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ORIGINAL PAPER

Photocatalytic degradation of azo dye Orange II in aqueous solutions using copper-impregnated titania

N. Divya · A. Bansal · A. K. Jana

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Abstract During dyeing process, industries consume large quantity of water and subsequently produce large volume of wastewater. This wastewater is rich in color and contains different dyes. Orange II is one of them. In this article, metal-impregnated TiO_2 P-25 catalyst was used to enhance the photocatalytic degradation of Orange II dye. Photodegradation percentage was followed spectrophotometrically by the measurements of absorbance at $\lambda_{max} = 483$ nm. The effect of copper-impregnated TiO_2 P-25 photocatalyst for the degradation of Orange II has been investigated in terms of percentage removal of color, chemical oxygen demand (COD) and total organic carbon (TOC). As such 98 % color removal efficiency, 97 % percentage removal of COD and 89 % percentage removal of TOC was achieved with TiO_2 P-25/Cu catalysts under typical conditions. Copper-impregnated TiO_2 P-25 photocatalyst showed comparatively higher activity than UV/H_2O_2 homogeneous photodegradation. The relative electrical energy consumption for photocatalytic degradation was considerably lower with TiO_2 P-25/Cu photocatalyst than that with homogeneous photodegradation. Transmission electron microscopic analysis was used for catalyst characterization.

Keywords Degradation · Electrical energy requirement per order · Mineralization · Orange II · Photocatalyst · Transmission electron microscopic analysis

Introduction

An effective treatment is necessary for the degradation of harmful dye, which is discharged into the surface waters. In many industries (textile, leather, plastics, paper, food and cosmetics) dyes are used as a coloring agent. More than one million tons of dyes annually produced in the world are azo dyes (Cho and Zoh 2007; Somasiri et al. 2006). 10–15 % of the total used colorants are discharged into effluent during their synthesis and dyeing processes (Dave and Dave 2009; Divya et al. 2009). The resulting effluent may contain some components or moieties that could be toxic, carcinogenic or mutagenic to aquatic life. Photocatalysis has emerged as an effective and promising technique among advanced oxidation processes (AOPs) for the degradation of these organic pollutants in wastewater (Behnajady et al. 2008). During photocatalysis very powerful oxidizing agent hydroxyl radical ($OH^{\cdot}$) and/or superoxide radical ($O_2^{\cdot -}$) are generated. The oxidizing agent is responsible to destroys hazardous pollutants.

Complex organic pollutants such as dyes can completely be mineralized using suitable photocatalyst. The organic pollutants react with the oxidizers to form CO_2, water and dilute concentration of simple mineral acids. The semiconductor may be in the form of a powder suspended in the

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water or coated on a support. Heterogeneous photodegradation has proved to be an effective and promising method among AOPs for the degradation of various organic pollutants including dyes in wastewater (Daneshvar et al. 2004).

The combination of different semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS and ZnS) with UV/solar lights are used in photocatalysis. But titanium dioxide is the most widely studied catalyst using to its physical and chemical stability, low cost, eases of availability, non-toxicity an electronic and optical property (Goncalves et al. 2005). The mechanism of photodegradation of organic compounds by UV/TiO_2 as described by (Wu 2008) as follows:

$$TiO_2 + hv \rightarrow TiO_2(e^-_{cb} + h^+_{vb}) \quad (1)$$

$$TiO_2\left(h^+_{vb}\right) + OH^- \rightarrow TiO_2 + OH^{\cdot} \quad (2)$$

$$TiO_2\left(h^+_{vb}\right) + H_2O_2 \rightarrow TiO_2 + H^+ + OH^{\cdot} \quad (3)$$

$$TiO_2\left(e^-_{cb}\right) + O_2 \rightarrow TiO_2 + O_2^{\cdot -} \quad (4)$$

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \quad (5)$$

$$TiO_2\left(e^-_{cb}\right) + H^+ + O_2^{\cdot -} \rightarrow TiO_2 + HO_2^- \quad (6)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (7)$$

The $OH^{\cdot}$ radicals are principally responsible for the degradation of organic compounds. Oxygen serves as an efficient electron trap (Eq. 4), which prevents the recombination of electrons and photogenerated holes. If oxygen is limited, rapid recombination of photo produced electrons and holes in TiO_2 lowers the efficiency of the photocatalytic reactions; consequently the usefulness of such a system has limited practical application (Wu 2008). The addition of oxidants eliminates the recombination process as the added oxidants rapidly react with conduction band electrons, generating extremely reactive oxidizing radicals, which increases the efficiency of TiO_2. Some times TiO_2 catalysts have been used with supported adsorbent (Bhattacharyya et al. 2004).

The photoactivity of TiO_2 is altered by doping with transition metals like Pt, Pd, Au, Ag, Mn, Fe and Cu or oxides such as WO_3, which act as charge separators of the photo-induced electron/hole pair (Arabatzis et al. 2003; Arana et al. 2005; Galindo et al. 2000; Gracien et al. 2007; Gupta et al. 2006; Tokumura et al. 2006; Zhao et al. 2007). The combination of semiconductor substrate and metal cluster gives improved photocatalytic activity by trapping the photo-induced charge carriers, thereby improving the charge transfer processes (Nasr-Esfahani and Habibi 2008). They may enhance the electron–hole separation by acting as electron traps, extend the light absorption into the visible range, enhance surface electron excitation and modify the surface properties of photocatalysts.

In the recent years, copper ions are used for metal doping/deposition, because of their novel effects on the improvement of photoactivity of semiconductor photocatalysis nanocrystallites (Sahoo et al. 2005). It effectively retards the recombination of photogenerated electrons and holes. This process has shown to improve the overall efficiency for a number of photocatalytic reactions (Behnajady et al. 2008; Sahoo et al. 2005; Menendez-Flores et al. 2008).

