}$$

4. Oxidation of the organic reactant via successive attacks by $^{\cdot}$OH radicals or by direct reaction with holes.

$$\text{Reactant} + {}^{\cdot}\text{OH} \rightarrow \text{R}^{\cdot} + \text{H}_2\text{O} \quad (8)$$

$$\text{Reactant} + \text{h}_{\text{vb}}^{+} \rightarrow \text{R}^{+} + \text{degradation products} \quad (9)$$

The present study reveals the potential of UV illumination-based photocatalytic degradation of MR dye using commercially available ZnO obtained from Merck. The photocatalytic kinetic studies have been carried out to optimize reaction system by varying various physical parameters, such as initial dye concentration, ZnO dose, pH of the reaction medium, interfering ions, and radical scavengers. The amount of oxidation of MR dye was investigated through the determination of chemical oxygen demand (COD) of degraded solution. A comparative account is also made to understand the applicability of the material under solar and UV illumination to degrade MR. It is important to note that while "solar irradiation" is more green, "UV illumination" is more controllable.

2. Materials and methods

2.1. Materials

MR purchased from S.D. Fine Chemicals was used without further purification. The commercial ZnO from Merck was used as photocatalyst. Double distilled water was used throughout the experiment. Other chemicals used in the study such as NaOH, KNO_3, NaCl, Na_2SO_4. KNO_3, KH_2PO_4, $CaCl_2$, and $FeSO_4$ were purchased from Merck. Humic acid, oxalic acid, maleic acid, malic acid, citric acid, *p*-benzoquinone, sodium azide, and *t*-butanol were obtained from Aldrich. All the chemicals used in the study were of analytical reagent grade. For determination of COD, potassium dichromate ($K_2Cr_2O_7$), conc. H_2SO_4, mercuric sulfate ($HgSO_4$), and silver sulfate (Ag_2SO_4) were used. Solution pH was adjusted with HCl (0.1 N) and NaOH (0.1 N) solution as and when required.

2.2. Instrumentation

The instruments used in the study were UV–vis spectrophotometer (Chemito, spectrascan 2600), UV fluorescent lamp (Phillips, 25-W and 15-W), centrifugation machine (REMI, India), COD digester (SPECTROQUANT 320, MERCK), Cyberscan 510 digital pH meter, electrical balance (Afcoset), orbital shaking incubator (REMI Instruments), and magnetic stirrer (REMI-2 MLH).

2.3. Experimental procedure

The photocatalytic degradation was carried out in a 500-mL borosil beaker (with 12.5-cm height and 10-cm diameter, placed on a magnetic stirrer). On the top of the beaker, a low-pressure 25-W UV fluorescent tube (wavelength ~365 nm) was placed at a distance of 13 cm from the bottom surface of the beaker. Upon addition of 30 mL of MR dye solution (conc. ≈30 mg/L) in the beaker, the effective distance between the solution surface and light source remained as 12.2 cm. The experimental setup for the photodegradation of MR is shown in Fig. 1. After the photo irradiation, the solution was centrifuged and the supernatant was collected. The absorption spectrum of irradiated solution was measured in standard quartz cuvette. The degradation of MR was recorded with respect to the absorption at $\lambda_{\max} = 435$ nm. The concentration of MR was found out from the absorbance value using the pre-established calibration curve.

To find out the time required to attain the adsorption–desorption equilibrium, the MR solution (30 mL, ~30 mg/L) was stirred in presence of ZnO (4.0 mg/L) under dark, and the decrease of absorbance of the MR solution was monitored at 435 nm at a regular time interval. The absorbance reached at a stable position at 60 min and no further change in absorbance was observed beyond this point, which indicated that the equilibrium was reached. This time was considered as the "zero time of irradiation" for photocatalytic degradation.

The extent of oxidation of the dye was determined by COD measurement. The aqueous solution of MR at an initial concentration of 20 and 30 mg/L individually was mixed with ZnO (4.0 g/L) and exposed to UV light. Aliquots were then taken at 10 min interval

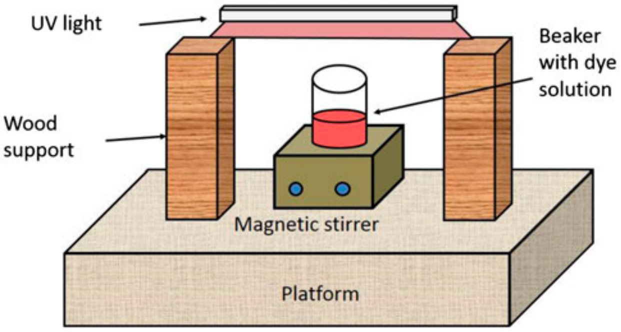

Fig. 1. Experimental setup for UV-catalyzed degradation.

and COD was measured using closed reflux titrimetric method [35].

To examine the effects of interfering substances and the scavengers on the MR degradation, 30 mL of MR solution (conc.: 30 mg/L) was stirred with ZnO (4.0 g/L) in presence of interfering substances at required concentrations. The color removal (%) was found out by measuring the absorbance at 435 nm.

