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Photocatalytic degradation of an organic pollutant by zinc oxide – solar process

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Abstract The photocatalytic degradation of 4-nitrophenol over irradiated ZnO suspensions was investigated in aerated aqueous solution. Complete degradation was achieved after irradiation with solar light, being the reaction rate dependent on the initial pH. The effect of various parameters such as catalyst loading, pH and initial concentration of 4-nitrophenol on degradation has been determined. The degradation was strongly enhanced in the presence of electron acceptors such as H_2O_2, $K_2S_2O_8$ and $KBrO_3$. The kinetics of heterogeneous photocatalytic degradation is discussed interms of Langmuir–Hinshelwood (L–H) kinetic model. The intermediates formed during the photodegradation were identified by GC–MS analysis. The mineralization of 4-nitrophenol has also been confirmed by COD measurements.

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1. Introduction

4-Nitrophenol (4-NP) is used for the synthesis of medicines, dye, explosives, leather coloring agents, and it is also generated during the formulation of pesticides or photodegradation of pesticides that contain the nitrophenol moiety (Uberoi and Bhattacharya, 1997; Kidak and Ince, 2006). Consequently, 4-NP occurs widely in industrial and agricultural wastewater, rivers and soils (Dieckmann and Gray, 1996; Oturan et al., 2000). The presence of substituent groups, e.g., nitro groups, on phenols increases the toxic effects on ecosystem and human health due to their persistence in the environment. Therefore,

4-NP is notified as priority organic pollutants by the United States Environmental Protection Agency (EPA, 2008). The conventional approaches for wastewater treatment have been carried out to degrade 4-NP. Biological degradation methods were proved to be ineffective especially at high concentrations (Spain, 1995; Yi et al., 2006). Physical processes such as adsorption (Pan et al., 2007), solvent extraction (Shen et al., 2006), and membrane separation (Ghosh et al., 2006) are also used for 4-NP removal, but these methods have one major disadvantage that they do not provide a real degradation of the compounds but only transfer them from a diluted to a concentrated stream which needs further treatment.

Alternative pollutants destructive technologies are advanced oxidation processes (AOPs). AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of ·OH radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants.

Efficient treatment technologies are required to reduce 4-nitrophenol (4-NP) concentration in wastewater to acceptable

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levels because it is hazardous even at low concentrations. Heterogeneous photocatalysis, a very promising advanced oxidation process developed in the past years, allows performing the efficient degradation and in most cases the complete mineralization of a great variety of organic pollutants present at low concentration levels in aqueous wastes (Hoffman et al., 1995; Fujishima et al., 2000; Malato et al., 2002; Liotta et al., 2009; Lu et al., 2009; Mai et al., 2008). It is based on the use of proper semiconductor materials, which upon activation with suitable light sources give rise to the formation of various reactive species. Advanced oxidation processes (AOPs) have following advantages (i) complete mineralization, (ii) no waste disposal problem, (iii) no expensive oxidants needed, (iv) low cost and (v) only mild temperature and pressure are necessary.

In the present study, an attempt has been made to investigate the advanced oxidative degradation of 4-nitrophenol using zinc oxide as heterogeneous photocatalyst under different conditions using Solar light as radiation source.

2. Experimental

2.1. Materials and methods

4-Nitrophenol (Merck) (molecular formula $C_6H_5O_3N$ molecular weight 139.11) is extensively used as a disinfectant. It has the absorption maxima at 316 nm. The photocatalyst zinc oxide (Merck), which has a particle size 0.1–4 μm and surface area 5 m^2/g, was used for the study. AnalaR grade reagents H_2O_2, $K_2S_2O_8$, $KBrO_3$ were used. The pH of the solution was measured by HANNA Phep digital pH meter. The pH of the solution was adjusted before irradiation using NaOH or H_2SO_4.

For solar experiments, all photocatalytic degradations were carried out under similar conditions on sunny days between 11 A.M to 2 P.M. During the illumination time no volatility of the solvent was observed. Solar light intensity was measured for every 15 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set at the position of maximum intensity. The intensity of solar light was measured using LT Lutron LX-10/A digital Lux meter. The intensity was nearly constant during the experiments.

2.2. Apparatus

For GC analysis, Perkin–Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used. GC/MS analysis was carried out using GC model: Varian GC–MS-Saturn 2200 Thermo, capillary column VF5MS (5% phenyl–95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness, temperature of column range from 50 to 280 °C (10 °C min^{-1}), and injector temperature 250 °C.

2.3. Procedure

For the photolysis experiment, 50 ml of the 4-nitrophenol solution [2×10^{-4} M] containing appropriate quantity of the catalyst dispersion was used. The interval time of 20 min, 2–3 ml of sample was withdrawn and ZnO particles were removed by centrifugation. 1 ml of the centrifugate was diluted to 10 ml. Changes in the concentration of 4-nitrophenol are observed from its characteristic absorption at 316 nm using UV–visible

spectrophotometer. All photocatalytic experiments were carried out at pH 5.

2.4. Chemical oxygen demand

Chemical oxygen demand (COD) is a widely used parameter to characterize the organic content of an industrial effluent. It is an aggregate measure of the organic compounds that can be oxidized to inorganic (mineral) end-products and therefore, it was used to assess the degree of mineralization that had occurred during the photocatalytic process. The COD was determined at the beginning and end of the experimental runs which agrees with standard methods (American Public Health Association, 1992) using the volumetric titration methodology.