Orange II azo dye is one of the organic compounds found in the textile wastewaters. It has a high photo and thermal stability. It is carcinogenic and mutagenic and affects the aquatic life seriously. In the present study the degradation of Orange II has been investigated for homogeneous and heterogeneous conditions involving UV/H_2O_2 and TiO_2 P-25. TiO_2 P-25 catalyst has been impregnated with copper metal ions to study the degradation of Orange II dye in aqueous solution. H_2O_2 has been used to inhibit the recombination of electron/hole pairs and improve the photodegradation efficiency (Luo et al., 2002).

The effect of impregnated TiO_2 on dye degradation has been discussed in terms of color removal, percentage removal of COD and TOC. The degradation kinetics was also studied. This research has been carried out in the Chemical Engineering Department, National Institute of Technology, Jalandhar (Punjab, India), from February to April 2009.

Materials and methods

Reagents

Degussa TiO_2 P-25, procured from Evonic (Degussa), Germany, was used as a photocatalyst. It is 80 % anatase and 20 % rutile and has a BET surface area of 50 m^2/g. The Orange II (85 % dye content), H_2O_2 (30 % w/v), HCl (34 %), sodium hydroxide pellets purified (NaOH), ferrous ammonium sulphate ($NH_3(FeSO_4)_2 \cdot 6H_2O$), potassium dichromate ($K_2Cr_2O_7$), silver sulphate ($AgSO_4$), mercury sulphate ($HgSO_4$), sulphuric acid (H_2SO_4) were procured from S.D. Fine Chemicals Limited, Mumbai, India. Ferroin indicator, copper nitrate [$Cu(NO_3)_2$] were procured from Qualigens Fine Chemicals Limited, Mumbai, India. They were used without any further treatment or purification.

Preparation of TiO_2 P-25/Cu-modified nano-size titania-based catalyst

Modification of catalyst was done using impregnation method. Metal ion doped TiO_2 (Degussa P-25) was prepared using the following procedure. The titania-based photocatalyst employed was commercial titanium dioxide powder (Degussa P-25). The doping was done using transition metal salt $Cu(NO_3)_2$. 0.0018 mol of $Cu(NO_3)_2$ was dissolved in 30 ml of distilled water in a porcelain bowl. 0.99 mol of TiO_2 was then added to the solution. The solution was stirred well and was allowed to stand for 24 h. The contents were heated at 100 ± 5 °C to evaporate all the water. The dried solids were first ground and then calcined at 400 °C for 6 h in a muffle furnace.

Irradiation experiments

All experiments were carried out in a batch photoreactor. The radiation source consisted of two 15 W UV tubes (F15T8/GL), positioned on opposite sides of the cabinet interior nearer to top. The details of photochemical reactor are available elsewhere (Divya et al. 2009; Liu and Chiou 2005).

Stock solution of the dye (1,000 ppm) was prepared with double distilled water from which working solution (50, 100 ppm, etc.) was prepared. Then solution pH value was adjusted to 3.0 using 0.1 N NaOH and 0.1 N HCl. For homogeneous photodegradation, 20 ml of the working solution of the dye (50 ppm) was taken in a beaker then H_2O_2 was added. The zero time reading was taken and the solution was then subjected to irradiation. Aliquots were taken at regular intervals to analyze the percent degradation of the dye. In case of heterogeneous photocatalysts, titania-based catalyst was added along with H_2O_2. The solution was then subjected to continuous stirring for 60 min in dark and the rest of the procedure was same as that for homogeneous photodegradation.

Analysis

The degradation of Orange II was measured with UV–vis spectrophotometer (LaMotte, USA). A calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. The measurement of maximum absorbance was taken for Orange II was 483 nm. The decolorization has been reported and discussed in terms of, η, photodegradation efficiency (Divya et al. 2009). The total mineralization of Orange II has been measured by using the disappearance of the total organic carbon (TOC) and chemical oxygen demand (COD). Estimation of TOC and COD had been done by standard methods. The efficiency of dye mineralization was estimated using the following expressions (Aleboyeh et al. 2008):

$$\text{Mineralization}\ \% = \left[1 - \frac{\text{COD (or TOC)}}{\text{COD}_0\text{(or TOC}_0\text{)}}\right] \times 100 \qquad (8)$$

where COD, TOC correspond to time t and COD_0, TOC_0 correspond to initial conditions.

To check the reproducibility of the experimental system some sets of experiments were repeated under similar conditions. The uncertainty in experimental system was calculated in term of square root mean error (SRME), given as follows:

$$\text{Square root mean error} = \sqrt{\left\{\sum \frac{(\eta_1 - \eta_2)^2}{N}\right\}}$$

where, $\eta_1 =$ degradation efficiency during first run, $\eta_2 =$ degradation efficiency during second run and $N =$ no. of turn efficiency observed.

The SRME observed for the experimental system was found to be less than or equal to ±2 %.

Characterization of catalysts using transmission electron microscopy

Transmission electron microscopy (TEM) can give a real space image on the distribution of particles, their surface and shape. With a finely focused electron probe, not only imaging of materials is possible, but also a single particle can be identified. Besides, electron microscopy shows the shape and state of particles. Samples were placed onto a carbon-coated copper grid (400 holes) by physically interacting the grid and powders, and analyzed to see the particles that remained adhered to the grids. Detailed surface images of photocatalyst were obtained by transmission electron microscope (TEM). The TEM studies were performed using a Hitachi 7500 (SAIF, Panjab University, Chandigarh).