3. Results and Discussion

3.1. Characterization of commercial ZnO

The characterization of the photocatalyst by FE-SEM/XRD/DRS is reported by us very recently [25]. In the literature, the band gap (E_{bg}) for ZnO is reported to be in the range 3.06–3.3 eV [36]. In our case, the E_{bg} as calculated from DRS was 3.09 eV. The crystallites were of various sizes and shapes. Sphere-like shape with a few hundred nanometer diameter was noticed for smaller sized particles. The XRD pattern indicated that the catalyst had wurtzite structure having the diffraction peaks at $2\theta = 31.69$ (1 0 0), 34.36 (0 0 2), 36.18 (1 0 1), and 56.56 (1 1 0) confirming the hexagonal structure [37]. The relative high intensity of the peak corresponding to 101 planes indicates anisotropic growth implying a preferred orientation of the crystallites [38,39].

3.2. Parametric study of UV light-induced photocatalytic degradation of MR

3.2.1. Effect of ZnO dose

In most of the photocatalytic studies, initial rate of photodegradation is found to be proportional to the dose of the catalyst. However, above a certain dose of catalyst, the reaction rate decreases because of light scattering and screening [40]. With the increase of ZnO dose, the tendency of solid catalyst particles to agglomerate also increases, resulting in a reduction in catalyst effective surface area available for the light absorption leading to a drop in the photocatalytic degradation rate. It is important to choose the optimum catalyst dose in order to avoid excess of catalyst and to ensure minimum energy loss during degradation process. The influence of photocatalyst dose on the dye degradation was investigated for a dye solution at an initial concentration of 30 mg/L. The UV photoirradiation was done for 1 h with ZnO at varying doses in the range of 0.5–4.0 g/L. The total degradation of MR increased with the increase in ZnO dose (Table 1). Most commonly, in heterogeneous photocatalytic degradation process, an initial gradual increase in degradation with the increase in catalyst dose and subsequent decrease in degradation at higher catalyst dose are observed. In the present study, within the described range of catalyst dose and with 1 h irradiation, an increase in MR degradation was observed with increase in ZnO dose and 99.4% degradation of MR was achieved with 4.0 g/L ZnO dose. Thus, 4.0 g/L was selected as the optimum dose for ZnO for further studies. The increase in degradation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension with increase in ZnO dose.

3.2.2. Photocatalytic degradation of MR

Various processes, such as hydrolysis, adsorption, and photolysis, were investigated in the present study. In all cases, the experiment was carried out up to 1 h. The hydrolysis was done by simple stirring of the solution under the dark. In adsorption study, the solution was stirred in presence of ZnO under the dark. The photolysis was carried out by stirring the MR solution under UV light, without the addition of ZnO. The $\lambda_{\max}$ for MR was at 435 nm. In all the above three cases (Fig. 2), the absorbance of the MR solution was monitored at 435 nm at a regular time interval. The change in absorbance or concentration was not observed in case of hydrolysis and photolysis. But a nominal change (~1.3%) in concentration was observed in case of adsorption experiment. The decrease in concentration during adsorption experiment was almost negligible, though it was an obligatory step. After allowing the ZnO-MR solution to be stirred under the dark for 1 h to achieve the adsorption equilibrium (this is designated as zero time for photocatalytic degradation), the UV photocatalysis was performed, and an immediate change in the absorbance of MR solution was observed. These observations revealed the significance of ZnO as well as UV light in photocatalytic destruction of MR dye.

The systematic photocatalytic degradation of MR was carried out with 30 mL of MR solution (conc. 30 mg/L) using optimum dose i.e. 4.0 g/L of ZnO. As the reaction proceeds, the peak intensity decreases gradually (Fig. 3). At the end of 60 min of reaction, there was no evidence of absorption peak, and almost ~99% discoloration of MR dye occurred. It indicated that the main chromophore (i.e. the azo group) of MR in the solution had been eliminated with the photocatalytic reaction in UV/ZnO system, and the dye has been possibly transformed to other more simple organics. The common and practical problem of photocatalysis is the recombination of e^-_{cb}/h^+_{vb}, which may be avoided by the use of suitable electron acceptor [41]. In the present

Table 1
Effects of catalyst (ZnO) dose and initial MR concentration

Dose of catalyst (g/L)	Concentration of MR (mg/L)	Removal of color (%)
0.5	[a]	71.5
1	[a]	74.9
1.5	[a]	85.9
2	[a]	89.5
3	[a]	93.1
4	[a]	99.4
[b]	10	99.6
[b]	20	99.5
[b]	30	99.1
[b]	40	82.2
[b]	50	70.6

[a] Concentration of MR: 30 mg/L.
[b] Optimized dose of catalyst: 4.0 g/L.

