Effect of operational parameters and kinetic study on the photocatalytic degradation of *m*-cresol purple using irradiated ZnO in aqueous medium

Sajjad Khezrianjoo and Hosakere Doddarevanna Revanasiddappa

ABSTRACT

A detailed investigation of photocatalytic degradation of *m*-cresol purple (*m*CP) dye has been carried out in aqueous heterogeneous medium containing zinc oxide (ZnO) as the photocatalyst in a batch reactor. The effects of some parameters such as amount of photocatalyst, dye concentration, initial pH of solution, ethanol concentration and temperature were examined. The most efficient pH in removal of the dye with photocatalytic degradation and dark surface adsorption processes was observed to be 8. The adsorption constant calculated from the linear transform of the Langmuir isotherm model was similar to that obtained in photocatalytic degradation at pH = 8; hence, the Langmuir–Hinshelwood model was found to be accurate for photocatalytic degradation at this pH. Dark surface adsorption and degradation efficiency were increased by enhancement in the temperature at the optimum pH of 8 and the apparent activation energy (E_a) for the photocatalytic degradation of *m*CP was determined as 14.09 kJ/mol at this pH. The electrical energy consumption per order of magnitude (E_{EO}) for photocatalytic degradation of *m*CP was also determined.

Key words | dark surface adsorption, decolorization, energy consumption, kinetic model, optimization, photodecomposition

Sajjad Khezrianjoo
Hosakere Doddarevanna Revanasiddappa
(corresponding author)
Department of Chemistry,
University of Mysore,
Mysore 570006,
India
E-mail: *hdrevanasiddappa@yahoo.com*

INTRODUCTION

An important source of environmental concern is dye pollutants. The release of wastewater containing dye in the ecosystem is a dramatic source of esthetic pollution and perturbations in aquatic life (Herrmann 1999; Galindo *et al.* 2001). Most of the organic dyes are not easily biodegradable. Nevertheless methods such as reverse osmosis, adsorption on activated carbon, ion exchange and ozonation do not destruct the pollutant molecule efficiently (Galindo *et al.* 2001). Heterogeneous photocatalysis appears as an emerging solution to destruction of dyes and many other organic compounds from wastewater in the presence of semiconductors (TiO$_2$, ZnO, CdS, etc.) and ultraviolet (UV) light (Khezrianjoo & Revanasiddappa 2013). Among the semiconductors, titanium dioxide (TiO$_2$) is found to be efficient for photocatalytic degradation of pollutants due to superior photocatalytic oxidation ability, non-photo-corrosive and non-toxic characteristics (Saien & Khezrianjoo 2008). However, widespread use of TiO$_2$ is uneconomical for large scale water treatment; thereby interest has been drawn towards the search for suitable alternatives to TiO$_2$. Zinc oxide (ZnO) appears to be a suitable alternative to TiO$_2$ since its photodegradation mechanism has been proven to be similar to that of TiO$_2$ (Dindar & Icli 2001; Pirkanniemi & Sillanpaa 2002). The biggest advantage of ZnO in comparison with TiO$_2$ is it adsorbs over a larger fraction of the UV spectrum and the corresponding threshold of ZnO is 425 nm (Behnajady *et al.* 2006). Meanwhile, ZnO has been reported, sometimes, to be more efficient than TiO$_2$

(Khodja *et al.* 2001; Kansal *et al.* 2009; Krishnakumar & Swaminathan 2011). When ZnO is irradiated with light having energy equal to or more than the band gap energy (3.37 eV), a heterogeneous photocatalytic reaction occurs at the solid solution contact surface (Sobana & Swaminathan 2007).

For engineering purposes, it is useful to find out a simple and easy-to-use rate equation that fits the photocatalytic degradation rate data. Many authors have used the modified Langmuir–Hinshelwood (L-H) kinetic expression to analyze the heterogeneous photocatalytic reaction with ZnO successfully (Chakrabarti & Dutta 2004; Vasanth Kumar *et al.* 2007; Habib *et al.* 2013). This model is subject to the assumptions that adsorption of both the oxidant and the reductant are rapid equilibrium processes and that the rate-determining step of the reaction involves both species present in a monolayer at the solid–liquid interface (Chakrabarti & Dutta 2004). The L-H kinetic model could describe the solid–liquid reaction as:

$$r = k_c \frac{K_{LH}C}{1 + K_{LH}C_o} = k_{obs}C \qquad (1)$$

where C_o and C are the initial pollution and concentration at a given time; K_{LH} is the L-H adsorption equilibrium constant and k_c is the surface kinetic rate constant of reaction. However, the fitting of experimental data with the L-H type kinetic model using zinc oxide photocatalyst has so far only been demonstrated for the photocatalytic degradation of organic substrates in single-component systems. Another point to check is dark surface adsorption; if the kinetically obtained K_{LH} is different from that obtained by dark adsorption measurement, the L-H mechanism cannot be adopted (Ohtani 2008; Khezrianjoo & Revanasiddappa 2012). Therefore, for L-H kinetic analysis, the dark adsorption measurement is always required (Ohtani 2008; Khezrianjoo & Revanasiddappa 2012).

The aim of the present work is to study the removal of an indicator dye, *m*-cresol purple (*m*CP) in the presence of ZnO photocatalyst as a suitable alternative to TiO$_2$ irradiated by UV. Effects of operational parameters as well as degradation kinetics are investigated and 'Electrical Energy per Order' is also determined.