The crystallite morphology of the P-25 TiO_2 in solid-state and transition metal modified P-25 TiO_2 based catalysts were observed by transmission electron microscopy (TEM) (Fig. 1). TEM of powder catalyst was performed at 100 kV. It was observed that the mean particle size of P-25 TiO_2 was 10 ± 2 nm (Fig. 1a) observed at 300,000× direct magnification. Deposited Cu particle (Fig. 1b) size was in the range of 3–4 nm at 500,000× direct magnification (Fig. 1b). The nano-sized modified photocatalyst was subjected to the removal of color, COD and TOC of Orange II in aqueous solution. The results obtained are discussed as follows.

Results and discussion

Series of experiments were conducted for the photocatalytic degradation of Orange II azo dye. The physical and

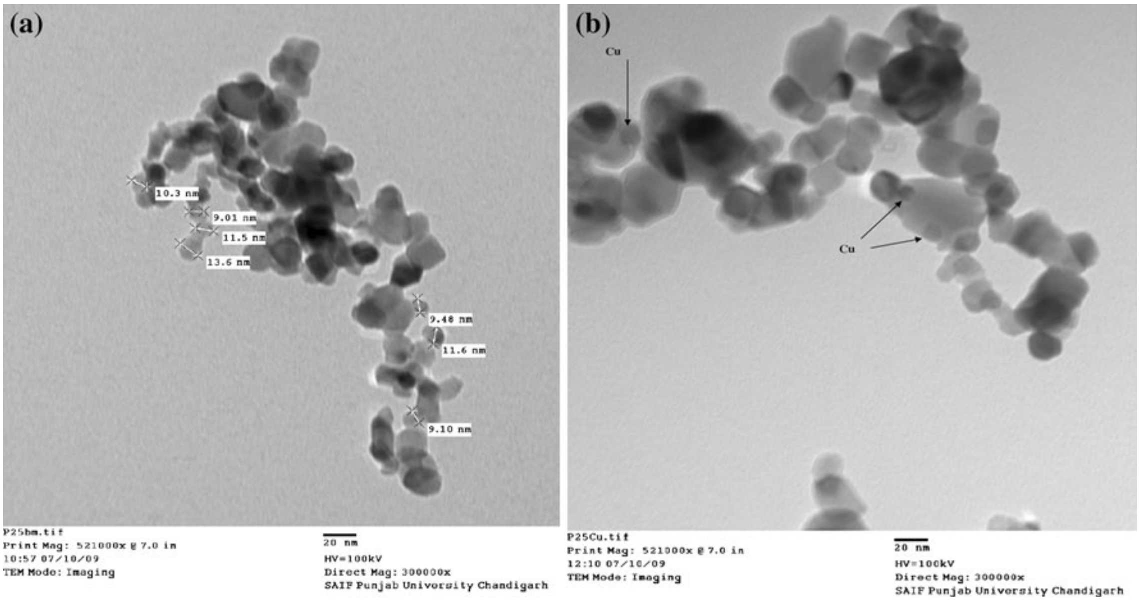
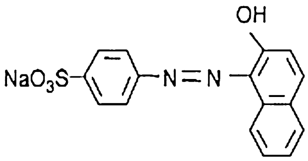


Fig. 1 Transmission electron microscopy (TEM) of **a** TiO_2 P-25 and **b** copper modified TiO_2 P-25/Cu and modified catalysts

Table 1 Physical and chemical characteristics of dye

Title	Properties
Dye name	Orange II
Abbreviation	AO7, OII
Generic name	Acid Orange 7
Color index (CI)	15,510
Appearance	Orange powder
Chemical formula	$C_{16}H_{11}N_2NaO_4S$
Molecular weight	350.33
λ_{max}, nm	483
Toxic fumes	Carbon monoxide, carbon dioxide, nitrogen oxides, sulphur oxides
Chemical structure	

chemical characteristics of Orange II azo dye are reported in Table 1. Experiments were conducted to find out the effect of homogeneous and heterogeneous photodegradation in the removal of color, COD and TOC due to Orange II azo dye in aqueous solutions. All parameters were kept identical under pre-optimized operational conditions (pH 3, Concentration = 50 ppm, H_2O_2 = 0.5 % of total used sample, volume of sample used = 20 ml) in different sets of experiments for all the studies (Divya et al. 2009). 10 mg/L catalyst dose was used for the studies (Bansal et al. 2010). The degradation studied has been discussed as under.

Color removal efficiency

Homogeneous photodegradation

A series of experiments were conducted for different concentrations of Orange II in the range of 50–400 ppm (Fig. 2). The decolorization of dye was found to depend on the concentration of the dye. As the initial concentration of dye increases the color removal efficiency decreases. The results indicated that the low concentration solution degraded fast. The time needed for color removal depended on the initial dye concentration. For higher concentration of Orange II (400 ppm), it took rather long time of more than 450 min for near total degradation in comparison to 90 min for 50 ppm solution. Probably it happened because at the high initial concentration of dye, the color might have hindered the penetration of light into the bulk of the reaction sample (Divya et al. 2009). Consequently, the degradation of the dye decreased as the initial dye concentration increased. The present result agreed with various previous studies (Lachheb et al. 2002; Kiriakidou et al. 1999; Mahmoodi et al. 2005; Muruganandham and Swaminathan 2004; Tokumura et al. 2006).

