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Solar light-induced photocatalytic degradation of methyl red in an aqueous suspension of commercial ZnO: a green approach

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ABSTRACT

The potential of commercial ZnO as a heterogeneous photocatalyst for the degradation of methyl red (MR; C. I. Acid Red 2) under solar light irradiation was considered. The effect of initial concentration of MR, catalyst loading, pH, light intensity, radical scavengers, and inorganic salts was studied. The rate of decolorization followed first-order kinetics with respect to dye concentration. Under ambient and neutral pH condition, the catalyst at a dose of 0.5 g/L could decolorize MR (initial conc. 30 mg/L) up to 99% in 1 h. The COD removal under similar situation was ~53%. The mineralization of MR was found to be dependent on catalyst dose and time of solar light irradiation. Thus, mineralization up to 80% was possible for the same solution using catalyst at 1 g/L dose. The method was free from interference due to Cl^-, SO_4^{2-}, NO_3^-, Ca^{2+}, $Fe^{2+/3+}$, humic acid, oxalic acid, and citric acid. However, it was strongly interfered by $H_2PO_4^-$, maleic acid, malic acid, and tartaric acid. Studies showed that the reaction was mostly governed by singlet oxygen and superoxide radical. High turnover frequency and recycle ability of the catalyst made the process economical. The recovered ZnO could degrade MR up to 86 and 79% after the first and second cycle under identical experimental conditions. A cost-benefit analysis was made to evaluate the efficacy of the catalyst in relation to the commercial TiO_2 and silver-doped TiO_2. Further, the efficiency of the present method for MR degradation was compared with those of the other methods involving UV and visible light, and in the presence of nano-ZnO and commercial ZnO.

Keywords: Methyl red degradation; Solar light; Commercial ZnO; Color removal; COD removal

1. Introduction

Quality of available surface and ground water ($1.4 \times 10^9\,km^3$) is continuously deteriorating because of many anthropogenic activities like discharge of various industrial pollutants, agricultural activities, and mining operations. Various kinds of dyes are being introduced in the environment each day from different industries such as textile, leather, paper, rubber, plastics, ceramic, cosmetics, and paints causing threat to the aquatic life [1–4]. At present, a huge volume of wastewater is being generated by the textile industries. Even at a very low concentration (1–2 mg/L), these colored compounds remain visible, and interfere with flora and fauna of water bodies. Among all the dyes

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classified as acidic, basic, azo, diazo, anthraquinone, and metal complex-based dyes, the basic and azo dyes show the highest rate of toxicity. The azo dyes, which contain one or more azo groups (–N=N–) in their structure [2,5–11], generally show mutagenic or carcinogenic activity.

Various conventional or biological treatment processes may be either selective and/or incomplete due to recalcitrant behavior of the dye molecules. Moreover, some of the biodegradation products might be even more toxic than the dye molecule itself [3,6]. Because of stringent environmental standards, the methods based on coagulation/flocculation, adsorption, ultra-filtration, nano-filtration, reverse osmosis are being encouraged for treating dye wastewater. However, these methods are costly and simultaneously produce a waste stream that requires further treatment or disposal. Furthermore, bio-treatment of azo dyes is less adopted because of their resistance to aerobic degradation. On the other hand, anaerobic degradation of many dyes can lead to carcinogenic aromatic amines. Due to all these reasons, the effluents (either in treated or partially treated form) from many dye industries are being discharged either directly to the waterways or in municipal sewage treatment plants [10,12–14].

During the last two decades, several advanced oxidation processes (AOPs) have been proposed as alternative routes for treating recalcitrant organic pollutants, including dyestuffs [15]. These AOPs generate active free radicals such as hydroxyl radicals, which is the second strongest known oxidant after fluorine (2.87 V vs. standard hydrogen electrode). As compared to biological processes, these AOP-based techniques seem to have relatively high operating cost. Many such AOPs used to treat different industrial wastewaters are expensive because they need UV generation by lamps [4,11,16–19]. Common AOPs use ozonation, UV/H_2O_2, Fenton's reagent (Fe^{2+}/H_2O_2), and UV/TiO_2 [7,20,21].

Recently the heterogeneous photocatalysis has become most popular for pollutant degradation [15,22,23]. In this process, a semiconductor catalyst is mixed with the contaminated solution and then irradiated by solar or UV light ($\lambda < 400$ nm) [5]. Mechanism of heterogeneous photocatalysis involves reactions between adsorbed water, hydroxyl anions, and oxygen molecules or other substances with electron-hole pairs produced at semiconductor surface under UV/solar irradiation. These electron-hole pairs are capable of initiating a series of chemical reactions and eventually mineralize the pollutants [24,25]. The proposed mechanism is presented pictorially in Fig. 1. The complete degradation of many organic pollutants is provided by the following mechanism [26–29]:

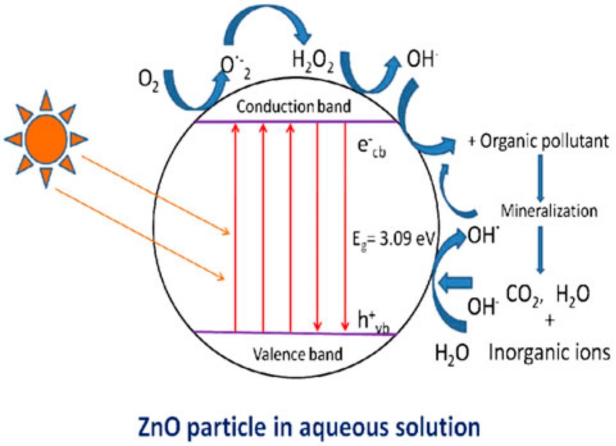

Fig. 1. Pictorial presentation of degradation mechanism.