MATERIALS AND METHODS

Reagents and chemicals

All reagents were used as received. The *m*CP indicator dye $C_{21}H_{17}NaO_5S$ (CAS No. 2303-01-7, MW = 382.43) was provided from S.D. Fine Chemical Company, India, with purity of more than 97%. The molecular structure of this dye is shown in Figure 1. The ZnO catalyst was a Lobal Chemie, India product; with particle size of $<5\,\mu m$ and purity of more than 99%. Hydrochloric acid, sodium hydroxide and ethanol were of laboratory reagent grade (Merck products). Distilled water was used to prepare the solutions.

Photo-reactor

For the degradation process a circulating photo-reactor made of glass with a cube body shape (27 cm length, 20 cm width and 4 cm height) was used. The reactor was equipped with a water-flow jacket for regulating the temperature, by means of the external circulating flow of a thermostat bath, having an accuracy of $\pm 0.1\,^{\circ}C$. The 18 watt low pressure mercury UV lamp (Philips TUV PL-L) was positioned on top of the reactor with a 15 cm distance from the surface of the solution. The liquid film in the reactor was 19 mm thick. The photocatalytic reactor system was operated in a batch mode and after each experiment the reactor solution was disposed of. A pump circulated the solution; in this way, both fluidizing and good mixing of the catalyst particles were provided. The whole reactor body was covered with thin polished aluminum reflectors. Since the photocatalysis is sustained by a ready supply of dissolved oxygen, air was supplied to the center and four corners of the reactor at constant flow-rate using a micro air compressor.
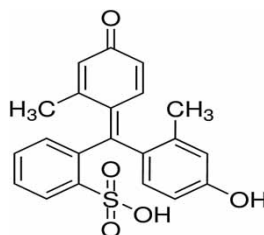

Figure 1 │ Chemical structure of *m*CP.

Photocatalytic experimental procedure

To perform the experiments, one liter of a solution containing 20 mg/L of mCP (5.23×10^{-5} M), and a known amount of ZnO mass were prepared. The pH was adjusted to the desired value by using a pH meter (Elico LI 127). To start the degradation, the solution was transferred to the reactor, and the lamp was switched on while adjusting the temperature. During each experiment, circulation of the suspension was maintained to keep the suspension homogeneous. Samples (4 mL) were taken at regular time intervals and then centrifuged, to separate the ZnO particles from the solution. Analyses were performed with a UV-Vis spectrophotometer (Systronics 168) provided with 1 cm matched quartz cells. The degradation efficiency or conversion (X) of mCP with respect to its initial concentration at any time was obtained by:

$$X = \frac{C_o - C}{C_o} \tag{2}$$

where C_o and C are the initial mCP and concentration at a given time.

Adsorption isotherm

All batch equilibrium experiments were conducted in the dark. At the time of 15 minutes, the study of mCP adsorption was performed on ZnO at different initial concentrations and pH. Data obtained from the adsorption experiments was fitted to the modified empirical Langmuir equation:

$$Q = \frac{Q_{max}K_{ads}C}{1 + K_{ads}C} \tag{3}$$

where Q_{max} is the maximum absorbable dye quantity and K_{ads} is the equilibrium constant for adsorption. This relationship (Equation (3)) can be written in linear form as:

$$\frac{C}{Q} = \frac{1}{Q_{max}K_{ads}} + \frac{C}{Q_{max}} \tag{4}$$

and the adsorbed quantity (Q in mg/g) was calculated as:

$$Q = \frac{V\Delta C}{m} \tag{5}$$

where ΔC is the difference between the initial concentration (C_o) and the equilibrium concentration (C), V is the volume (L), and m is the mass of ZnO (g).

The dimensionless separation factor (R_L) (Equation (6)) has been used to describe the shape of the Langmuir isotherm (L-shape) to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{1 + K_{ads}C_o} \tag{6}$$

where K_{ads} is the Langmuir adsorption constant and C_o is the highest initial dye concentration (20 mg/L).

RESULTS AND DISCUSSION

Effect of catalyst concentration

In the presence of both ZnO and UV light, 97.2% of dye was degraded at the irradiation time of 240 min. This was contrasted with only 3.6% decolorization for the same experiment performed without ZnO as photocatalyst. Figure 2 shows a plot of the reaction rate constant k_{obs} as a function of the catalyst mass for the mCP degradation under UV illumination. The rate constant increases with an increase in the amount of catalyst up to a level corresponding to the complete absorption of incident light by the catalyst. With an increase in the catalyst mass, the density of particles in the area of illumination increases; meanwhile, the greater number of the dye molecules that
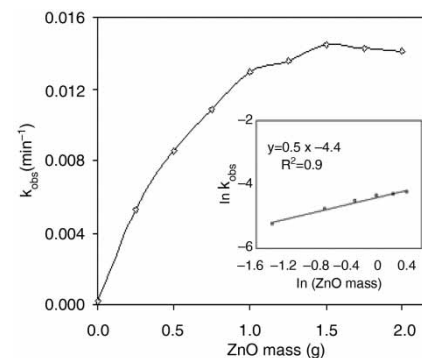
Figure 2 | Effect of the amount of ZnO on degradation rate constant of mCP. Inside: relationship between $\ln(k_{obs})$ and $\ln$(ZnO mass) [mCP]$_o$ = 20 mg/L, [ZnO] = 1.5 g/L, T = 25 °C and pH = 6.7.

will be adsorbed on catalyst surface. Above 1.5 g, the degradation rate constant of mCP decreases mildly. The reason for this can be due to the screening effect of excess catalyst particles, which masks reduction in the light intensity throughout the solution (Daneshvar *et al.* 2004).