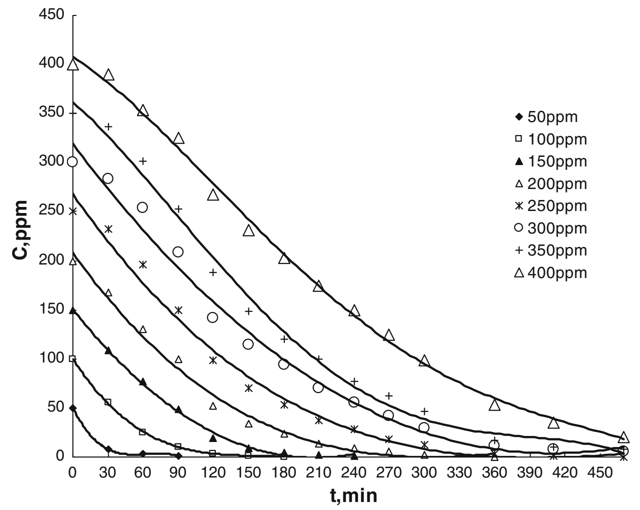


Fig. 2 Effect of different initial concentrations of Orange II (pH = 3, $H_2O_2 = 0.5$ % of total sample)

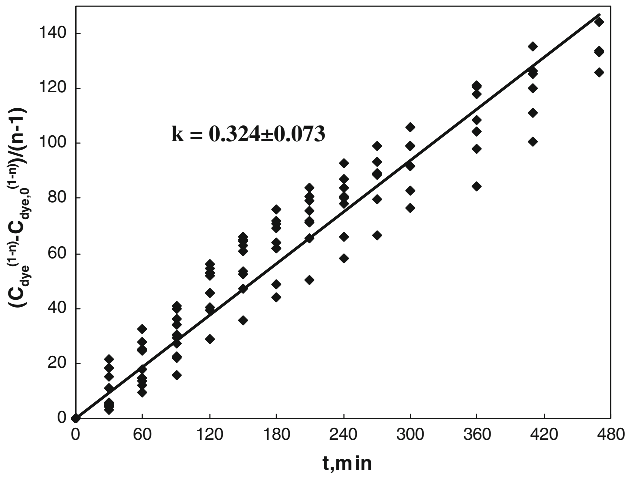


Fig. 3 *n*th order kinetics model of decolorization for Orange II (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample)

The experimental data were well fitted to an *n*th order rate equation (Levenspiel 1995). The rate of reaction was calculated using the expressions given below.

$$-r_{\mathrm{dye}} = -\frac{\mathrm{d}C_{\mathrm{dye}}}{\mathrm{d}t} = kC_{\mathrm{dye}}^{n} \tag{9}$$

$$-r_{\mathrm{dye}} = -\frac{\mathrm{d}C_{\mathrm{dye}}}{C_{\mathrm{dye}}^{n}} = k\mathrm{d}t \tag{10}$$

$$-\int_{C_{\mathrm{dye},o}}^{C_{\mathrm{dye}}} \frac{\mathrm{d}C_{\mathrm{dye}}}{C_{\mathrm{dye}}^{n}} = k\int_{o}^{t} \mathrm{d}t \tag{11}$$

$$C_{\mathrm{dye}}^{(1-n)} - C_{\mathrm{dye},0}^{(1-n)} = (n-1)kt \quad n \neq 1 \tag{12}$$

$$\frac{\left[C_{\mathrm{dye},0}^{(1-n)} - C_{\mathrm{dye}}^{(1-n)}\right]}{(1-n)} = kt \tag{13}$$

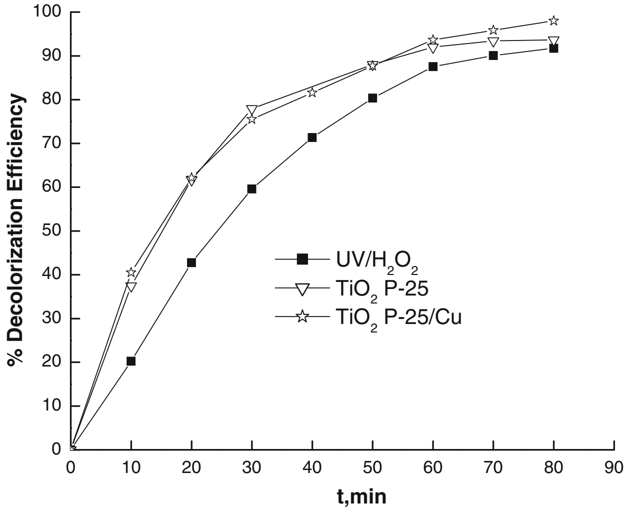


Fig. 4 Percent degradation efficiency for orange II with UV- H_2O_2 and different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample, amount of catalyst = 10 mg L^{-1})

The linear fit of *n*th order reaction rate was plotted $\frac{\left[C_{\mathrm{dye},0}^{(1-n)}-C_{\mathrm{dye}}^{(1-n)}\right]}{(1-n)} - Vs - t$. The decolorization rate of Orange II follows the *n*th order kinetics (Fig. 3). The values of $k = 0.324 \pm 0.073$ and $R^2 = 0.97$ for $n = 0.204 \pm 0.042$.

Heterogeneous photocatalysis

The catalysts used for Orange II degradation are P-25 TiO_2 and P-25 TiO_2/Cu (10 mg/L). The copper-impregnated nano-size catalyst enhanced the color removal efficiency of Orange II (Fig. 4). The color removal efficiency of Orange II azo dye was higher, i.e., 98 % with P-25 TiO_2/Cu catalysts. As discussed, the presence of Cu^{2+}-ions can help to efficiently separate the electron/hole pairs by attracting the conduction band photoelectrons, thus avoiding the recombination. The valence band photogenerated holes are free to react with OH^- adsorbed onto the TiO_2 to create hydroxyl radicals (OH^-) and the conduction band electrons (at least a number of them) react with electron acceptors such as oxygen creating oxygen radicals ($O_2{}^-$). These radicals (OH, $O_2{}^-$) present extremely strong oxidizing properties and probably lead to degradation of Orange II dye. Simultaneously, H_2O_2-trapped photogenerated electrons and inhibited the recombination of photogenerated electron/hole pairs.