1. Absorption of efficient photons where $h\nu \geqslant E_{bg} = 3.09\,\text{eV}$ by zinc oxide, where E_{bg} = band gap energy

$$\text{ZnO} + h\nu \rightarrow e^-_{cb} + h^+_{vb} \tag{1}$$

2. Oxygen ionosorption

$$(O_2)_{ads} + e^-_{cb} \rightarrow O_2^{\cdot -} \tag{2}$$

3. Neutralization of OH^-groups into $^{\cdot}OH$ radical by photo-holes

$$(H_2O \rightarrow H^+ + OH^-)_{ads} + h^+_{vb} \rightarrow H^+ + ^{\cdot}OH \tag{3}$$

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

$$\text{Reactant} + ^{\cdot}OH \rightarrow R^{\cdot} + H_2O^{\cdot} \tag{4}$$

$$\text{Reactant} + h^+_{vb} \rightarrow R^+ + \text{degradation products} \tag{5}$$

Recently, the process of pollution control mediated by solar light has drawn tremendous attention because of its destructive nature, low-energy consumption, milder condition, easy controllability, and handy operation [30]. Treatment of industrial wastewater, ground water, and contaminated air by heterogeneous photocatalysis under solar light has been reported already [26]. In addition, life-cycle analysis of AOPs shows that heterogeneous photocatalysis using UV light consumes huge amount of electricity, although the expenditure on reagent and catalysts is comparatively low [3,31,32]. On the other hand AOPs can be performed with solar irradiation, as the Sun provides photons with the wavelength required for these processes. Typically in the whole solar spectrum, 3–5% is the UV flux with an intensity of 20–30 W/m^2. In UV induced processes the Sun makes 0.2–0.3 mol photons/m^2 hr within the 300–400 nm range. This suggests that the solar light can be an economical and ecologically sensible light source. Consequently, as a green approach, the use of solar energy is being encouraged for photoactivation which helps in reducing the energy consumption by 90% required for generating UV radiation for this process [3,18,20,33–37].

Different semiconductor materials, especially TiO_2 and ZnO, have been tried [38,39] for detoxification of various contaminants present in aqueous phase. The main problem with TiO_2 is that it can absorb only a small portion of solar spectrum in the UV region, and has a high recombination rate of photoinduced electron-hole pairs at or near its surface. On the other hand ZnO, which is a suitable alternative to TiO_2, has been reported to exhibit higher photocatalytic activity compared to that of TiO_2. The biggest advantage of ZnO is that it can absorb a larger portion of solar spectrum [3,40].

Methyl red (MR) dye has been used in textile, dying, paper, and printing industries; however, it causes irritation in eyes, skin, and digestive tract (if inhaled/swallowed) [2]. The present study reports the photocatalytic degradation of MR using commercially available ZnO under solar irradiation. For large-scale applications, this commercial ZnO might be a better choice (compared to nano ZnO) because of its low cost, non-toxic nature, and easy availability. The effect of various parameters such as initial dye concentration, ZnO dose, pH of the reaction medium, interfering ions, and low molecular weight organic acids has been examined. The amount of mineralization of MR dye was indicated by the chemical oxygen demand (COD) of the degraded solution.

2. Materials and methods

2.1. Materials

The commercial sample of MR (C.I. Acid Red 2; molecular weight = 269.3) obtained from S.D. Fine Chemicals, India was used without further purification. The commercially available photocatalyst zinc oxide (ZnO) from Merck, India was used as received. All other chemicals used in the study such as NaOH, KNO_3, NaCI, Na_2SO_4, KH_2PO_4, $CaCl_2$, and $FeSO_4$ were obtained from Merck, India. Humic acid, oxalic acid, maleic acid, malic acid, citric acid, p-benzoquinone, sodium azide, t-butanol obtained from Aldrich were used as received. All the chemicals were of reagent grade quality. The reagents potassium dichromate ($K_2Cr_2O_7$), conc. H_2SO_4, mercuric sulfate ($HgSO_4$), and silver sulfate (Ag_2SO_4) used for COD analyses were from S. D. Fine Chemicals. Double-distilled water was used throughout the entire studies. Solution pH was adjusted with HCl (0.1 N) and NaOH (0.1 N) solution whenever required.

2.2. Instrumentation

The instruments used in the study were UV–vis spectrophotometer (Chemito, spectrascan 2600), JEOL JSM - 5800 field emission scanning electron microscope (FESEM), X-ray diffraction (PANalytical B.V., Netherland), 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-2MLH). A diffuse reflectance UV-visible spectrum (DRS) was collected in an ultraviolet–visible–near infrared Cary 5000 spectrophotometer. The intensity of solar light was measured using a Lux Meter (Lutron LX 105) at various time intervals between 10 AM and 3 PM.

2.3. Experimental procedure

The photocatalytic experiments were carried out in a 500 mL capacity borosilicate beaker having dimensions 12.5×10 cm (height × diameter). Sunlight was used as the energy source for catalyst excitation. Upon the addition of 30 mL of MR dye solution (conc. ≈30 mg/L) in the beaker, the optimized dose of ZnO catalyst was introduced into the solution. This setup was placed on a magnetic stirrer to further enhance the agitation of the dye solution. The whole set-up was placed under sunlight exposure between 10 AM and 3 PM and the average intensity of sunlight during this period was 50,000 Lux units. The heat up of the reacting solution during the process of photocatalytic reaction was not much and the temperature varied within ± 3˚C between the starting and ending point of 1 h reaction. However, to make the situation simpler and more practical for real field applications, no cooling system (such as water jacket or water trough) was used. During the course of reaction the samples were withdrawn from beaker time to time and analyzed after centrifugation to find out the degradation efficiency. All experiments were performed at solution pH and under ambient condition.

Studies were conducted to know the extent of dye adsorption onto the surface of the catalyst. After 60 min, adsorption–desorption equilibrium was reached in the presence of ZnO, and this was considered to be the "zero time of irradiation". Additional experiments were carried out to verify that the observed removal of dye from solution was indeed photocatalysis. Two separate experiments were conducted: in one experiment the MR solution was irradiated under the Sun without photocatalyst (direct photolysis); in the second experiment the MR dye was stirred with ZnO in the dark for adsorption studies. After 1 h of solar irradiation, direct photolysis contributed ~7% dye degradation while the adsorption could remove ~3% of dye after reaching the adsorption–desorption equilibrium in 1 h. The progress of the photocatalytic degradation of MR was monitored by measuring the absorbance ($\lambda_{\max} = 435$ nm) of irradiated supernatant solution after the separation of suspended ZnO by centrifugation. The concentration of MR was determined from the absorbance value using the pre-established calibration curve. The extent of mineralization of the dye was examined by COD measurement following the closed reflux titrimetric method.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. FESEM analysis

The surface morphology and structure are two very important parameters for photocatalyst as they influence its activity. Moreover the catalytic activity of semiconductor material is strongly dependent on particle size. This is because the particle size represents the surface area available for phototocatalytic reactions. The FESEM image (Fig. 2(a)) of commercial ZnO indicates the presence of crystallites having various shapes and sizes. Different shapes were observed for particles having size in sub-micrometer range.