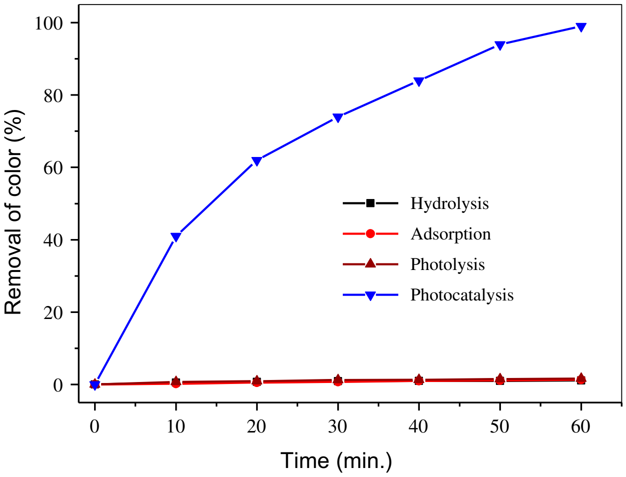

Fig. 2. Degradation of MR during hydrolysis (no catalyst, no light), adsorption (catalyst, no light), photolysis (light, no catalyst), and photocatalysis (catalyst, light) experiments (MR conc. = 30 mg/L; catalyst dose = 4.0 g/L).

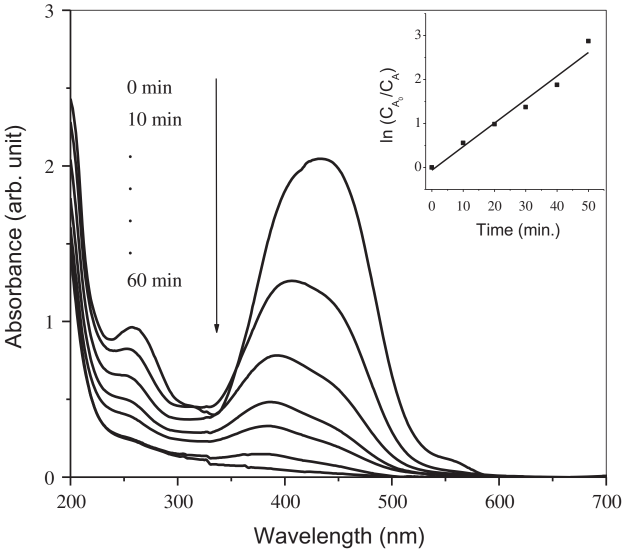

Fig. 3. Time-dependent UV–visible absorption spectra of MR during 1 h degradation (MR conc. = 30 mg/L; catalyst dose = 4.0 g/L) (Inset: Linear fit for first-order rate equation).

study, the experiment was carried out in aerobic condition where the reaction mixture was always in contact with air/oxygen. The dissolved oxygen has a tendency to work as an electron sink and thus it participates in the formation of ROS such as super oxide radical ($O_2^{\bullet -}$) and subsequently leading to other reactive species like H_2O_2, $HO_2^{\bullet}$, $^{\cdot}OH$, and HO_2^- [42,43]. This process reduces the recombination of charges and favors the oxidation of the substrate. Slight darkening of the catalyst during the irradiation revealed that the reaction occurred on ZnO surface. Experiment had also been done in absence of UV light and under that condition, the color of the catalyst did not change.

The absorption spectrum was monitored at a regular interval of time and the data were fitted in various linear equations of reaction rates, and compared (Table 2). For the heterogeneous photocatalytic degradation processes, many authors have used the Langmuir–Hinshelwood (L–H) rate equation to analyze the photocatalytic reaction. In the present case, the degradation followed the first-order reaction kinetics (as shown in the inset of Fig. 3), which is an obvious phenomenon in semiconductor photocatalysis [44,45].

3.2.3. Effect of initial MR concentration

The effect of initial concentration (10–50 mg/L) of MR on its photocatalytic degradation under UV light

Table 2
Models used for degradation kinetics

Kinetic model	Equation[a] for the linear fit	Rate constant (k)	Coefficient of correlation (R^2)
Zero order	$C_A = C_{A0} - kt$	0.522	0.889
First order	$\ln C_A = \ln C_{A0} - kt$	0.0534	0.971
Second order	$(1/C_A) = (1/C_{A0}) + kt$	0.0094	0.721
L–H	$(1/r) = (1/KkC_A) + (1/k)$	1.492	0.412

[a] C_{A0} = conc. at zero time; C_A = conc. at time t; k = rate constant; t = time; K = adsorption constant; r = rate of reaction.

was investigated where a decrease in overall degradation was observed at a concentration ≥30 mg/L, with the increase in concentration of MR. One of the reasons is that the increase in MR concentration prevents the penetration of UV light through the solution. The other reason may be the reduction in radical density relative to target pollutant on to the surface of catalyst. It is obvious that, when concentration of MR increases, the ROS (e.g. $^{\cdot}OH$ and $O_2^{\bullet -}$) required for the degradation of MR also increases. However, the formation of ROS on the catalyst surface remains constant under a specified condition. Table 1 shows the percent degradation of MR at various initial concentrations after 1 h of irradiation.