$$(\mathrm{TiO_2}) \cdots \mathrm{OH} + h_{\mathrm{vb}}^{+} \rightarrow \mathrm{OH}^{\cdot} \tag{14}$$

$$\mathrm{OH}^{\cdot}/\mathrm{O_2^-} + \mathrm{OH} \rightarrow (\mathrm{Intermediates}) \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{15}$$

The results indicate that the color removal efficiency was higher with heterogeneous photocatalysis in comparison to

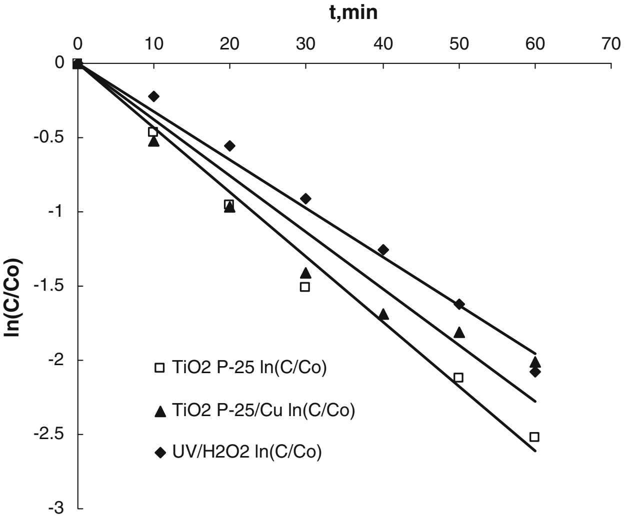


Fig. 5 Pseudo first order kinetics model of degradation for Orange II with different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample)

Table 2 Correlation coefficient 'R^2' and 'k' value for Orange II dye for different catalysts

Photocatalyst	Decolorization		COD removal		TOC removal	
	R^2	k/min	R^2	k/min	R^2	k/min
TiO_2 P-25/Cu	0.95	0.041	0.85	0.0032	0.97	0.0044
TiO_2 P-25	0.98	0.045	0.93	0.0007	0.97	0.0025

homogeneous photodegradation (Fig. 4). Further an efficiency of 98 % (with TiO_2 P-25/Cu as a catalyst in 80 min), is significantly much higher for similar studies on biodegradation of Orange II by Sharma et al. (2009) (85 % dye removal in 5 days for 100 ppm Concentration, using *Phanerochaete chrysosporium*) and Oranusi and Ogugbue (2005) (79.29 % decolorization efficiency using *Pseudomonas* sp.).

Heterogeneous photocatalysis followed the pseudo-first-order kinetics for OII degradation (Fig. 5). The correlation coefficients and reaction rate constants are tabulated in Table 2.

Percentages removal of chemical oxygen demand

The COD varies during the photocatalytic degradation of Orange II (50 ppm, 20 mL) (Table 3; Fig. 6). Within 9 h of irradiation, the percentage removal of COD with UV/H_2O_2, TiO_2 P-25 and TiO_2 P-25/Cu was 26, 42 and 97 %, respectively, indicating that the degradation of the Orange II with TiO_2 P-25/Cu was the highest. Although the catalytic activity of TiO_2 P-25 catalyst was slightly higher than that of UV/H_2O_2, it was noted that the very small amount of TiO_2 P-25-based heterogeneous photocatalytic degradation of the Orange II shows efficient changes in degradation efficiency, indicating that the titania-based transition metal modified catalysts particles in this process exhibit very good photocatalytic activity. Finally, it was found that the COD disappearance efficiency was better with heterogeneous photocatalysis against homogeneous photodegradation. The stoichiometry for the mineralization of Orange II could be suggested as:

$$C_{16}H_{11}N_2NaO_4S + 42H_2O_2 = 16CO_2 + 46H_2O + 2HNO_3 + NaHSO_4 \qquad (16)$$

The percentage removal of COD was much lower than that of decolorization under continuous UV radiation; it did not increase when complete decolorization of the solution was achieved. This is expected since the photosensitization mechanism is operable only when dye molecules are present on the photocatalyst surface. When this is the case, electron injection from the excited molecule into the conduction band of the semiconductor takes place, and the dye molecule converts into its cationic radical. The injected electron may then reduce surface chemisorbed oxidants, usually oxygen, to yield oxidizing species ($O_2^{\cdot-}$, $HOO^{\cdot}$ and $OH^{\cdot}$ radicals) which can cause photodegradation (Stylidi et al. 2003). It was observed that there was small decrease in COD during the first few hours under irradiation. This indicates that decolorization is due to decomposition of Orange II molecules to lower molecular weight compounds, such as formic acid, which eventually decompose to yield CO_2. Formation of CO_2 probably takes

Table 3 Percent COD and TOC removal, color removal, relative EE/O for color and COD removal with different photocatalysts after UV irradiation

Photocatalyst/process	% COD removal (9 h)	% TOC removal (9 h)	% color removal (80 min)	Relative EE/O value for color removal (80 min)	Relative EE/O value for COD removal (9 h)
TiO_2 P-25/Cu	97	89	98	0.640	0.082
TiO_2 P-25	42	72	94	0.905	0.551
UV/H_2O_2	26	55	92	1	1