3.1.2. Powder X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) is a versatile, non-destructive technique which is being used for analyzing crystalline material. XRD analysis of commercial ZnO sample was carried out to determine the overall structure and degree of crystallization, i.e. size, composition, and crystal structure. Fig. 2(b) shows the XRD pattern of commercial ZnO. The XRD pattern indicated that crystallographic phase of commercial ZnO is similar as wurtzite-type ZnO. Diffraction peaks at $2\theta = 31.68$, 34.36, 36.18, and 56.56 correspond to (1 0 0), (0 0 2), (1 0 1), and (1 1 0) planes of ZnO confirming its hexagonal structure [41]. The higher intensity of the (1 0 1) peak is indicative of anisotropic growth and a preferential orientation of the crystallites [42,43].

3.1.3. Determination of band gap of ZnO

The band gape energy (E_{bg}) of the ZnO particles was probed by using UV–visible diffuse reflectance spectroscopy (DRS). To determine the band gap of commercial ZnO, the diffuse reflectance spectrum (DRS) was recorded and the cut-off wavelength at which absorption sharp edge rises was determined by drawing a tangent on this curve (Fig. 2(c)). The band gap energy was calculated by using this cut off wavelength which is found at 401 nm. The calculation of band gap energy is performed by the following equation:

$$E_{\mathrm{bg}} = \frac{1,240}{\lambda}\,\mathrm{eV} \tag{6}$$

where λ is the wavelength in nanometer and E_{bg} is the band gap energy.

The corresponding band gap energy was 3.09 eV which is low compared to that of TiO_2 (3.2 eV). The band gap energy for ZnO is reported to be in the range of 3.06–3.3 eV [44,45].

3.1.4. Determination of zero- point charge (pH_{ZPC}) of ZnO

The characteristics of a pollutant, particularly its solubility in water, hydrophilicity, and other physiochemical properties depend on the charge associated with the molecule. For example, an organic acid may exist in its protonated (nonionic) or unprotonated (ionic) form when the solution pH is below or above its pKa. The positive, neutral, and negative forms can be achieved for some organic compounds in aqueous solution, which could greatly influence their photocatalytic degradation behavior. On the other hand, the solution pH can strongly affect the surface charge of the photocatalyst. In the heterogeneous photocatalytic degradation processes, the interaction/adsorption of solvent molecule or organic compound with the semiconductor surface is a favorable step. The pKa value of MR is ~5.1, indicating that below pH 5.1 it remains as neutral molecule and above this pH it remains as negatively charged species in aqueous solution.

The MR is a well known pH indicator which reminds that with the change of pH the $\lambda_{\max}$ of MR solution will also change. The pH_{ZPC} (zero-point charge) is the pH at which the catalyst material has a net zero surface charge. The pH_{ZPC} of ZnO used in

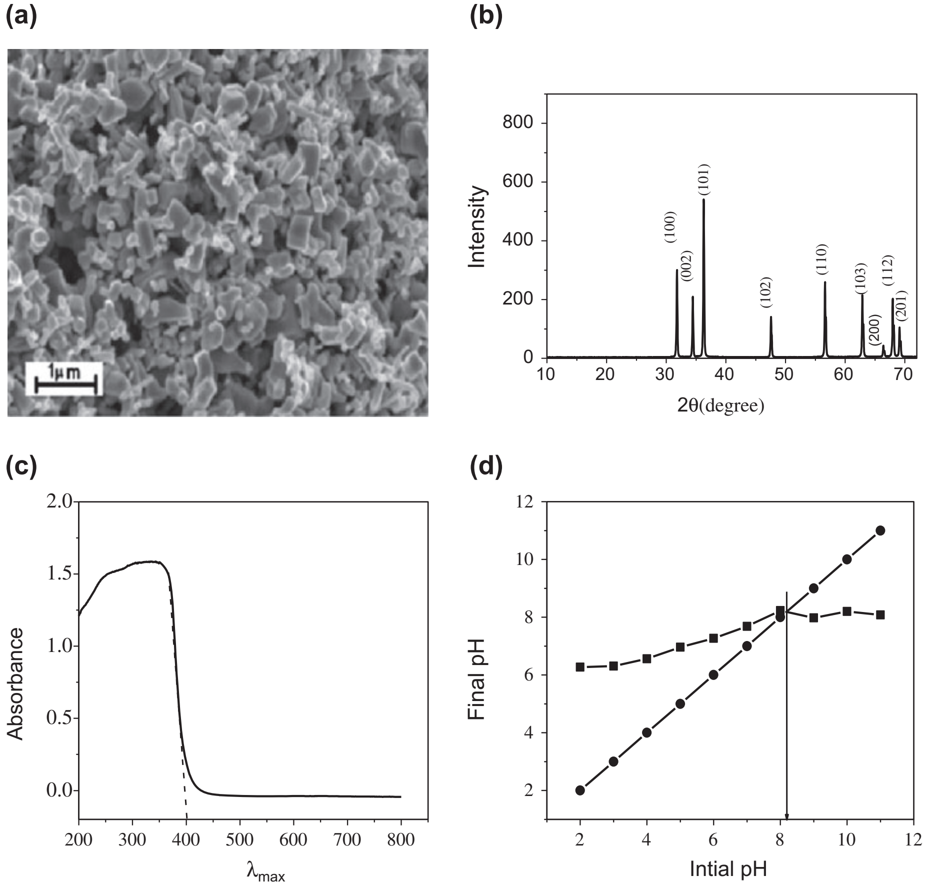

Fig. 2. Characterization of commercial ZnO by (a) FESEM, (b) XRD, (c) DRS, and (d) pH_{ZPC}.

our studies was determined experimentally following the reported procedure [45], and it was found to be 8.2 (Fig. 2(d)). This indicates that ZnO surface becomes positively charged below pH 8.2 and negatively charged above pH 8.2. The pH_{ZPC} value of ZnO and pKa of MR suggests that the optimum pH range for degrading MR should be 6–8. It is also important to mention here that in this pH range the UV–vis spectrum of MR shows a stable λ_{max}. Based on the above results/information, the optimum pH range for the photocatalytic degradation of MR with ZnO is chosen as 6–8.