3.2.4. Effect of intensity and wavelength of UV light on MR degradation

The extent of light absorption by catalyst and thereby the rate of photocatalysis depends on two factors: the wavelength of light and the intensity. It has already been reported that, at high intensity, the reaction rate becomes independent of light intensity [46]. Studies on photocatalytic degradation of MR were carried out using two different UV light sources (~254 and ~365 nm) of same radiant flux (25 W/m^2). As observed for the 1-h illumination of MR (30 mg/L) in presence of ZnO (4.0 g/L), between the two UV lights used, the higher photocatalytic degradation (~99%) was obtained with ~365-nm light source. The observed lower degradation (~86%) with light source having emission at ~254 nm under similar condition was attributed to the partial absorption at this range and wasting of light at ~254 nm by MR itself. Because of the better performance, the 365-nm UV light was selected for our studies. The incident light intensity is expected to be one of the rate-controlling parameters. The effect of intensity of UV light (~365 nm) on MR degradation efficiency was also examined at initial MR concentration of 30 mg/L, at pH ~6.5 and catalyst loading at 4.0 g/L. About 99% MR degradation was achieved with light intensity at 25 W/m^2 and 15 W/m^2. These results revealed that a light source with less intensity was enough for ~99% color removal. However, %COD removal (hence oxidation) was ~43% with the 25-W UV light and ~24.8% with 15-W UV light. It has already been reported that with increase in lamp power (and thus its light intensity) the rate of electron-hole pair formation at the ZnO surface increases and consequently its ability to oxidize organic pollutant also increases. Because of the better performance, the UV light (~365-nm) with higher intensity (25 W) was selected for our studies.

3.2.5. Effect of medium pH on MR degradation

The solution pH is an important factor for heterogeneous photocatalytic degradation. Both the characteristics of dye (viz., speciation behavior, solubility in water and hydrophobicity) and the charge on the photocatalyst surface depend on the pH. Thus MR remains mostly in its cationic form (i.e. the protonated form) below pH 5.3 (pK_a), and in anionic form (i.e. un-protonated form) above pH 5.3. It is already reported that the electrostatic interaction between the semiconductor surface, solvent molecules, the probe, and charged species formed during photocatalytic oxidation strongly depends on the solution pH [47].

The effect of pH on the $\lambda_{\max}$ and hence the color of the MR dye had been studied to determine the optimum pH range for the maximum photocatalytic degradation of the dye. While studying in the entire pH range (2–12), it was noticed that there was a blue shift of $\lambda_{\max}$ for MR when the solution pH changed from 5 to 6. As the pH was further increased, there was no more shift. The pH of the reaction mixture, as the reaction continued, was monitored up to 1 h and it was observed that the solution pH increased from ~6.5 to ~7.5. However, from earlier discussion there should not be any shift of $\lambda_{\max}$ of MR in this range of pH while the reaction proceeds. The used commercial ZnO has the pH$_{ZPC}$ 8.2 as reported in our previous study [25]. Hence, the particle surfaces are positively charged when the solution pH < 8.2 and negatively charged at pH > 8.2. That is why all of the photocatalytic degradation studies were performed in the pH range of 6.5–7.5, where dye was in anionic form and ZnO surface was positively charged. Under this situation, the interaction between two species favored the photocatalytic degradation. The observed change in pH during the reaction could be attributed to the formation of various intermediates.

3.2.6. *Effect of interfering substances*

Since the composition of wastewater varies widely, it is necessary to investigate the effects of different interfering inorganic ions (viz., Ca^{2+}, $Fe^{2+/3+}$, Cl^{-}, SO_4^{2-}, $H_2PO_4^{-}$, and NO_3^{-}), common organics such as humic acid, and some low molecular weight organic acids (LMWOA) (viz., malic acid, maleic acid, oxalic acid, and citric acid). These species may affect the photocatalytic degradation by getting adsorbed on the surface of ZnO. Furthermore, they may compete with the target pollutant and subsequently reduce the formation of $^{\cdot}OH$ radical. The hydroxyl radicals may also be scavenged by anions and this may result in the formation of new anion radicals. They have lower oxidation potential compared to the hydroxyl radical. Experiments were performed to examine the effects of these interfering substances on the degradation of MR (30 mg/L) under UV irradiation for 1 h using ZnO catalyst (4 g/L). The effect of different interfering substances on the percent color removal of dye is shown in Fig. 4. Under the conditions examined, the presence of NO_3^{-} (1,000 mg/L), SO_4^{2-} (100 mg/L), and Cl^{-} (1,200 mg/L) did not show any significant effect on the dye degradation. However, the degradation was strongly inhibited by $H_2PO_4^{-}$ (500 mg/L). This is due to the solubility of ZnO in presence of $H_2PO_4^{-}$ to form various phosphate complexes in aqueous solution [48]. With the increase in $H_2PO_4^{-}$ concentration, the dissolution of ZnO might have increased which caused the gradual decrease in photocatalytic degradation. No discernible effect was observed in presence of cations like Ca^{2+} (125 mg/L) and $Fe^{+2/+3}$ (60 mg/L). The presence of humic acid at a level of 10 mg/L reduced the dye degradation to a level of 85%. This result is contradictory to our earlier result of MR degradation by solar irradiation in presence of humic acid, where no interference was noticed [25]. Humic acid is UV sensitive and may produce some products which affect MR degradation. The interference of other LMWOA (Conc.: 1 mM) was also investigated and it was found that the presence of these acids in the reaction mixture significantly reduced the MR degradation. Results of these studies are shown in Fig. 4.