Hypothesizing that the rate of photocatalytic degradation depends on catalyst concentration, the initial rate of photocatalytic degradation of dye (r_o) with the homogeneous photochemical reaction can be expressed in the following form (Galindo *et al.* 2001):

$$r_o \alpha [catalyst]^n [dye]^m \tag{7}$$

Since the photocatalytic degradation of the dyes in aqueous ZnO can be described by the pseudo-first-order kinetic, the amount of m exponent is around one. The quantity of the n exponent can be evaluated from the dependence of $\ln k_{obs}$ values and the ZnO mass (Figure 2 inside). Consequently, in our case Equation (7) can be expressed as $(r_o \alpha [ZnO]^{0.56})$ where n is an exponent observed to be less than one for all the dyes studied, relative to low concentration of photocatalyst (Galindo *et al.* 2001; Sauer *et al.* 2002; Khezrianjoo & Revanasiddappa 2012).
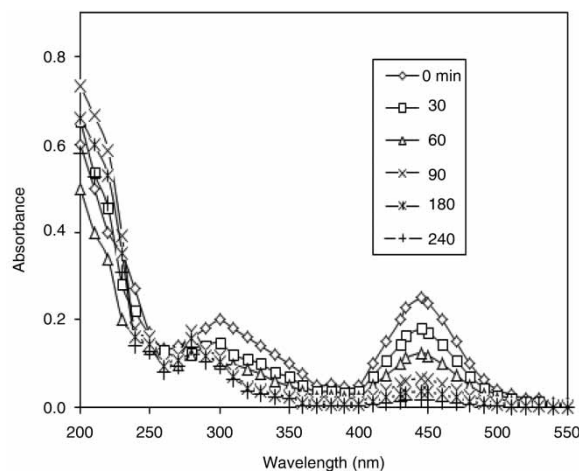
UV-Vis spectra

In the UV-Vis spectra of mCP dye, two maximum absorption peaks have been observed (Figure 3). Since mCP is an indicator dye, the appropriate maximum wavelength (λ_{max}) and absorbance at different pH values was measured; the results are indicated in Table 1.

Figure 3 shows the changes in the optical densities at 440 nm and at 300 nm of mCP at different irradiation times under natural pH of 6.7, T = 25 °C and ZnO concentration of 1.5 g/L. The decrease of the absorption peak at λ = 440 nm of the dye reveals decolorization in the presence of ZnO suspension after about 240 min. However, the degradation of the aromatic part of the dye molecule at λ = 300 takes more time.

Effect of pH

The pH is a complex parameter. It is related to the ionization state of the catalyst surface; the zero point charge

Figure 3 | Changes in UV-Vis spectra of mCP at different irradiation times; $[mCP]_o$ = 20 mg/L, [ZnO] = 1.5 g/L, T = 25 °C and initial pH of 6.7.

Table 1 | Observed maximum wavelength (λ_{max}) at different pHs for mCP; $[mCP]_o$ = 20 mg/L and T = 25 °C

pH	4	6.7 (natural)	8	10
λ_{max} (nm)	465	440	455	560
Absorbance	0.26	0.25	0.28	0.36

(pH_{zpc}) of ZnO particles is 9.0 ± 0.3 (Anandan *et al.* 2006) so the catalyst surface is positively charged in acidic media (pH < 9) whereas it is negatively charged under alkaline conditions (pH > 9). Meanwhile, pH can change the substrate properties. For the diprotic sulfonephthalein dye mCP, the reaction of interest at the pH range of 4 to 12 is the second dissociation:

$$HIn^-_{(aq)} \xleftrightarrow{pK'a} H^+_{(aq)} + In^{2-}_{(aq)} \tag{8}$$
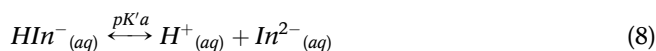
where HI^- and I^{2-} are the protonated (negative one ion) and unprotonated (negative two ion) forms of the indicator species and pK'_a is the second apparent dissociation constant of the dye. The pK'_a is a function of temperature T and salinity S.

$$pK'_a = \frac{1245.69}{T(K)} + 3.8275 + 0.00211(35 - S) \tag{9}$$

and valid for temperatures in the range from 293 °K to 303 °K and salinities from 30 to 37 psu (Abmann *et al.*

2011). According to Equation (9), the value of the pK'_a is around $8 \pm 1\%$; hence, the ratio of the negative two ion form of mCP concentration to its negative one ion form $\left(\frac{[In^{2-}]}{[HIn^-]}\right)$ can be estimated by Equation (10).

$$pH = 8 + \log\frac{[In^{2-}]}{[HIn^-]} \qquad (10)$$

Effect of pH on surface adsorption

To study the influence of substrate adsorption on the catalyst particle surface, a series of experiments was carried out at room temperature ($25\,°C$) and various pHs, while the UV light was absent. All isotherms showed (Figure 4) a type of Langmuir-shape.

The L-shape isotherms mean that there is no strong competition between solvent and the dye to occupy the ZnO surface sites. The data obtained from the adsorption experiments were fitted to the linear form of the Langmuir equation (Equation (4)); from which the K_{ads}, Q_{max} and R_L factors have been calculated; results are presented in Table 2.