3.2. ZnO-assisted photocatalytic degradation of MR under solar irradiation

3.2.1. Effect of ZnO loading

It has been already reported in literature that photocatalytic rate as well as degradation efficiency depend on catalyst loading. Increased surface area and absorption of light are mainly responsible for this type of behavior. At lower dose of catalyst, the absorption of light plays a dominating role compared to catalyst surface area. Initial rate of photodegradation is found to be proportional to the mass of the catalyst. When ZnO is overloaded, the reaction rate decreases due to an increase in particle aggregation, light scattering, and screening. In addition, the surface that absorbs the photons does not increase in a geometrical ratio [46,47]. That is why it becomes important to choose optimum dose of catalyst in order to avoid overloading of catalyst and to ensure optimum absorption of incident photons from the Sun. The influence of catalyst dose on the dye degradation efficiency of MR was studied for a dye solution with an initial concentration of 30 mg/L. The photoirradiation of dye solution was carried out for 1 h with varying ZnO doses from 0.3 to 3 g/L under solar irradiation with the same initial concentration of the dye. The obtained results are shown in Fig. 3. During the experiment, it was observed that decolorization of MR dye increased with the increase in ZnO dose from 0.3 to 0.5 g/L, and thereafter further increase in catalyst loading above 0.5 g/L had no effect. Studies on the COD removal were also performed to know the

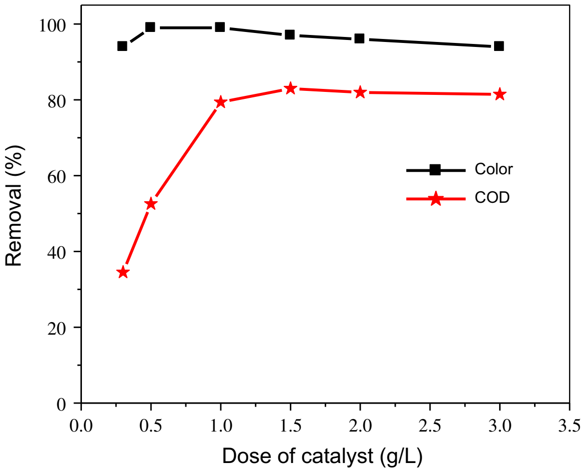

Fig. 3. Effect of catalyst dose on photocatalytic degradation of MR (pH = 7; MR conc. = 30 mg/L; Irradiation time = 1 h).

degree of mineralization of the dye. It shows that although dye color disappears in 1 h (~99%) but the solution bears residual COD. This type of behavior is not abnormal [47]. The increase in degradation with ZnO loading is attributed to the increased number of active sites on the catalyst surface and the absorption of solar light by the suspended particles, which in turn increased the number of holes and hydroxyl radicals in the reaction mixture. When the catalyst dose was increased to > 0.5 g/L, the photodegradation efficiency decreased to ~97%. This can be attributed to two factors: the agglomeration of catalyst particles, and the increase in the turbidity of the solution. The turbidity of the solution increases the scattering as well as the screening of incident light. This in turn reduces the penetration of solar light. Therefore, the most effective photodegradation (~99%) of MR in terms of decolorization was observed with 0.5 g/L ZnO upon 1 h of solar irradiation. Hence, an optimum ZnO dose of 0.5 g/L was selected for all further experiments.

3.2.2. Kinetic studies and the effect of initial concentration of MR

Two major processes, photolysis and adsorption, besides the photocatalytic degradation, can contribute to the removal of MR. Direct photolysis of MR (30 mg/L) for 1 h in the absence of ZnO led to ~7% degradation, whereas adsorption of MR on ZnO (in absence of light) caused ~3% removal of MR (Fig. 4). In both cases, the experiment was carried out up to 1 h and the progress of MR degradation / removal was monitored at 435 nm at a regular time interval.

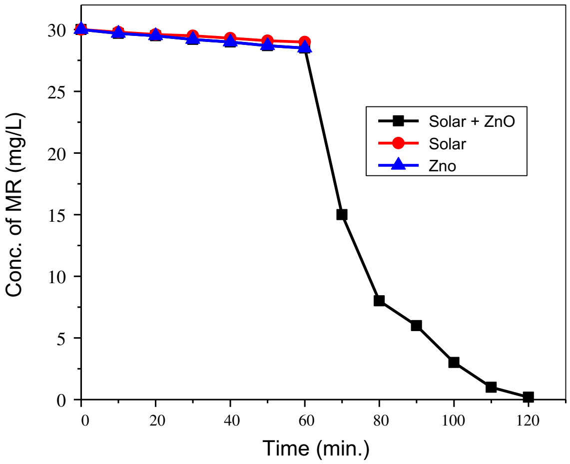

Fig. 4. Degradation of MR during photolysis (light, no catalyst), adsorption (catalyst, no light), and photocatalytic degradation (catalyst, light) experiments (MR conc. = 30 mg/L; catalyst dose = 0.5 g/L).

The decrease in concentration during adsorption and direct photolysis experiment was not so significant, though it was an obligatory step for our experiment to eliminate the contribution of these two processes for photodegradation. When the photocatalysis was performed after 1 h of adsorption/equilibrium experiment, the gradual change in absorbance of MR solution was instantly observed. These observations revealed the significance of ZnO as well as the efficacy of solar light in the photocatalytic destruction of MR dye.

The systematic photocatalytic degradation of MR under solar light was carried out with 30 mL of MR solution (conc. 30 mg/L) using optimum dose i.e. 0.5 g/L of ZnO. With the progress of the photocatalytic degradation, the absorption peak intensity decreased gradually. After 60 min of reaction, there was no evidence of absorption peak and almost ~99% degradation of MR dye occurred. It indicates that the main chromophore of MR in the solution is destroyed by solar light in the presence of ZnO. Upon irradiation with solar light, the electron from the valence band (VB) of ZnO goes to the conduction band (CB) creating a hole in the VB. The electrons in the CB and the holes in the VB then migrate to the surface of ZnO and react with the chemisorbed O_2 and/or OH^-/H_2O molecules to generate reactive oxygen species (ROS) such as $O_2^{\bullet-}$, $HOO^\bullet$, $^\bullet OH$ radicals, which attack dye molecules leading to their stepwise degradation, mineralization, and detoxification. Alternatively, the electrons in the CB can be picked up by the adsorbed dye molecules, thus forming dye radical anions. Subsequent reaction of the above radical anions can result in the degradation of the dye. The common and practical problem of photocatalysis is the recombination of $e^-_{\mathrm{cb}}/h^+_{\mathrm{vb}}$, which can be avoided by the use of suitable electron acceptor [48]. In the present study, all experiments were carried out under ambient conditions. The presence of dissolved oxygen in the reaction mixture is important because it has a tendency to work as an electron sink and participate in the formation of ROS such as super oxide radical $O_2^{\bullet-}$ and subsequently leading to other reactive species like H_2O_2, $HO_2^{\bullet}$, and HO_2^- [49,32]. This process also reduces the problem of recombination of hole and electron generated in the system. After the photocatalytic reaction it was observed that the color of the catalyst is slightly changed from white to dark grey. This implies that the reaction occurs on ZnO surface. Blank experiment was also conducted under solar irradiation on ZnO, and no change in color was observed on catalyst surface.