3.2.7. *Effect of radical scavengers on photocatalytic degradation of MR*

To understand the mechanistic pathway of the MR degradation, it is important to know the participation of ROS, such as singlet oxygen ($^1O_2$), superoxide ($O_2^{\bullet-}$), and hydroxyl radicals ($^{\cdot}OH$), under photocatalytic conditions. This was investigated using appropriate quenchers of these species in the reaction system. For this purpose, materials sodium azide (NaN_3, a quencher of singlet oxygen but may also interact with $^{\cdot}OH$), *p*-benzoquinone (BQ, a quencher of superoxide

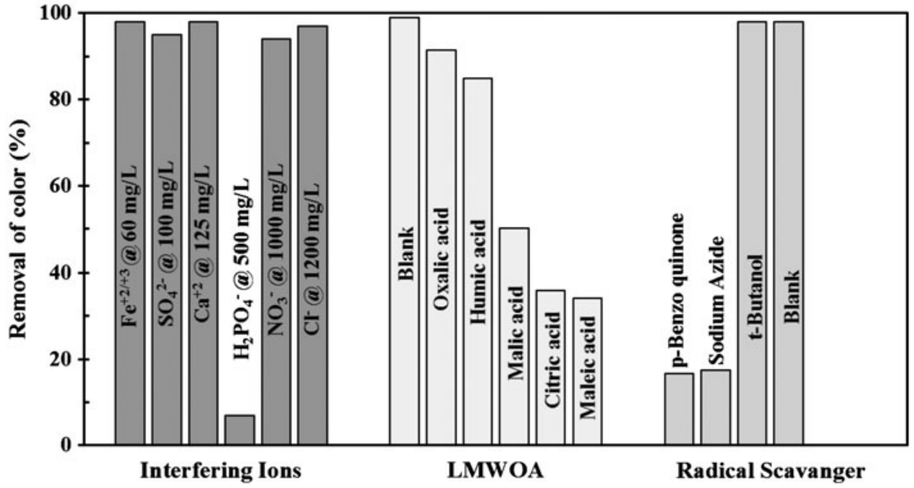

Fig. 4. Effect of different interfering ions, LMWOA, and radical scavengers on MR degradation under UV light (MR conc. = 30 mg/L; catalyst dose = 4.0 g/L; time of irradiation = 1 h).

radical), and *t*-butanol (a quencher of $^{\cdot}$OH) were used to examine the scavenging effect [49,50]. In this experiment, a comparison was made between the original decolorization of MR-ZnO system with those obtained after addition of quenchers (1 mM) in the initial solution, under otherwise identical condition. The results are shown in Fig. 4. The degradation of MR was highly suppressed in presence of *p*-benzoquinone, and ~18% of MR was decolorized within 1 h. Similarly, the addition of sodium azide also significantly inhibited the decolorization with ~19% degradation of MR. However, there was no significant effect of *t*-butanol on MR decolorization. These results confirmed that $^1O_2$ and $O_2^{\bullet-}$ serve as the main ROS in the MR degradation in suspension, while $^{\cdot}$OH played a little role. Similar results were also obtained in our previous study on MR degradation by solar light [25].

3.2.8. COD removal

The degree of MR oxidation with time is demonstrated by monitoring the change in COD. The COD removal for two different concentrations of MR (20 and 30 mg/L) was examined. During photodegradation the aliquots were withdrawn at 10 min interval and COD was measured using closed reflux titrimetric method. The COD removal was calculated as follows:

$$\%\text{COD Removal} = [(\text{COD}_0 - \text{COD}_t)/\text{COD}_0] \times 100$$

where COD_t and COD_0 were COD (mg/L) values at any given time t min and at time 0 min. The plot of COD removal with time during the photocatalytic treatment of MR is shown in Fig. 5. After 1 h of degradation, the COD removal was found to be ~42 and ~73% for MR solutions having initial concentration 30 and 20 mg/L, respectively. When the UV photocatalytic reaction was performed beyond 60 min with the MR solution having initial concentration of 30 mg/L, a gradual increase in COD removal was noticed, and at 8 h of UV photoirradiation ~80% of COD removal occurred.

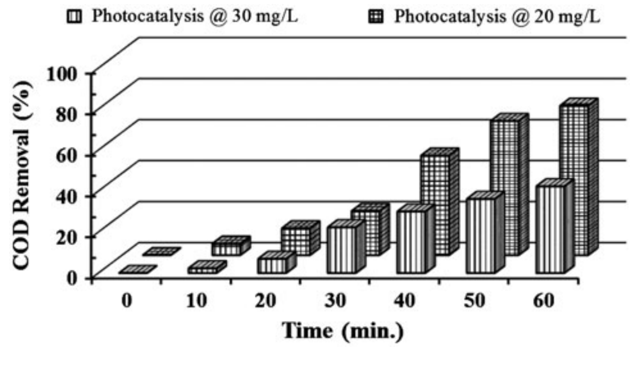

Fig. 5. COD removal kinetics for MR (MR conc. = 30 and 20 mg/L; catalyst dose = 4.0 g/L).

3.2.9. TOF and recycle ability of the catalyst

To examine the cost effectiveness of this method, the photocatalyst was regenerated and reused for dye degradation. It was observed that the catalyst could be reused for the second and the third cycle with an efficiency of ~80 and ~74%, sequentially. The regeneration of photocatalyst was easy. After degradation of the dye, the solution was centrifuged and supernatant was decanted. Then the catalyst was thoroughly washed many times with distilled water and was reused for the second and the third cycle of operations with a fresh lot of dye solution (30 mg/L). The catalyst could be used further with a decreased efficiency.