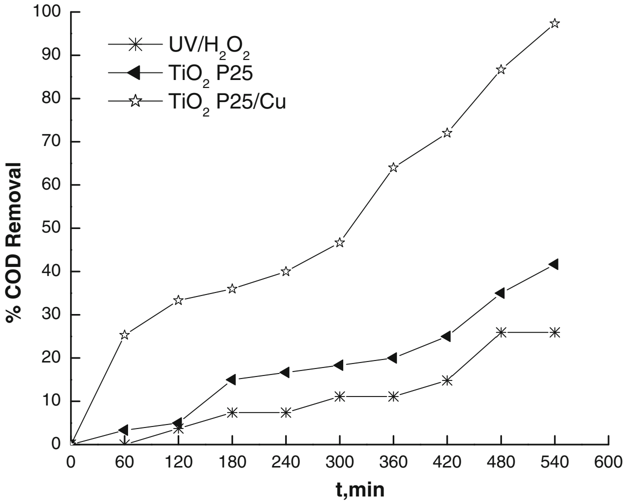


Fig. 6 Percent mineralization efficiency (% COD removal) for Orange II with UV-H_2O_2 and different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample, amount of catalyst = 10 mg L^{-1})

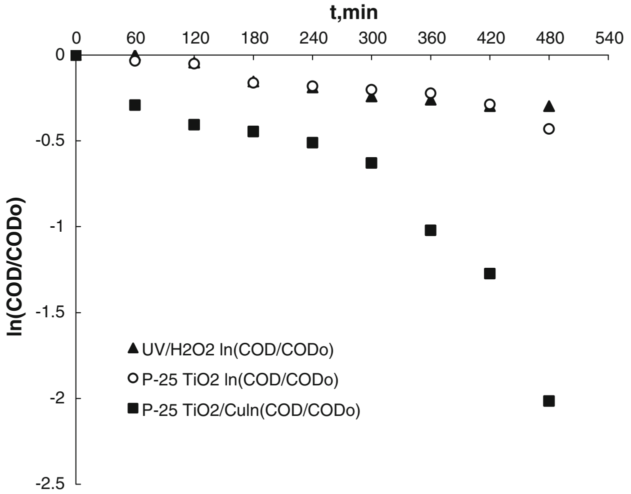


Fig. 7 Pseudo first order kinetics model of COD removal for Orange II with different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample)

place by decarbonylation of carboxylic acids via the "photo-Kolbe" reaction (Stylidi et al. 2003):

$$\mathrm{R-COO^-} + h^+ \rightarrow R^{\circ} + \mathrm{CO_2} \quad (17)$$

This may still be contributing to the COD of the solution. Complete decolorization was achieved at 90 min, and for nearly complete removal of COD it took rather long time. Prolonged irradiation of the suspension results in elimination of the COD of the solution, indicating that complete mineralization occurs after 9 h. Homogeneous and heterogeneous photodegradation (P-25 TiO_2) followed the pseudo-first-order kinetics for Orange II degradation (Fig. 7). But TiO_2 P-25/Cu photocatalysts do not follow the pseudo-first-order kinetics. The correlation coefficients (R^2) and reaction rate constants (k) are tabulated in Table 2.

Percentage removal of total organic carbon

Mineralization of Orange II was studied in terms of percentage removal of TOC with transition metal modified nano-size catalysts such as TiO_2 P-25 and TiO_2 P-25/Cu. TOC removal was also measured for the homogeneous photodegradation (Fig. 8). Within 9 h of UV irradiation, the TOC removal of the Orange II by UV/H_2O_2, TiO_2 P-25 and TiO_2 P-25/Cu is 55, 72 and 89 %, respectively (Table 3; Fig. 8). Results indicated that the TOC removal of the Orange II using TiO_2 P-25/Cu is the fastest, than that of UV/H_2O_2 for the degradation. TiO_2 P-25 catalysts show slightly higher catalytic activity than that of UV/H_2O_2. It indicated that the TOC removal was comparatively slow than decolorization of Orange II. TOC removal of Orange II under homogeneous and heterogeneous photodegradation followed the pseudo-first-order kinetics (Fig. 9). The correlation coefficients (R^2) and reaction rate constants (k) are tabulated in Table 2.

Electrical energy consumption

Photodegradation of aqueous organic pollutant is an electric energy-intensive process. A major fraction of the operating costs is represented by electrical energy. The values of electrical energy requirement per order (EE/O) for photocatalytic decolorization and mineralization of Orange II was calculated for a batch type photoreactor as (Daneshvar et al. 2007).

$$\mathrm{EE/O} = \frac{P \times t \times 1{,}000}{V \times 60 \times \log \frac{C_i}{C_f}} \quad (18)$$

where P is the input power (kW) to the AOP system, t is the irradiation time (min), V is the volume of water (liter) in the reactor, C_i and C_f is the initial and final concentration of organic pollutants, respectively. The relative electrical energy requirement was calculated for the low concentration (50 ppm) of Orange II solution. The relative EE/O value can be calculated through below give equation.

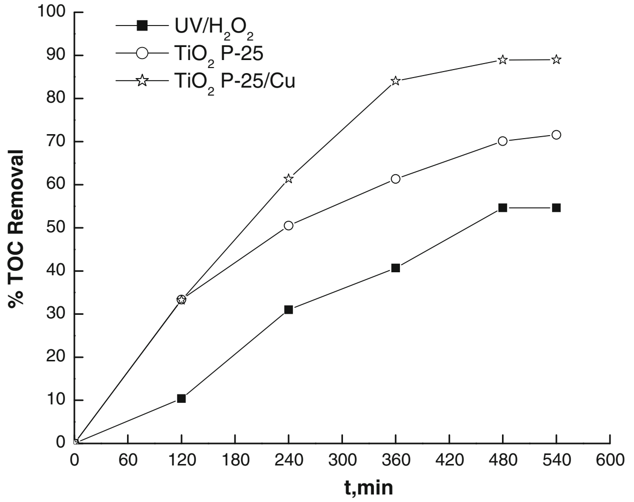


Fig. 8 Percent mineralization efficiency (% TOC removal) for Orange II with UV- H_2O_2 and different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample, amount of catalyst = 10 mg L^{-1})