As has been mentioned, the photocatalytic degradation of the dye was monitored by measuring the absorption spectrum at a regular interval of time. The photodegradation efficiency of MR was calculated from a mathematical equation adopted from measurements of decolorization used before [50]:

$$\%\ \text{Color removal} = [(C_0 - C_t)/C_0] \times 100 \tag{7}$$

where C_0 is the initial concentration of dye and C_t is the concentration of dye at time t.

The percent color removal after 1 h of irradiation in the presence of ZnO (dose: 0.5 g/L) and at different initial MR concentrations (10–50 mg/L) was evaluated and the results are shown in Fig. 5(a). The color removal up to 99% was achieved in the MR concentration range of 10–30 mg/L, and thereafter with further increase of MR concentration the removal efficiency decreased. This could be due to the fact that the increase in MR concentration prevents the penetration of solar light through the solution. The other reason may be the number of MR molecules adsorbed on the surface of ZnO increases, but the number of $^{\bullet}OH$ radicals formed on the surface of ZnO remains constant. It is obvious that when concentration of MR increases, the requirement of ROS ($^{\bullet}OH$ and $O_2^{\bullet-}$) for the degradation of MR also increases. However, the concentration of $^{\bullet}OH$ and $O_2^{\bullet-}$ on the catalyst surface remains constant under a specified condition. Finally, the kinetics of photodegradation at various MR concentrations (30, 40, and 50 mg/L) under solar light irradiation was performed after an adsorption period of 1 h in the dark, and the data were fitted in various linear equations of reaction rates (Table 1). From the results, it could be interpreted that the photodegradation of MR under solar light employing ZnO as the photocatalyst follows first-order kinetics (Fig. 5(b)) with respect to dye concentration. Many authors have reported Langmuir–Hinshelwood (L–H) model for the heterogeneous photocatalytic degradation [51,52]. The rate constant (k) for different orders of the MR degradation (30 mg/L) was calculated from the slopes of the linear plots and presented in Table 1. From the correlation coefficient, it is assumed that the decolorization follows first-order kinetics better compared to others under the described experimental condition.

3.2.3. Effect of solar light intensity on MR degradation

The incident light intensity is expected to be one of the rate-controlling parameters. The influence of sunlight intensity on photocatalytic degradation was investigated at a fixed dye concentration (30 mg/L)

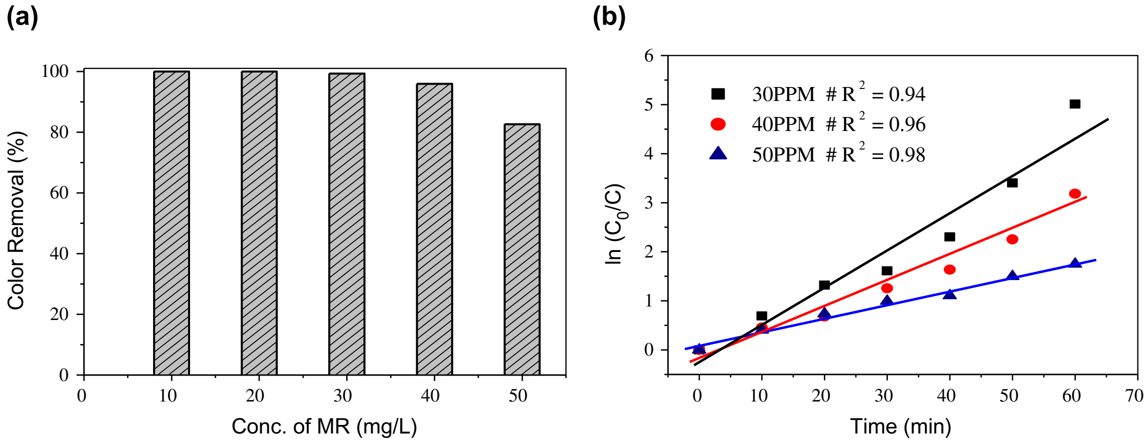

Fig. 5. (a) Effect of the initial dye concentration on photocatalytic degradation of MR, (b) First-order kinetics for MR degradation at different initial concentrations (pH = 7, catalyst dose = 0.5 g/L).

Table 1
Models used for degradation kinetics (MR conc. = 30 mg/L; catalyst dose = 0.5 g/L)

Kinetic model	Equation[a] for the linear fit	Rate constant	Correlation coefficient (R^2)
Zero-order	$C_t = C_0 - kt$	0.522	0.834
First-order	$\ln C_t = \ln C_0 - kt$	0.063	0.973
Second-order	$(1/C_t) = (1/C_0) + kt$	0.016	0.692
LH	$(1/r) = (1/Kkc) + (1/k)$	0.892	0.570

[a] C_0 = conc. at zero time; C_t = conc. at time t; k = rate constant; t = time; K = adsorption constant; r = rate of reaction

and catalyst dose (0.5 g/L). The solar irradiation generates the photons required for the electron transfer from the VB to the CB of a semiconductor photocatalyst. The energy of a photon is related to its wavelength, and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increased with the increase of light intensity as more radiation falls on the ZnO surface and hence more ROS are produced. One important aspect about the solar irradiation, however, is the control over the intensity. The light intensity varies during different hours of the day as well as it varies from day to day. To gain a quantitative idea about this aspect, two experiments were conducted. In our present studies all the experiments were conducted during January—March, 2012 when plenty of sunlight was available. The working hours of the day was selected between 10 AM and 3 PM when the Sun was bright. In the first experiment the intensity of the solar light was quantitatively measured (using a radiometer) during this time period, and recorded at an interval of 1 h (Table 2). The results indicate that during the 1 h time interval the variation lies within 5,000 Lux. Our experimental time scale for MR degradation was 1 h. Thus, it can be said that in this 1 h time scale the light intensity varied by ~5,000 Lux. The variation of intensity in 1 h time scale measured on different days was similar. The second experiment was conducted to examine the effect of solar light intensity on MR degradation. During this experiment, the intensity of light and the percent of MR decolorization were quantitatively measured. The plot of percent color removal vs. light intensity is shown in Fig. 6. It is obvious that the MR degradation is related to light intensity. The intension was to see the optimum light intensity that can result in maximum decolorization under the imposed experimental conditions. It was observed that the minimum light intensity required for 100% color removal under the experimental condition (conc. of MR = 30 mg/L; dose of ZnO = 0.5 g/L; time of irradiation = 1 h) was 45,000–50,000 Lux. Thus it was possible to relate the time of the day to conduct the experiment, the optimum intensity of the solar light required, and the percentage of decolorization. The solutions of MR were degraded on different days and under different intensity of sunlight, and similar results were obtained.