According to the Langmuir model, adsorption of mCP on ZnO at pH of 4, natural (6.7) and 8 was fairly good; however best fitting with the L-shape model was observed at pH of 8 ($R_L = 0.95$); meanwhile maximum amount of dye
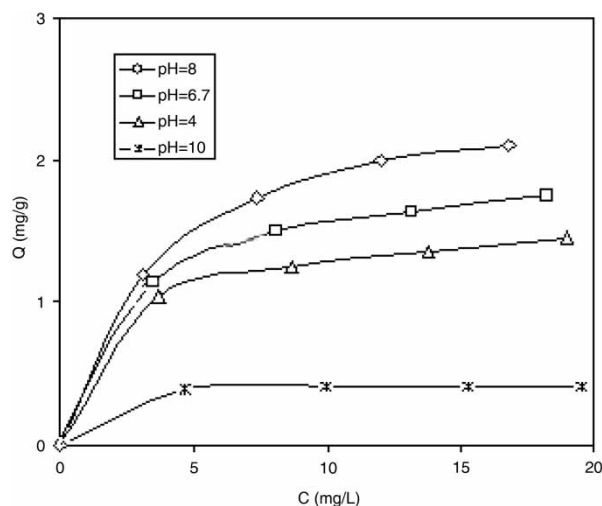
**Figure 4** │ Adsorption isotherm of mCP on catalyst surface at different pHs; [ZnO] $= 1.5$ g/L and T $= 25\,°C$.

Table 2 │ Effect of pH on the Langmuir equilibrium constant (K_{ads}), maximum absorbable dye quantity (Q_{max}) and R_L factor of mCP adsorption on ZnO surface; [ZnO] $=$ 1.5 g/L and T $= 25\,°C$

pH	K_{ads}	Q_{max}	R_L
4	0.462	1.547	0.91
6.7	0.377	1.959	0.92
8	0.292	2.541	0.95
10	4.383	0.405	0.53

adsorption on the catalyst surface has been observed at this pH ($Q_{max} = 2.541$ mg/g). Since at pH $= 8$ the dye molecules are negatively charged $\left(\frac{[In^{2-}]}{[HIn^-]} = 1\right)$, strong adsorption of dye molecules on the positively charged catalyst surface was observed. As the pH of the solution decreases from 7 to 4, the $\left(\frac{[In^{2-}]}{[HIn^-]}\right)$ will decrease from 10^{-1} to 10^{-4}, so the dye adsorption amount on the positively charged catalyst surface decreases. At pH $= 10$, the catalyst surface is negatively charged. On the other hand, the mCP molecules lose the proton under this condition $\left(\frac{[In^{2-}]}{[HIn^-]} = 10^2\right)$, hence the low tendency ($Q_{max} = 0.405$ mg/g) to be adsorbed on the catalyst surface due to electrostatic repulsion forces.

Effect of pH on photocatalytic degradation

As illustrated in Figure 5, the maximum degradation (97%) was observed at pH 8 after 150 min of irradiation. Generally, in alkaline solutions photodegradation efficiency was greater than that in acidic solutions. This is because photodecomposition of ZnO particles takes place in acidic and neutral solutions (Khodja et al. 2001). Meanwhile, increasing the pH up to 8 provides a higher level of adsorption on the catalyst surface. It should be mentioned that more efficient formation of hydroxyl radicals also occurs in alkaline solutions (Khodja et al. 2001). The photodegradation efficiency decreases at pH $= 10$; the reason for this can be due to the low-level of dye adsorption on the catalyst surface. The sharp decrease in the photodegradation efficiency at the pH of 4 can be related to the complete photodecomposition of ZnO under highly acidic (pH at or lower than 4) conditions (Khodja et al. 2001).
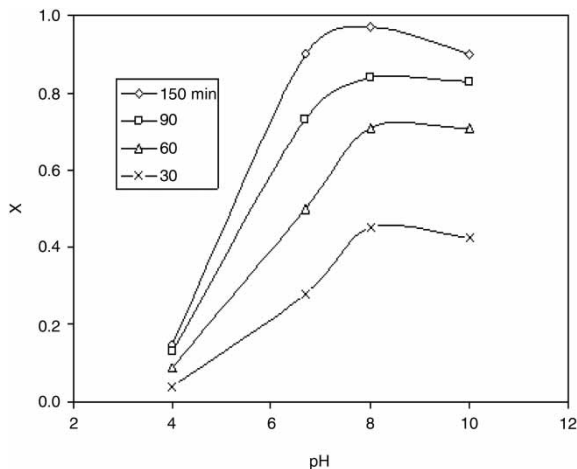
Figure 5 │ Effect of pH on degradation of *m*CP at different irradiation times, [*m*CP]ₒ = 20 mg/L, T = 25 °C and [ZnO] = 1.5 g/L.

Kinetics of photocatalytic degradation of *m*CP

Photodegradation experiments of *m*CP by UV/ZnO process at pH = 8 exhibited pseudo-first-order kinetics with respect to the initial concentration of the dye (Equation (11)).

$$\ln\left(\frac{[mCP]_o}{[mCP]}\right) = k_{obs}t \tag{11}$$

where k_{obs} is the pseudo-first-order rate constant, and $[mCP]$ and $[mCP]_o$ are the concentration at time (t) and ($t = 0$), respectively. Figure 6 shows a plot of $\ln([mCP]_o/[mCP])$ versus time for the experiments with different initial concentrations of *m*CP.

The values corresponding to different initial concentration rate constants, along with the regression coefficients are listed in Table 3.