Catalyst turnover number (TON) and turnover frequency (TOF) are two important parameters to compare catalyst activity [20]. For heterogeneous catalysis, TON is the number of reactant molecules that is converted to products in presence of 1 g catalyst. The TOF is TON/time. For the degradation of MR (30 mg/L) with ZnO (4.0 g/L), the TOF was found to be 4.4×10^{15} molecules/g/s.

3.2.10. Comparative study on MR degradation under UV and solar irradiation with TiO_2 and Ag–TiO_2 and other catalysts

In our earlier studies [19], we used "commercial TiO_2 (Merck)" and "Ag^+ doped TiO_2", (later on designated as nano silver impregnated TiO_2 [20]) for MR degradation using UV light. Other ZnO based catalysts viz., Ag-doped ZnO (Ag-ZnO), N-doped ZnO (N-ZnO), and Ag-N co-doped ZnO nanoparticles (Ag-N-ZnO) for MR degradation under UV and solar irradiation were also reported [51]. A comparative account of the catalyst used in the present study was made with the earlier used catalysts (i.e. commercial TiO_2, Ag^+ doped TiO_2, Ag-ZnO, N-ZnO, and Ag-N-ZnO) in terms of their MR degradation ability and cost (Table 3). The cost of ZnO photocatalyst was comparable to that of commercial TiO_2. However, it is to be noted that although Ag^+-doped TiO_2 was a good photocatalyst, it contained silver. So proper treatment after its use was required.

A comparative account of the experimental conditions and the performance of the present method with solar light-induced photocatalytic degradation method [25] using the same ZnO catalyst is also made (Table 4).

Table 3
Comparative account on MR degradation under UV irradiation using commercial/modified photocatalysts

Catalyst	Size	pH_{ZPC}[a]	Separability	Degradation (%)	Cost (Rs./100 g)	Irradiation time (min)	Rate constant (k)	MR conc. (mg/L)	Catalyst dose (g/L)
TiO_2	~2 μm[a]	6.2[a]	[b]	~85[d]	50[a]	45[d]	1.1×10^{-1}[d]	20[d]	1
Ag–TiO_2	~2 μm[a]	7.1[a]	[c]	~99[d]	88[a]	45[d]	4.9×10^{-2}[d]	20[d]	1
ZnO	<1 μm	8.2	[c]	~99[e]	89[e]	60[e]	5.3×10^{-2}[e]	30[e]	4
Ag–ZnO	44 nm	NR	[c]	~56[f]	NR	180[f]	5.0×10^{-3}[f]	NR	NR
N–ZnO	20 nm	NR	[c]	~51[f]	NR	180[f]	4.2×10^{-3}[f]	NR	NR
Ag–N–ZnO	16 nm	NR	[c]	~60[f]	NR	180[f]	6.3×10^{-3}[f]	NR	NR

[a] Ref. [20].

[b] Requires 0.45 μm membrane filtration.

[c] Requires settling or centrifugation.

[d] Concentration of MR: 20 mg/L, Catalyst dose: 1.0 g/L, Ref. [19].

[e] Concentration of MR: 30 mg/L, Catalyst dose: 4.0 g/L [present method].

[f] Ref. [51].

NR: not reported.

Table 4
Comparative account of UV–vs. solar light-induced ptotocatalytic degradation of MR using commercial ZnO

Parameter	Unit	UV	Solar
Optimum pH	–	6.5–7.5	~7
Optimum dose	g/L	4	0.5
Conc. of MR	mg/L	30	30
Time of irradiation	min	60	60
Color removal	%	~99	~99
COD removal	%	~42	~53
Intensity of light	W/cm^2	0.0025	0.00658
Wavelength	nm	365	Visible range
Dominating ROS	NA	$^1O_2$ and $O_2^{\bullet -}$	$^1O_2$ and $O_2^{\bullet -}$
Turnover frequency (TOF)	molecules/g/s.	4.4×10^{15}	3.6×10^{16}
Interfering ions	–	$H_2PO_4^-$	$H_2PO_4^-$

4. Conclusions

The present study describes the degradation of MR using commercial ZnO in the presence UV light. The discoloration of the dye follows first-order equation. The COD measurement reveals that on UV irradiation for 1 h the dye is oxidized by ~42 and ~73% in case of dye concentrations 30 and 20 mg/L, respectively. Low-intensity (15 W) UV light is enough for successful degradation of MR under optimized conditions but higher COD removal can be achieved in high-intensity (25 W) UV light. The effects of various ions, humic acid, and LMWOA (generally found in the waste stream) are examined. The organic acids and $H_2PO_4^-$ anion inhibit the degradation of MR significantly. It is also found with the use of appropriate radical scavengers that the photocatalytic degradation of the dye is caused by singlet oxygen and super oxide ion generated in the reaction system. The photocatalyst can be recovered easily, and can be reused for dye degradation with slightly less efficiency. A comparative account of MR degradation is also made with respect to earlier used photocatalysts, and the present catalyst is found to be good in terms of both efficiency and easy availability. A comparative account of the present method of UV irradiation and the solar light irradiation recently reported [25] is made.