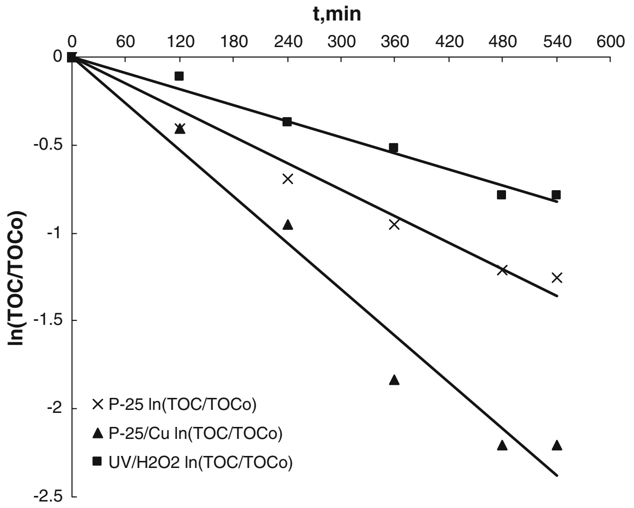


Fig. 9 Pseudo first order kinetics model of TOC removal for Orange II with different catalysts (pH = 3, concentration = 50 ppm, H_2O_2 = 0.5 % of total sample)

$$\text{Relative EE/O} = \frac{\text{EE/O(withcatalysts)}}{\text{EE/O(homogeneous photodegradation)}} \quad (19)$$

The relative EE/O values for photocatalytic decolorization and mineralization of Orange II with TiO_2 P-25/Cu process were 0.64 and 0.082 and for other combinations values are tabulated in Table 3. The

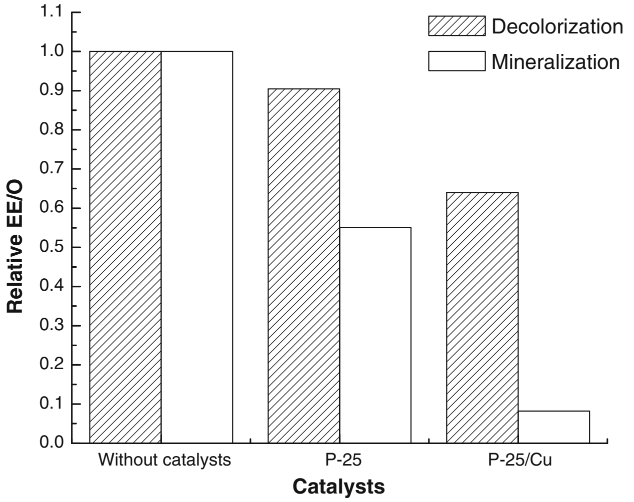


Fig. 10 Relative electrical energy requirements for the decolorization and mineralization of Orange II azo dye

relative EE/O value for Orange II decolorization was very high with homogeneous photodegradation, but it decreased with modification of nano-sized titania-based catalyst (such as TiO_2 P-25 > TiO_2 P-25/Cu). It is also clear that TiO_2 P-25/Cu catalysts offered the best energy efficiency (Fig. 10). In case of removal of COD relative EE/O values was high with UV/H_2O_2 and gradually decreased with TiO_2 P-25, TiO_2 P-25/Cu, photocatalysts similar to decolorization (Fig. 10).

It is clear from the calculation of relative EE/O value that the modified TiO_2 P-25/Cu-based catalyst offered best energy efficiency for both decolorization and mineralization (Fig. 10).

Conclusion

TEM analysis performed on copper-impregnated TiO_2 P-25 photocatalysts indicated that particles were nano-sized. The sizes of the particles are in the range of 10 ± 2 nm TiO_2 P-25, and 3–4 nm Cu. Kinetic studies of homogeneous photodegradation revealed that the degradation of Orange II follows *n*th order kinetics with *n* close to 0.204 ± 0.042. The concentration of dye had the effect on its degradation. The removal efficiency was higher for low concentration dye solutions. In case of heterogeneous photocatalysis TiO_2 P-25/Cu-modified catalyst showed better photocatalytic degradation activity as compared with TiO_2 P-25 catalyst. Pseudo-first-order reaction kinetics followed the heterogeneous photocatalysis reasonably well.

The results show that the COD, TOC and color removal efficiency was faster with heterogeneous photocatalysis (transition metal modified nano-sized catalysts) than that for homogeneous photodegradation. The best results, however, were obtained corresponding to TiO_2 P-25/Cu.

The relative electrical energy consumption for photocatalytic degradation of Orange II with TiO_2 P-25/Cu catalyst was lesser than that of other combinations of catalysts and homogeneous photodegradation.

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References

Aleboyeh A, Olya ME, Aleboyeh H (2008) Electrical energy determination for an azo dye decolorization and mineralization by UV/H_2O_2 advanced oxidation process. Chem Engg J 137: 518–524

Arabatzis IM, Stergiopoulos T, Bernard MC, Labou D, Neophytides SG, Falaras P (2003) Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl Catal B Environ 42:187–201

Arana J, Fernandez Rodrıguez C, Gonzalez Diaz O, Herrera Melian JA, Perez Pena J (2005) Role of Cu in the Cu-TiO_2 photocatalytic degradation of dihydroxybenzenes. Catal Today 101:261–266

Bansal A, Divya N, Jana AK (2010) Performance of titania based Nano-Photocatalysts on the degradation of Orange G azo dye. The 5th IASME/WSEAS international conference on energy and environment. 23–25 February, Cambridge University, UK, 140–146