As can be seen in Table 3, the lower *m*CP concentrations provide the better agreement with the first-order reaction.

The linearity plotted of the L-H kinetic model (Equation (1)) can be used as:

$$\frac{1}{k_{obs}} = \frac{1}{k_c K_{LH}} + \frac{[mCP]_o}{k_c} \tag{12}$$

The data reported in Table 3 were plotted in Figure 7 as $1/k_{obs}$ versus $[mCP]_o$. Using a least square best fitting
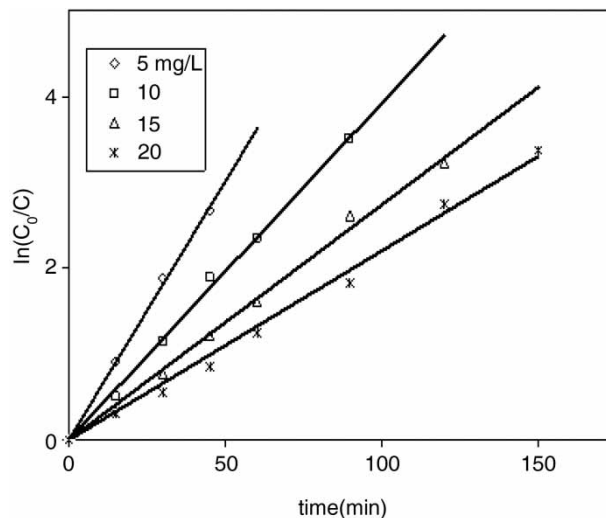
Figure 6 │ Linear variation of $\ln(C_o/C)$ versus time for the photocatalytic degradation of *m*CP at different initial concentrations, [ZnO] = 1.5 g/L, T = 25 °C and pH = 8.

Table 3 │ Pseudo-first-order kinetic rate constants in photocatalytic degradation of *m*CP with different initial concentrations at pH = 8, [ZnO] = 1.5 g/L and T = 25 °C, along with the regression coefficients

C_o (mg/L)	$k_{obs} \times 10^2$ (1/min)	R^2
5	6.03	0.9992
10	3.98	0.9975
15	2.74	0.9928
20	2.20	0.9903
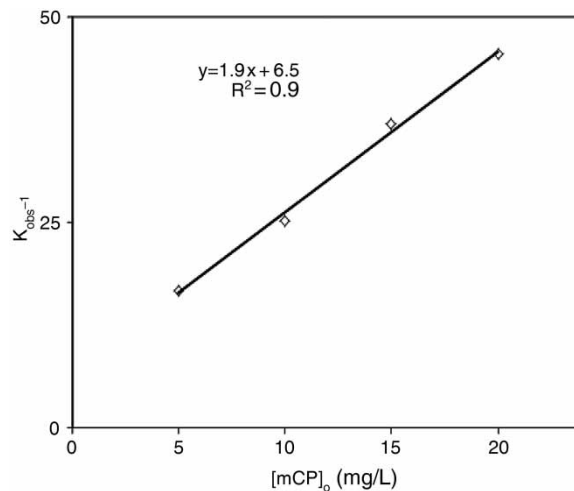
Figure 7 │ Variation of reciprocal of constant rate versus different initial concentrations of *m*CP; [ZnO] = 1.5 g/L, T = 25 °C and pH = 8.
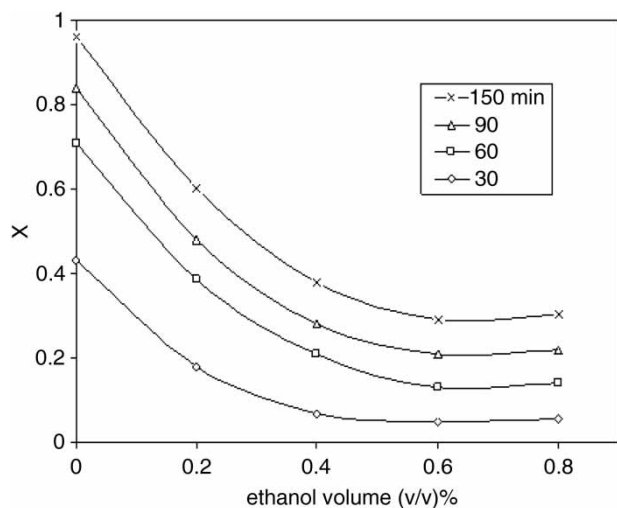
procedure, at pH of 8, the values of the adsorption equilibrium constant, K_{LH}, and the kinetic rate constant of surface reaction, k_c, were calculated as $K_{LH} = 0.302$ L/mg and $k_c = 0.508$ mg/L min.

According to the L-H model, if K_{HL} truly reflected the adsorption affinity of the dye on the catalyst surface, K_{ads} and K_{LH} would be identical (Ohtani 2008; Khezrianjoo & Revanasiddappa 2012). Since the adsorption constant in the kinetic model was determined in our case to be close to that obtained in the dark ($K_{LH} = 1.03K_{ads}$), the photocatalytic degradation of 20 mg/L of mCP at pH = 8, T = 25 °C and 1.5 g/L of ZnO follows the L-H model satisfactorily. It should be mentioned that, in other studies, it was reported that K_{LH} measured under irradiation could be substantially different from K_{ads} measured in the dark (Sauer *et al.* 2002; Kusvuran *et al.* 2005; Gora *et al.* 2006).