Table 2
Variation of sunlight intensity at different time period of the day

Time period[a]	Intensity (Lux)
10–11 AM	40,000–45,000
11 AM–12 noon	45,000–50,000
12 noon–1 PM	50,000–55,000
1–2 PM	55,000–65,000
2–3 PM	55,000–60,000

[a] Sunlight intensity as measured in the period of January—March (2012) during 10 AM–3 PM.

3.2.4. Effect of pH of dye solution on MR degradation

It is known that pH of solution plays a crucial role in photocatalytic degradation of many organic compounds [53]. This prompted us to study the influence of pH on the photocatalytic degradation of MR. Moreover due to the amphoteric behavior of ZnO [47], the pH of the solution is a crucial parameter which governs the degradation rate on semiconductor particle surface since it determines the charge on the surface of the ZnO as well as the size of the aggregates formed. Characteristics of MR viz. speciation behavior, solubility in water, and hydrophobicity can also vary with the pH of the medium. The reported value of pK_a of MR is 5.3. Thus, below pH 5.3 it will remain in neutral form whereas above this pH it will exist in its anionic form. Charge on MR also has significant influence on its photocatalytic degradation behavior. It is also known that protonation and deprotonation of MR can take place depending on the pH of the reaction medium.

The effect of pH on the color as well as the λ_{max} of the MR dye was also studied to determine the optimum pH range for the maximum photocatalytic

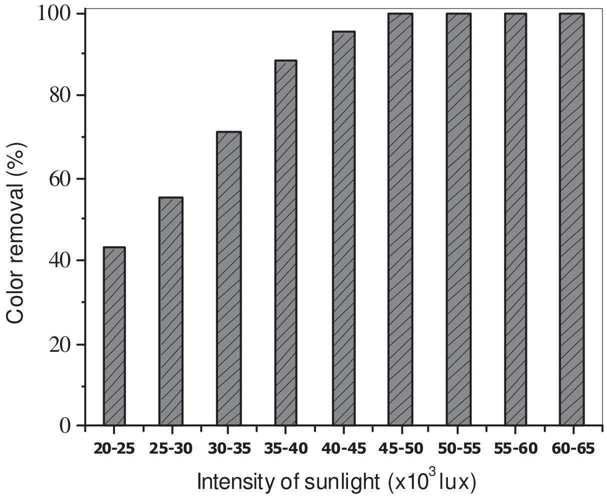

Fig. 6. Effect of solar light intensity on photocatalytic degradation of MR (30 mg/L) with optimized ZnO dose (0.5 g/L).

degradation of the dye. The effect of initial pH of the reaction medium on the degradation of MR was studied in the pH range from 2 to 12 with 30 mg/L MR concentration and 0.5 g/L ZnO loading. The pH of the MR solution was adjusted using dilute (0.1 N) HCl and (0.1 N) NaOH solutions. It was noticed that there is a shift of $\lambda_{\max}$ for MR at pH 5–6 (Fig. 7(a)). When the pH is further increased there is no further shift. The pH of the medium as the reaction proceeds was also monitored up to 1 h and it was observed that there was a shift of 1 unit in the pH of solution (Fig. 7(b)). However, as is obvious from Fig. 7(a) there should not be any shift of $\lambda_{\max}$ of MR due to this slight change of pH during the reaction. The $\mathrm{pH_{zpc}}$ of commercial ZnO is 8.2, which indicates that below pH 8.2 the particle surfaces remain positively charged and above 8.2 remain negatively charged. That is why all photocatalytic degradation reactions in our studies were carried out at pH ~7, where dye was in anionic form and ZnO surface was positively charged. Under this condition, the photocatalytic degradation would be more effective. As observed in Fig. 7(b), the pH increases significantly during 1 h irradiation, from pH 6.5 (at $t = 0$ h) to pH 7.5 (at $t = 1$ h). The observed change in pH may be attributed to the formation of various intermediates during the progress of the reaction.

3.2.5. Effect of interfering substances

Presence of common dissolved inorganic solids in dye-bearing wastewater can significantly influence the photocatalytic degradation. To investigate the applicability of this green approach to the treatment of real wastewater, the effect of different inorganic ions viz. Ca^{2+} (up to 100 mg/L), $Fe^{2+/3+}$ (up to 45 mg/L), Cl^- (up to 800 mg/L), SO_4^{2-} (up to 80 mg/L), $H_2PO_4^-$ (up to 400 mg/L), and NO_3^- (up to 800 mg/L), common organics such as humic acid (10 mg/L), and some low molecular weight organic acids like malic acid, maleic acid, oxalic acid, tartaric acid, and citric acid (each at 1 mM) was studied on the photodegradation of MR (initial conc.: 30 mg/L and ZnO dose: 0.5 g/L) for 1 h.

The presence of certain ions / molecules can affect the photocatalytic degradation in many ways such as by getting adsorbed on the surface of the catalyst, by competing with the dye molecule, and subsequently reduce the formation of ROS. In some cases, the ions in the reaction mixture can force scavenging hydroxyl radicals, thus decreasing the efficiency. The results show that in the described range Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+} did not show any significant effect on the dye degradation. However, maximum reduction (up to ~80%) in degradation efficiency was observed in the

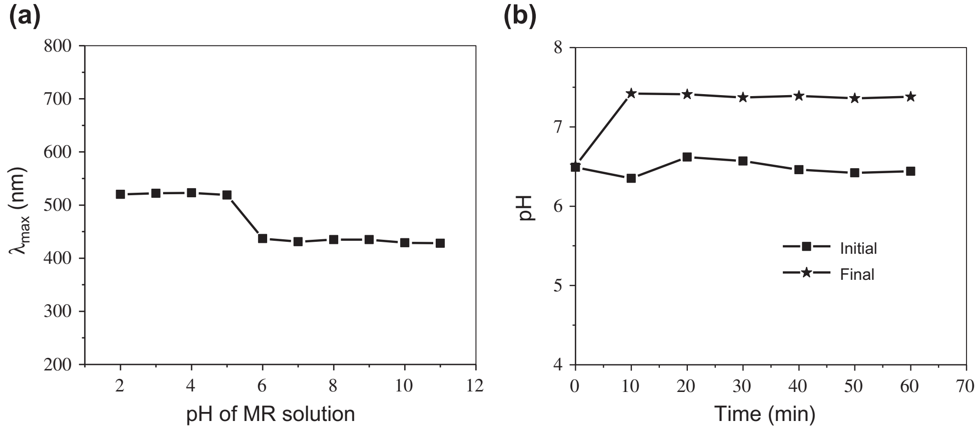

Fig. 7. (a) Effect of pH on $\lambda_{\max}$ of MR, (b) Effect of MR degradation on the final pH of solution.

presence of $H_2PO_4^-$ ion, even at a concentration of 100 mg/L, which is attributed to the binding ability of ZnO with dihydrogen phosphate [54]. The presence of $Fe^{2+/3+}$ (at a concentration of 45 mg/L), on the other hand, caused up to only 5% decrease in efficiency. It is important to mention that MR degradation under UV light also produced similar results.