Behnajady MA, Modirshala N, Shokri M, Rad B (2008) Enhancement of photocatalytic activity of TiO_2 nanoparticles by silver doping: photodeposition versus liquid impregnation methods. Glob Nest J 10:1–7

Bhattacharyya A, Kawi S, Ray MB (2004) Photocatalytic degradation of Orange II by TiO_2 catalysts supported on adsorbents. Catal Today 98:431–439

Cho I-H, Zoh K-D (2007) Photocatalytic degradation of azo dye (Reactive Red 120) in TiO_2/UV system: optimization and modeling using a response surface methodology (RSM) based on the central composite design. Dyes Pigments 75:533–543

Daneshvar N, Salari D, Khataee AR (2004) Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. J Photoch Photobio A Chem 162:317–322

Daneshvar N, Aber S, Dorraji MSS, Khataee AR, Rasoulifard MH (2007) Preparation and investigation of photocatalytic properties of ZnO nanocrystals: effect of operational parameters and kinetic study. Int J Chem Bio Engg 1:24–29

Dave SR, Dave RH (2009) Isolation and characterization of *Bacillus thuringiensis* for Acid red 119 dye decolourisation. Bioresour Technol 100:249–253

Divya N, Bansal A, Jana AK (2009) Degradation of acidic Orange G dye using UV-H2O2 in batch photoreactor. Int J Bio Chem Sci 3(1):54–62

Galindo C, Jacques P, Kalt A (2000) Photodegradation of the aminoazobenzene acid Orange 52 by three advanced oxidation processes: UV/H_2O_2, UV/TiO_2 and VIS/TiO_2 Comparative mechanistic and kinetic investigations. J Photochem Photobio A Chem 130:35–47

Goncalves MST, Pinto EMS, Nkeonye P, Oliveira-Campos AMF (2005) Degradation of C.I. reactive Orange 4 and its simulated dyebath wastewater by heterogeneous photocatalysis. Dyes Pigment 64:135–139

Gracien EB, Shen J, Sun X, Liu D, Li M (2007) Effect of additive oxidant agent on the discoloration and mineralization of acid Orange 7 by using iron-doped titanium dioxide produced by re-anodization method. Chem Engg J. doi:10.1016/j.cej.2007.05.050

Gupta AK, Pal A, Sahoo C (2006) Photocatalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using Ag^+ doped TiO_2. Dyes Pigment 69:224–232

Kiriakidou F, Kondarides DI, Verykios XE (1999) The effect of operational parameters and TiO_2-doping on the photocatalytic degradation of azo-dyes. Catal Today 54:119–130

Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C, Herrmann JM (2002) Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. Appl Catal B Environ 39:75–90

Levenspiel O (1995) Chemical reaction engineering, 2nd edn. Wiley, Singapore

Liu H-L, Chiou Y-R (2005) Optimal decolorization efficiency of Reactive Red 239 by UV/TiO_2 photocatalytic process coupled with response surface methodology. Chem Engg J 112:173–179

Luo J, Yartym J, Hepel M (2002) Photoelectrochemical degradation of Orange II textile dye on nanostructured WO_3 film electrodes. J New Mat Elect Syst 5:315–321

Mahmoodi NM, Arami M, Nargess YL, Nooshin ST (2005) Decolourisation and aromatic ring degradation kinetics of Direct Red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO_2 as a photocatalyst. Chem Eng J 112:191–196

Menendez-Flores VM, Friedmann D, Detlef WB (2008) Durability of Ag-TiO_2 photocatalysts assessed for the degradation of dichloroacetic acid. Int J Photoenergy 1–11. doi:10.1155/2008/280513

Muruganandham M, Swaminathan M (2004) Photochemical oxidation of reactive azo dye with UV-H_2O_2 process. Dyes Pigment 62:269–275

Nasr-Esfahani M, Habibi MH (2008) Silver doped TiO_2 nanostructure composite photocatalyst film synthesized by Sol–Gel Spin and Dip Coating Technique on Glass. Int J Photoenergy 1–11. doi: 10.1155/2008/628713

Oranusi NA, Ogugbue CJ (2005) Effect of pH and nutrient starvation on biodegradation of azo dyes by *Pseudomonas* sp. J Appl Sci Environ 91:39–43

Sahoo C, Gupta AK, Pal A (2005) Photocatalytic degradation of Crystal Violet (C.I. Basic Violet 3) on silver ion doped TiO_2. Dyes Pigment 66:189–196

Sharma P, Singh L, Dilbaghi N (2009) Biodegradation of Orange II dye by *Phanerochaete Chrysosporium* in simulated wastewater. J Sci Ind Res 68:157–161

Somasiri W, Ruan W, Xiufen L, Jian C (2006) Decolorization of textile wastewater containing acid dyes in UASB reactor system under mixed anaerobic granular sludge. Electron J Environ Agric Food Chem 5:1224–1234

Stylidi M, Kondarides DI, Verykios XE (2003) Mechanistic and kinetic study of solar-light induced photocatalytic degradation of acid Orange 7 in aqueous TiO_2 suspensions. Int J Photoenergy 5:59–67

Tokumura M, Znad HT, Kawase Y (2006) Modeling of an external light irradiation slurry photoreactor: UV light or sunlight-photoassisted

Fenton discoloration of azo-dye Orange II with natural mineral tourmaline powder. Chem Engg Sci 61:6361–6371

Wu C-H (2008) Effects of operational parameters on the decolorization of C.I. Reactive Red 198 in UV/TiO_2-based systems. Dyes Pigment 77:31–38

Zhao D, Zhou J, Liu N (2007) Surface characteristics and photoactivity of silver-modified palygorskite clays coated with nano-sized titanium dioxide particles. Mater Charact 58:249–255