Effect of ethanol as radical scavenger

The activity of two main species (electron and hole, and hydroxyl radical) can be distinguished using ethyl alcohol as a radical scavenger (Saien & Soleymani 2007). The importance of these species depends on the substrate structure and operational parameters. It was observed in Figure 8 that small amounts of ethanol inhibited the photocatalytic degradation of 20 mg/L of mCP in the presence of 1.5 g/L of catalyst, T = 25 °C and pH of 8. The photodegradation
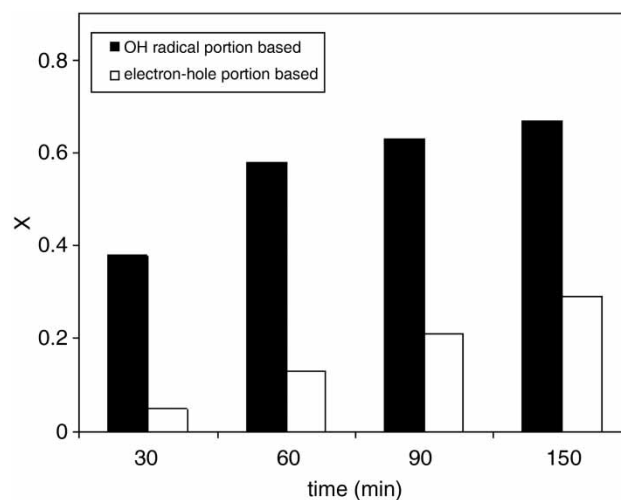
efficiency decreases with an increase of ethanol until 0.6% (v/v). On the other hand, adding an extra amount of ethanol leads to a mild increase in the process efficiency due to the formation of ethoxy radicals ($C_2H_5O^{\bullet}$) from direct photocatalytic oxidation of ethanol; meanwhile, the ethanol molecules can produce hydroxyl radicals in direct photolysis with respect to the level of C–O energy bond (Saien & Soleymani 2007).

From data given in Figure 8, the contributions of hydroxyl radicals and electron-holes in the photocatalytic degradation process at different times are determined and compared in Figure 9. As can be seen in Figure 9, hydroxyl radicals play a major role in photocatalytic degradation of mCP for all times. Another species involved which does not react with alcohols most probably provides the positive holes (h_{VB}^+) formed on the irradiated photocatalyst, which react with the adsorbed dye molecules. Since, the direct oxidation part with h_{VB}^+ increases with respect to the time, it can be assumed that the dye is more strongly adsorbed on the catalyst surface than the intermediate products.

Effect of temperature

It is generally accepted that temperature is a critical parameter determining the photocatalytic reaction rate (Nakashima *et al.* 2003). The effect of temperature on the

Figure 8 | Inhibitory effect of ethanol on photocatalytic degradation efficiency of mCP, $[m$CP$]_o = 20$ mg/L, [ZnO] = 1.5 g/L, T = 25 °C and pH = 8.

Figure 9 | The contribution of active species in degradation efficiency of mCP, $[m$CP$]_o = 20$ mg/L, [ZnO] = 1.5 g/L, T = 25 °C and pH = 8.

photocatalytic degradation rate constant and dark surface adsorption of mCP at the initial pH of 8 has been studied and results are presented in Table 4. At 60 min, about 33% enhancement in the dye degradation efficiency was observed; and 45% increase for surface adsorption was achieved at 15 min, between 5 and 45 °C. Temperatures higher than 45 °C caused significant evaporation of the solution during the experiments; so a higher operating temperature was not applied.

Increase in temperature increases the amount of mCP adsorbed on the surface of the catalyst. On the other hand, an increase in temperature decreases the solubility of oxygen in water and helps the reaction to compete more efficiently with electron and hole pairs recombination, which is not desirable (Saien & Khezrianjoo 2008).
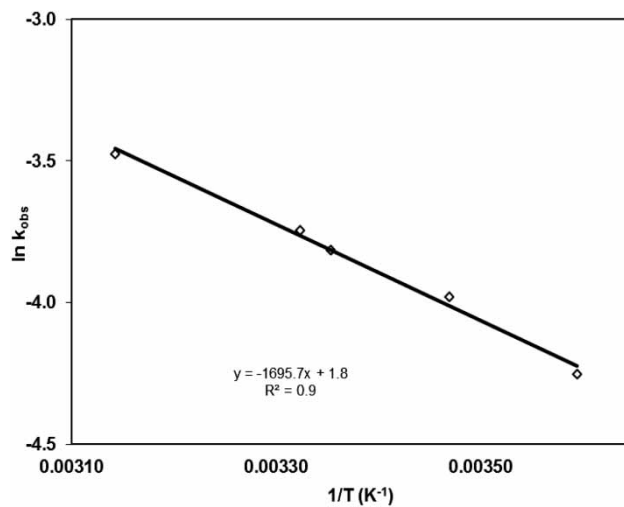
The apparent activation energy (E_a) for the photocatalytic degradation of mCP has been calculated from the Arrhenius equation:

$$k_{obs} = A \exp\left(-\frac{E_a}{RT}\right) \quad (13)$$

where k_{obs} (1/min) is the rate constant, A is the temperature independent frequency factor, E_a is the apparent activation energy of the photocatalytic degradation (J/mol), R is the gas constant (8.31 J/K mol) and T is the solution temperature in Kelvin. The linear transform $\ln(k_{obs})$ versus $(1/T)$, which is shown in Figure 10, gives a straight line whose slope is equal to $-E_a/R$. From the data obtained, the apparent activation energy was determined ($E_a = 14.09$ kJ/mol). This apparent energy represents the total activation energy of adsorption and photocatalytic degradation of mCP.