Wastewaters in many cases are found to contain organic acids having lower molecular weights. Moreover, during the degradation of organic contaminants, sometimes these acids are produced. Thus, a set of experiments was performed to see the effect of such acids viz. oxalic acid, citric acid, maleic acid, malic acid and tartaric acid. Because humic acid also occurs in nature, so the effect of humic acid on MR degradation under solar light irradiation is also investigated. The results are shown in Fig. 8. Although there was not much effect in the degradation of MR in the presence of humic acid, oxalic acid and citric acid, but a significant reduction in degradation was observed in presence of malic acid, maleic acid, and tartaric acid. It is clear from the plot (Fig. 8) that the MR degradation was 62, 51 and 39% in the presence of malic acid, maleic acid, and tartaric acid, respectively. Further investigation is warranted to understand such interferences.

3.2.6. Mineralization

The degree of MR mineralization with time was estimated by measuring the change in COD of the degraded solution. Kinetic studies on COD removal were performed with optimized dose of catalyst (i.e. 0.5 g/L) for 30, 40, and 50 mg/L solutions of MR. Aliquots were taken at 10 min interval and COD was measured using closed reflux titrimetric method. The COD removal was measured as follows:

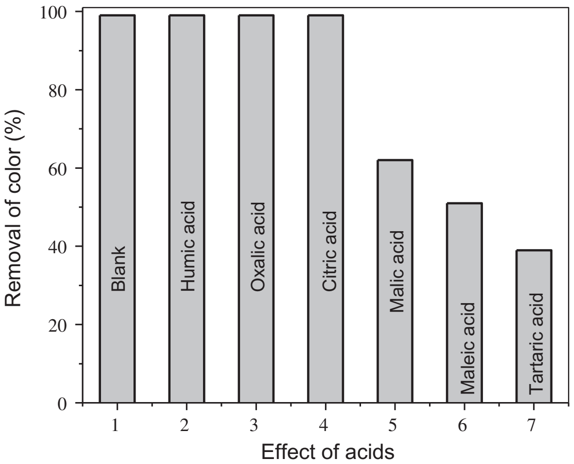

Fig. 8. Effect of low molecular weight organic acids on color removal of MR under solar light irradiation.

$$\text{COD removal} = [(1 - \text{COD}_t)/\text{COD}_0] \times 100 \quad (8)$$

where COD_t and COD_0 are COD (mg/L) values at any given time *t* min and at time 0 min, respectively.

It is noticed that in the MR concentration range of 30–50 mg/L and with ZnO dose 0.5 g/L, the COD removal was ~43–56% upon 1 h of solar irradiation. It is to be mentioned here that upon 30 min irradiation, the color removal was ~80, 68, and 60% for the MR solution having concentration 30, 40, and 50 mg/L, whereas for the same solutions the COD removal (i.e. mineralization) was ~33, 31, and 25%. Similarly for an MR solution having 30 mg/L concentration, in the presence of 0.5 g/L of ZnO and upon 1 h irradiation, the color removal was ~99% and the COD removal was ~53%. However, the percentage of mineralization could greatly be enhanced (~80%) by increasing the catalyst dose to 1 g/L (Fig. 3). Removal of color at a much faster rate compared to that of COD is common because degradation takes place in steps, and thus in most cases complete mineralization requires much longer time [55].

3.2.7. Studies on the mechanism of the photocatalytic degradation of MR

To gain insight into the mechanism of photocatalytic degradation and to know the role of various ROS such as singlet oxygen ($^1O_2$), superoxide ($O_2^{\cdot -}$), and hydroxyl ($^\cdot OH$) radicals under photocatalytic conditions, a detailed study was carried out. It has already been reported in literature that superoxide radicals, singlet oxygen, and hydroxyl radicals are mainly responsible for photocatalytic oxidation of dyes on semiconductor surfaces. To figure out the role of these ROS in aqueous suspension of MR and ZnO under solar light, appropriate quenchers of these species were used. Sodium azide, p-benzoquinone, and t-butanol were selected as $^1O_2$, $O_2^{\cdot -}$, and $^\cdot OH$ radical scavengers [56,57]. The reaction rate constant of t-butanol with hydroxyl radicals is already reported to be $6.0 \times 10^8\,M^{-1}\,s^{-1}$ [57]. In this experiment, a comparison was made between the original decolorization graphs of MR obtained in the presence of ZnO (only) with those in the presence of ZnO and quenchers (separately, and at a conc. of 1 mM), under otherwise identical conditions (Fig. 9).

It was clear that the degradation of MR was quite suppressed in the presence of p-benzoquinone and only 36% of MR was decolorized within 60 min. On the other hand, the addition of sodium azide caused the degradation of MR with 60% decolorization efficiency. It was noted that there was no difference in

MR decolorization in MR–ZnO system with and without t-butanol. These results confirmed that $^1O_2$ and $O_2^{\cdot -}$ were the main ROS in the decolorization of MR in MR–ZnO suspension, and the role of ·OH was not significant.

3.2.8. Turnover frequency (TOF) and recycle ability of the catalyst

Solar photocatalysis seems to be a greener technology and practically feasible. Catalyst used in this process can be recycled. The cost effectiveness of the solar photocatalytic process depends on two factors: first, recycle ability of the catalyst without sacrificing its efficiency, and secondly, the ease of regeneration of the catalyst. To examine the cost-efficiency of this method, the photocatalyst was recycled for MR degradation. The photodegradation efficiencies of the recycled ZnO catalyst were found to be 86 and 79% after first and second cycle of operations compared to 99% obtained with the fresh material under the same experimental conditions. The used photocatalyst could be generated very easily. After degradation of the dye, the solution was first centrifuged and then the supernatant was decanted. After that the catalyst was thoroughly washed several times with distilled water till a colorless wash liquid was obtained. Then the catalyst was dried in a hot air oven at a temperature of 90–100˚C for 24 h. The efficiency of the catalyst was slightly less compared to that of the fresh one. The decrease in the efficiency of the recycled catalyst may be attributed to the deposition of degradation products (fouling) on the ZnO surface blocking its active sites. This type of problem with photocatalyst has already been reported in literature [58].