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References

[1] A. Sumartono, Degradation of standard dyes and textile wastewater as a pollutant model using gamma radiation, Atom Indo. J. 34 (2008) 1–20.

[2] P.P. Vijaya, S. Sandhya, Decolorization and complete degradation of methyl red by a mixed culture, Environmentalist 23 (2003) 145–149.

[3] Y. Badr, M.G. Abd El-Wahed, M.A. Mahmoud, Photocatalytic degradation of methyl red dye by silica nanoparticles, J. Hazard. Mater. 154 (2008) 245–253.

[4] B.E. Reed, M.R. Matsumoto, R. Viadero, R.L. Segar, R. Vaughan, D. Masciola, Physicochemical Processes, Water Environ. Res. 71 (1999) 584–618.

[5] H. Choi, S.R. Al-Abed, D.D. Dionysiou, E. Stathatos, P. Lianos, TiO_2-based advanced oxidation nanotechnologies for water purification and reuse, Sustain. Sci. Eng. 2 (2010) 229–254.

[6] M. Schiavello (Ed.), Photocatalysis and Environment, Trends and Applications, Kluwer Academic Publishers, Dordecht, 1988.

[7] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis, Fundamentals and Applications, John Wiley & Sons, New York, NY, 1989.

[8] J.M. Herrmann, C. Guillard, P. Pichat, Heterogeneous photocatalysis: An emerging technology for water treatment, Catal. Today. 17 (1993) 7–20.

[9] A. Uygur, An overview of oxidative and photooxidative decolorisation treatments of textile waste waters, J. Soc. Dyers Colour. 113 (1997) 211–217.

[10] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.

[11] X. Cai, Y. Cai, Y. Liu, S. Deng, Y Wang, Y. Wang, I. Djerdj, Photocatalytic degradation properties of Ni$(OH)_2$ nanosheets/ZnO nanorods composites for azo dyes under visible-light irradiation, Ceram. Int. 40 (2014) 57–65.

[12] S.D. Marathe, V.S. Shrivastava, Removal of hazardous Ponceau S dye from industrial wastewater using nano-sized ZnO, Desalin. Water Treat. (2014) 1–5, doi: 10.1080/19443994.2014.896293.

[13] P. Singla, M. Sharma, O.P. Pandey, K. Singh, Photocatalytic degradation of azo dyes using Zn-doped and undoped TiO_2 nanoparticles, Appl. Phys. A: Mater. Sci. Process. 116 (2014) 371–378.

[14] P.C. Ribeiro, A.C.F. Costa, R.H.G.A. Kiminami, J.M. Sasaki, H.L. Lira, Synthesis of TiO_2 by the Pechini Method and photocatalytic degradation of methyl red, Mater. Res. 16 (2013) 468–472.

[15] J. Wang, F. Qu, X. Wu, Controlled synthesis and photocatalytic properties of three dimensional hierarchical ZnO microflowers, Mater. Express 3 (2013) 256–264.

[16] P. Bansal, P. Kaur, D. Sud, Heterostructured TiO_2/ZnO–excellent nanophotocatalysts for degradation of organic contaminants in aqueous solution, Desalin. Water Treat. (2013) 1–11, doi: 10.1080/19443994.2013.822330.

[17] A. Petrella, G. Boghetich, M. Petrella, P. Mastrorilli, V. Petruzzelli, D. Petruzzelli, Photocatalytic degradation of azo dyes. Pilot plant investigation, Ind. Eng. Chem. Res. 53 (2014) 2566–2571.

[18] R.D.C. Soltani, A. Rezaee, M. Safari, A.R. Khataee, B. Karimi, Photocatalytic degradation of formaldehyde in aqueous solution using ZnO nanoparticles immobilized on glass plates, Desalin. Water Treat. (2013) 1–8, doi: 10.1080/19443994.2013.855674.

[19] C. Sahoo, A.K. Gupta, A. Pal, Photocatalytic degradation of methyl red dye in aqueous solutions under UV irradiation using Ag^+ doped TiO_2, Desalination 181 (2005) 91–100.

[20] S. Saha, J.M. Wang, A. Pal, Nano silver impregnation on commercial TiO_2 and a comparative photocatalytic account to degrade malachite green, Sep. Purif. Technol. 89 (2012) 147–159.

[21] M.L. Curri, R. Comparelli, P.D. Cozzoli, G. Mascolo, A. Agostiano, Colloidal oxide nanoparticles for the photocatalytic degradation of organic dye, Mater. Sci. Eng. C 23 (2003) 285–289.

[22] C.A. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, N. Nagata, P.P. Peralta-Zamora, Semiconductor assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433–440.

[23] N. Sobana, M. Swaminathan, The effect of operational parameters on the photocatalytic degradation of acid red 18 by ZnO, Sep. Purif. Technol. 56 (2007) 101–107.

[24] R. Comparelli, E. Fanizza, M.L. Curri, P.D. Cozzoli, G. Mascolo, A. Agostiano, UV induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates, Appl. Catal. B-Environ. 60 (2005) 1–11.