Figure 10 │ Linear variation of $\ln(k_{obs})$ versus $1/T$; [ZnO] = 1.5 g/L, pH = 8.

Electrical energy efficiency

Photodegradation with a UV lamp is an electric-energy-intensive process. Accordingly, a figure-of-merit of the process based on electric energy consumption can be very useful and informative. Recently, the Photochemistry Commission of the International Union of Pure and Applied Chemistry (IUPAC) proposed the parameter for advanced oxidation processes (AOPs) on the use of electrical energy. The energy demand, in a certain reactor, is described by the 'Electrical Energy per Order' (E_{EO}). For the case of low pollutant concentration (i.e., cases that are overall pseudo-first-order in concentration of pollutant), this parameter is the electric energy in kilowatt hours (kWh) required to remove the concentration of pollutant by one order of magnitude (90%) in 1 m³ of contaminated water or air (Mahamuni & Adewuyi 2010). The simplified form of the equation that gives E_{EO} (kWh/m³) is:

$$E_{EO} = \frac{16.667 \times P \times t}{V \times \log(C_o/C)} \quad (14)$$

where P is the lamp power (kW), V is the treated volume (L), C_o and C are the initial and final mCP concentrations and t is the time of irradiation (min). The time required for 90% degradation of the pollutant, in the pseudo-first-order

Table 4 │ Effect of temperature on the rate constant and dye removal percentage with photocatalytic degradation and surface adsorption processes; $[m\mathrm{CP}]_{in} = 20$ mg/L, [ZnO] = 1.5 g/L, pH = 8

Temperature (°C)	$k_{obs} \times 10^2$ (1/min)	Degradation% ($t = 60$ min)	Adsorption% ($t = 15$ min)
5	1.42	62.3	11
15	1.87	66.1	14
25	2.20	71.4	16
35	2.36	76.2	18
45	3.09	82.9	20

degradation of pollutants is given by (Mahamuni & Adewuyi 2010):

$$t_{90} = \frac{2.3025851}{k_{obs}} \tag{15}$$

where k_{obs} is the pseudo-first-order rate constant (1/min). The E_{EO} values for photocatalytic decolorization of mCP at different pH levels are listed in Table 5.

The higher electrical energy consumption means lower process efficiency. The low level of energy consumption at pH $= 8$ confirms the optimum pH as discussed above. The actual electrical energy consumption for photocatalytic degradation of organic pollutions depends on the operational parameters and initial concentration of pollutant; increase in the pollution initial concentration causes an increase in the electrical energy consumption (Mahmoud & Ismail 2012; Mohammadi et al. 2015). The E_{EO} values for photocatalytic degradation of 20 mg/L of amoxicillin trihydrate in the presence of different catalysts have been reported in the range of 10.15 to 40.66 kWh/m^3 (Mohammadi et al. 2015) and the E_{EO} value for photocatalytic degradation of 50 mg/L of Acid Yellow 36 has been determined as 27.9 kWh/m^3 (Khezrianjoo & Revanasiddappa 2013).

CONCLUSIONS

The dye mCP is easily degraded by zinc oxide (ZnO) assisted photocatalysis in aqueous dispersion under irradiation by UV light. Dye removal efficiency was negligible when the photolysis was carried out and it was small in the presence of ZnO in darkness. We learned that optimal amount of photocatalyst in the natural pH of 6.7 was 1.5 g/L, with dye concentration of 20 mg/L, and dependence of the initial decolorization rate on the ZnO concentration can be explained as $(r_o\alpha[ZnO]^{0.56})$. The most efficient pH for the

photocatalytic decomposition and dark surface adsorption of mCP was 8, and zinc oxide cannot be used in highly acidic solution (pH $\leq$ 4). The L-H kinetic model showed a good agreement for the initial rates of degradation at pH of 8 with the appropriate rate constant of surface reaction and the substrate adsorption constant values of $k_c = 0.508$ mg/L min and $K_{LH} = 0.302$ L/mg, respectively. The adsorption constant in the kinetic model at pH of 8 was found to be similar to that obtained in the dark; thus, the photocatalytic degradation of mCP follows the L-H model satisfactorily at this pH. Our results showed that ethanol inhibited the photodegradation of dye, and we concluded from the inhibitory effect of ethanol that hydroxyl radicals play a major role in photocatalytic degradation of mCP with UV/ZnO processes for all times. The degradation and dark surface adsorption efficiency were affected by temperature; at the pH of 8, the activation energy (E_a) of this degradation was calculated as 14.09 kJ/mol. The complete removal of color, after selection of optimal concentration of catalyst and pH of 8 could be achieved in a relatively short time of about 150 min. The lowest energy consumption for photocatalytic decolorization of dye was also observed at this pH.

REFERENCES

Abmann, S., Frank, C. & Kortzinger, A. 2011 Spectrophotometric high-precision seawater pH determination for use in underway measuring systems. *Ocean Sci.* **7**, 597–607.

Anandan, S., Vinu, A., Venkatachalam, N., Arabindoo, B. & Murugesan, V. 2006 Photocatalytic activity of ZnO impregnated HB and mechanical mix of ZnO/HB in the degradation of monocrotophos in aqueous solution. *J. Mol. Catal. A: Chem.* **256**, 312–320.

Behnajady, M. A., Modirshahla, N. & Hamzavi, R. 2006 Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. *J. Hazard. Mater.* **133**, 226–232.