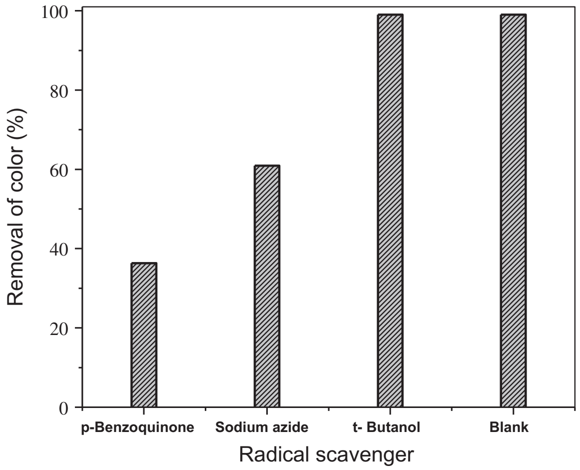

Fig. 9. Effect of radical scavengers on MR degradation (Initial conc. = 30 mg/L; catalyst dose = 0.5 g/L; time of irradiation = 1 h).

Catalyst turnover number (TON) and turnover frequency (TOF) are two important parameters to compare catalyst activity [59]. For heterogeneous catalysis, TON is the number of reactant molecules that is converted to products in the presence of 1 g catalyst. The TOF is TON/time. For the degradation of MR (30 mg/L) with ZnO (0.5 g/L), the TOF was found to be 3.6×10^{16} molecules/g/s.

3.2.9. Comparison of the photocatalytic efficacy of commercial ZnO and ZnO nanoparticles

The present study utilizes the commercially available ZnO (Merck) for MR degradation under solar light. Earlier works [60–63] for MR degradation using nano ZnO and commercial ZnO (either in the free or supported form) under UV light and visible light were compared with the present work and compiled in Table 3. It has been observed that the present procedure is better compared to other methods in terms of efficiency and the time required for exposure. In case of large-scale applications commercial ZnO and solar irradiation are always preferable because of low cost of the ZnO and easy availability of the solar light. Furthermore, utilization of the solar light for the degradation can make the process more energy efficient and green.

3.2.10. Cost-benefit analysis of solar degradation process

In our earlier studies, we used "commercial TiO_2 (Merck)" and "Ag^+ doped TiO_2 (later on designated as nano silver impregnated TiO_2) [55]" for the MR degradation using UV light or solar light (250-W Philips tungsten-halogen lamp) [64]. A comparative account of the catalyst used in the present study was made with commercial TiO_2 and Ag^+-doped TiO_2 in terms of their MR degradation ability and cost (Table 4). The cost of ZnO photocatalyst was comparable to that of commercial TiO_2 but the latter showed very poor activity under solar irradiation. The Ag^+-doped TiO_2 is known as a good photocatalyst, but the works reported earlier [64] encountered less degradation as well as prolong reaction time in case of MR dye.

4. Conclusions

MR, a widely used azo dye was efficiently degraded in the presence of commercial ZnO under solar irradiation. The method qualifies as a green approach as it requires no UV light in the dye

Table 3
Comparison of the photocatalytic efficacy of commercial ZnO and ZnO nanoparticles for MR degradation

Materials	Particle size	Light source	MR concentration (M)	Solution pH	Degradation (%)	Time of irradiation (min)
Nano-ZnO[a]	7 nm	UV	3.0×10^{-5} M	6	–50	145
Commercial ZnO[a] (Aldrich)	<1 μm	UV	3.0×10^{-5} M	6	–80	145
Nano-ZnO[b]	NR[f]	UV	3.7×10^{-5} M	NR[f]	–30	180
Nano-ZnO[c]	6 nm	UV	NR[f]	NR[f]	60	140
Commercial ZnO[c] (Aldrich)	<1 μm	UV	NR[f]	6	76	NR[f]
Nano-ZnO (hydrolytic & non-hydrolytic)[d]	6 nm	UV	3.0×10^{-5} M	6	100 & 54	145
Commercial ZnO[d] (Aldrich)	>200 nm	UV	3.0×10^{-5} M	6	93	145
Commercial ZnO[e] (Merck)	<1 μm	Solar	11.1×10^{-5} M	–7	99	60

[a]Ref. [60]; [b]Ref. [61]; [c]Ref. [62]; [d]Ref. [63]; [e]Present work; [f]NR = not reported

Table 4
Efficiency and cost evaluation of different photocatalyst under solar irradiation

Photocatalyst	pH_{ZPC}[a]	Separability[b,c]	Degradation of MR (%)[d,e]	Cost (Rs./100 gm)[a]	Degradation time (h)[d]
TiO_2	6.2[a]	b	Very less[d]	50[a]	10[d]
Ag–TiO_2	7.1[a]	c	90[d]	88[a]	10[d]
ZnO	8.2	c	99[e]	89	1

[a]Ref. [55]. [b]Requires 0.45 μm membrane filtration. [c]Requires settling or centrifugation. [d]Concentration of MR: 20 mg/L, catalyst dose: 1 g/L [64]. [e]Concentration of MR: 20 or 30 mg/l, catalyst dose: 0.5 g/L.

degradation process. The used ZnO catalyst was characterized by SEM, XRD, DRS, and the pH_{zpc} was determined. The studies confirm that all ZnO particles are in sub-micron range and the band gap of commercial ZnO is 3.09 eV. It is important to choose the optimum condition to maximize the degradation rate and to minimize the cost of the process. MR solution of 30 mg/L concentration has been successfully degraded with 99% color removal in 1 h irradiation with a catalyst dose of 0.5 g/L. The COD removal for the same solution under similar condition was ~53%. However, ~80% COD removal for the same solution was possible when the catalyst dose was increased to 1.0 g/L. Effect of intensity of the solar light on MR degradation was also investigated. Color removal was found to be increased with increasing intensity of solar light. ZnO can be easily recycled without sacrificing much photoactivity. The photodegradation followed first-order kinetics under the experimental condition. The effect of various low molecular weight organic acids and common inorganic interfering agents on MR degradation under solar light was studied. The role of ROS was also investigated to understand the reaction mechanism. Studies indicated the participation of $^1O_2$, $O_2^{\bullet -}$ species during the photocatalytic reaction, $O_2^{\bullet -}$ being the more dominant. The catalyst showed high TOF. A cost-benefit analysis was made to evaluate the efficacy of the catalyst with respect to the earlier used catalysts [64] viz. "commercial TiO_2" and Ag^+ doped TiO_2. While the present method for MR degradation is compared with the existing methods which make use of nano-ZnO and commercial ZnO, the present method stands to be more economical and greener.

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