[25] N.K. Singh, S. Saha, A. Pal, Solar light-induced photocatalytic degradation of methyl red in an aqueous suspension of commercial ZnO: A green approach, Desalin. Water Treat. (2013) 1–14, doi: 10.1080/19443994.2013.838520.

[26] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO_2 assisted degradation of textile dye reactive blue 4, Chemosphere 46 (2002) 1173–1181.

[27] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, J. Hazard. Mater. 112 (2004) 269–278.

[28] C. Hu, J.C. Yu, Z. Hao, P.K. Wong, Effects of acidity and inorganic ions on the photocatalytic degradation of different azo dyes, Appl. Catal. B-Environ. 46 (2003) 35–47.

[29] W.S. Kuo, P.H. Ho, Solar photocatalytic decolorization of methylene blue in water, Chemosphere 45 (2001) 77–83.

[30] G. Mascolo, R. Comparelli, M.L. Curri, G. Lovecchio, A. Lopez, A. Agostiano, Photocatalytic degradation of methyl red by TiO_2: Comparison of the efficiency of immobilized nanoparticles versus conventional suspended catalyst, J. Hazard. Mater. 142 (2007) 130–137.

[31] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar/UV-induced photocatalytic degradation of three commercial textile dyes, J. Hazard. Mater. 89 (2002) 303–317.

[32] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. Energ. Mat. Sol. C. 77 (2003) 65–82.

[33] Y. Abdollahi, A.H. Abdullah, Z. Zainal, N.A. Yusof, Photodegradation of m-cresol by zinc oxide under visible-light irradiation, Int. J. Chem. 3 (2011) 33–43.

[34] T.A. Konovalova, J. Lawrence, L.D. Kispert, Generation of superoxide anion and most likely singlet oxygen in irradiated TiO_2 nanoparticles modified by carotenoids, J. Photochem. Photobiol., A: Chem. 162 (2004) 1–8.

[35] A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg (Eds.), Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.

[36] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[37] D. Sridevi, K.V. Rajendran, Synthesis and optical characteristics of ZnO nanocrystals, Bull. Mater. Sci. 32 (2009) 65–168.

[38] B. Krishnakumar, B. Subash, M. Swaminathan, AgBr–ZnO–An efficient nano-photocatalyst for the mineralization of acid black 1 with UV light, Sep. Purif. Technol. 85 (2012) 35–44.

[39] A.K. Sinha, M. Basu, M. Pradhan, S. Sarkar, T. Pal, Fabrication of large-scale hierarchical ZnO hollow spheroids for hydrophobicity and photocatalysis, Chem. Eur. J. 16 (2010) 7865–7874.

[40] S. Lathasree, A.N. Rao, B. SivaSankar, V. Sadasivam, K. Rengaraj, Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions, J. Mol. Catal. A: Chem. 223 (2004) 101–105.

[41] J. Fenoll, P. Hellín, C.M. Martínez, P. Flores, S. Navarro, Semiconductor-sensitized photodegradation of s-triazine and chloroacetanilide herbicides in leaching water using TiO_2 and ZnO as catalyst under natural sunlight, J. Photochem. Photobiol. A: Chem. 238 (2012) 81–87.

[42] J. Yang, J. Dai, C. Chen, J. Zhao, Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO_2-film electrodes, J. Photochem. Photobiol. A: Chem. 208 (2009) 66–77.

[43] Y. Wang, C.S. Hong, Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO_2 suspensions, Water Res. 33 (1999) 2031–2036.

[44] D. Robert, B. Dongui, J.V. Weber, Heterogeneous photocatalytic degradation of 3-nitroacetophenone in TiO_2 aqueous suspension, J. Photochem. Photobiol. A: Chem. 156 (2003) 195–200.

[45] Q.J. Geng, X.K. Wang, S.F. Tang, Heterogeneous photocatalytic degradation kinetic of gaseous ammonia over nano-TiO_2 supported on latex paint film, Biomed. Environ. Sci. 21 (2008) 118–123.

[46] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review, J. Environ Manage. 92 (2011) 311–330.

[47] M. Qamar, M. Muneer, D. Bahnemann, Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueous suspensions of titanium dioxide, J. Environ Manage. 80 (2006) 99–106.

[48] S.E. Ziemniak, M.E. Jones, K.E.S. Combs, Zinc(II) oxide solubility and phase behavior in aqueous sodium phosphate solutions at elevated temperatures, J. Solution Chem. 21 (1992) 1153–1176.

[49] M. Stylidi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic degradation of acid orange 7 in aqueous TiO_2 suspensions, Appl. Catal. B-Environ. 47 (2004) 189–201.

[50] L. Zhang, Y. Nie, C. Hu, X. Hu, Decolorization of methylene blue in layered manganese oxide suspension with H_2O_2, J. Hazard. Mater. 190 (2011) 780–785.

[51] T. Welderfael, O.P. Yadav, A.M. Taddesse, J. Kaushal, Synthesis, characterization and photocatalytic activities of Ag-N-codoped ZnO nanoparticles for degradation of methyl red, Bull. Chem. Soc. Ethiop. 27 (2013) 221–232.