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

Daneshvar, N., Salari, D. & Khataee, A. R. 2004 Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO$_2$. *J. Photochem. Photobiol. A* **162**, 317–322.

Dindar, B. & Icli, S. 2001 Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight. *J. Photochem. Photobiol. A* **140**, 263–268.

Table 5 │ The E_{EO} values for photocatalytic decolorization of mCP at different pHs; $[m$CP$]_o =$ 20 mg/L, [ZnO] = 1.5 g/L and T $= 25$ °C

pH	6.7	8	10
E_{EO} (kWh/m^3)	47.4	31.2	45.0

Galindo, C., Jacques, P. & Kalt, A. 2001 Photooxidation of the phenylazonaphthol AO20 on TIO$_2$: kinetic and mechanistic investigations. *Chemosphere* **45**, 997–1005.

Gora, A., Toepfer, B., Puddu, V. & Puma, G. L. 2006 Photocatalytic oxidation of herbicides in single-component and multicomponent systems: reaction kinetics analysis. *Appl. Catal. B* **65**, 1–10.

Habib, M. A., Muslim, M., Shahadat, M. T., Islam, M. N., Ismail, I. M. I., Islam, T. S. A. & Mahmood, A. J. 2013 Photocatalytic decolorization of crystal violet inaqueous nano-ZnO suspension under visible light irradiation. *J. Nanostructure Chem.* **3**, 1–10.

Herrmann, J. M. 1999 Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today* **53**, 115–129.

Kansal, S. K., Kaur, N. & Singh, S. 2009 Photocatalytic degradation of two commercial reactive dyes in aqueous phase using nanophotocatalysts. *Nanoscale Res. Lett.* **4**, 709–716.

Khezrianjoo, S. & Revanasiddappa, H. D. 2012 Langmuir-Hinshelwood kinetic expression for the photocatalytic degradation of Metanil Yellow aqueous solutions by ZnO catalyst. *Chem. Sci. J.* **2012**, 1–8.

Khezrianjoo, S. & Revanasiddappa, H. D. 2013 Photocatalytic degradation of Acid Yellow 36 using zinc oxide photocatalyst in aqueous media. *J. Catal.* **2013**, 1–6.

Khodja, A. A., Sehili, T., Pihichowski, J. F. & Boule, P. 2001 Photocatalytic degradation of 2-phenylphenol on TiO$_2$ and ZnO in aqueous suspensions. *J. Photochem. Photobiol. A* **141**, 231–239.

Krishnakumar, B. & Swaminathan, M. 2011 Influence of operational parameters on photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions. *Spectrochim. Acta Mol. Biomol. Spectros.* **81**, 739–744.

Kusvuran, E., Samil, A., Atanur, O. M. & Erbatur, O. 2005 Photocatalytic degradation kinetics of di- and tri-substituted phenolic compounds in aqueous solution by TiO$_2$/UV. *Appl. Catal. B* **58**, 211–216.

Mahamuni, N. N. & Adewuyi, Y. G. 2010 Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation. *Ultrason. Sonochem.* **17**, 990–1003.

Mahmoud, G. E. A. & Ismail, L. F. M. 2012 Photocatalytic degradation of Direct Yellow 50 on TiO$_2$ and Fe^{3+}-doped TiO$_2$ semiconductor nanoparticles under UV light irradiation. *J. Am. Sci.* **8** (10), 83–99.

Mohammadi, R., Massoumia, B. & Eskandarloo, H. 2015 Preparation and characterization of Sn/Zn/TiO$_2$ photocatalyst for enhanced amoxicillin trihydrate degradation. *Desalination Water Treat.* **53** (7), 1995–2004.

Nakashima, T., Ohko, Y., Kubota, Y. & Fujishima, A. 2003 Photocatalytic decomposition of estrogens in aquatic environment by reciprocating immersion of TiO$_2$-modified polytetrafluoroethylene mesh sheets. *J. Photochem. Photobiol. A* **160**, 115–120.

Ohtani, B. 2008 Preparing articles on photocatalysis – beyond the illusions misconceptions and speculation. *Chem. Lett.* **37**, 217–229.

Pirkanniemi, K. & Sillanpaa, M. 2002 Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere* **48**, 1047–1060.

Saien, J. & Khezrianjoo, S. 2008 Degradation of the fungicide carbendazim in aqueous solutions with (UV/TiO$_2$) process: optimization, kinetics and toxicity studies. *J. Hazard. Mater.* **157**, 269–276.

Saien, J. & Soleymani, A. R. 2007 Degradation and mineralization of Direct Blue 71 in a circulating upflow reactor by UV/TiO$_2$ process and employing a new method in kinetic study. *J. Hazard. Mater.* **144**, 506–512.

Sauer, T., Cesconeto Neto, G., Jose, H. J. & Moreira, R. F. P. M. 2002 Kinetics of photocatalytic degradation of reactive dyes in a TiO$_2$ slurry reactor. *J. Photochem. Photobiol. A* **149**, 147–154.

Sobana, N. & Swaminathan, M. 2007 The effect of operational parameters on the photocatalytic degradation of Acid Red 18 by ZnO. *Sep. Purif. Technol.* **56**, 101–107.

Vasanth Kumar, K., Porkodi, K. & Selvaganapathi, A. 2007 Constrain in solving Langmuir–Hinshelwood kinetic expression for the photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst. *Dyes Pigm.* **75**, 246–249.