2.5. GC–MS analysis

For identification of intermediate products of 4-nitrophenol photocatalytic degradation, the sample taken after complete degradation was analyzed. The sample for analysis was prepared by the following method. The centrifugate obtained with different times of irradiation was extracted 5 times with HPLC grade chloroform. The extract was dried over anhydrous sodium sulfate to remove the water present in the solution. The solvent was removed by evaporation under reduced pressure. The final residual mass was taken for GC–MS analysis.

3. Results and discussion

3.1. Photocatalytic degradability of 4-nitrophenol

In the absence of the photocatalyst, the 4-nitrophenol solution on irradiation with the solar light has been found to be stable even after 90 min. In the presence of zinc oxide and in the absence of light there is a small decrease in 4-nitrophenol concentration initially and then found to be stable. The initial decrease is due to the adsorption of 4-nitrophenol by zinc oxide and the pollutant undergoes 97.7% degradation in 90 min on irradiation with ZnO in the presence of UV light of 365 nm. The photodegradation of 4-nitrophenol as a function of time is shown in Figs. 1 and 2 shows the changes in the UV–visible spectrum of 4-nitrophenol on solar radiation with ZnO under different irradiation times.

3.2. Effect of initial pH of the solution

The most important parameter that influences the photocatalytic degradation is the solution pH. The efficiency of the catalyst is affected by the pH of the solution. The pH of the solution is adjusted before irradiation and it is not controlled during the course of reaction. The effect of varying the pH from 1 to 11 on the degradation of 4-nitrophenol is shown in Table 1. It is found that the degradation efficiency increases with an increase in pH from 1 to 11. Increase of pH of the 4-nitrophenol solution from 1 to 5 increases the degradation from 54.9% to 79.9% at the time of 60 min. A slight increase in the degradation rate was observed for further rise in pH from 5 to 11. Many authors observed similar behavior in their studies (Sharma et al., 1995; Pandurangan et al., 2001; Sakthivel et al., 2003; Akyol et al., 2004). At low pH, ZnO particle agglomeration
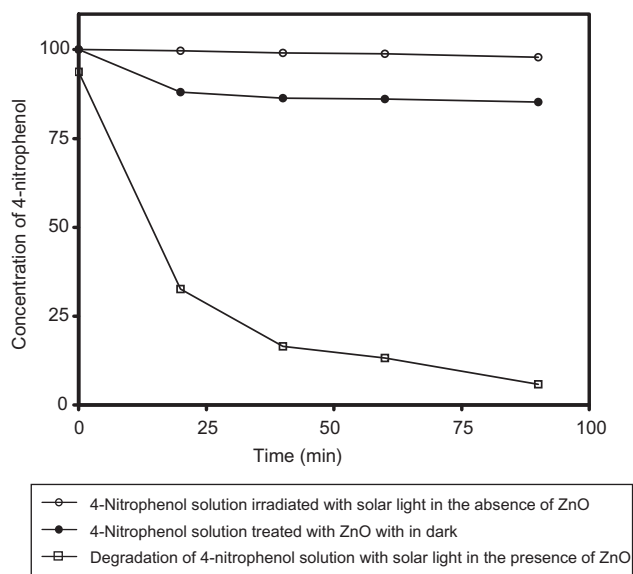
Figure 1 Photodegradability of 4-nitrophenol using Solar light and ZnO ZnO = 75 mg/50 ml; [4-NP] = 2×10^{-4} mol/l; pH 5.0 ± 0.1.

reduces the pollutant adsorption as well as photon absorption. The increased efficiency in the alkaline pH range may be explained on the basis of increase in the formation of ·OH radicals with an increase in pH. In acid and neutral solutions the formation of ·OH radical can be given by the equation.

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \qquad (1)$$

In alkaline solution the ·OH radical is also formed from hydroxide ion

$$OH^- + h^+ \rightarrow \cdot OH \qquad (2)$$

3.3. Effect of catalyst weight

The amount of catalyst is one of the main parameters for the degradation studies. In order to avoid the use of excess catalyst

Table 1 Effect of pH on the photocatalytic degradation of 4-nitrophenol using solar light.

pH	Percentage of degradation
1	54.9
3	64.2
5	79.9
7	85.7
9	90.3
11	98.3

4-Nitrophenol = 2×10^{-4} mol/L; ZnO = 75 mg/50 mL; irradiation time = 60 min.

it is necessary to find out the optimum loading for efficient removal of pollutant. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic degradation process (San et al., 2001; Gouvea et al., 2000; Saquib and Mumner, 2002). The effect of the amount of catalyst on the photocatalytic degradation of 4-nitrophenol has been carried out in the range of 25–150 mg of the catalyst for 50 ml of solution. The results are given in Fig. 3. As the concentration of the catalyst is increased from 25 mg to 75 mg/50 ml, degradation increases from 56.8% to 79.9 % at 60 min of irradiation time. This is due to an increase in the number of ZnO particles, which increases the absorption of photons and adsorption of pollutant molecules. Further increase of ZnO loading decreases the removal rate. Increase of the catalyst loadings beyond 75 mg/50 ml may cause screening effect. These effects reduce the specific activity of the catalyst. At high loadings of catalyst, particle aggregation may also reduce the catalytic activity. The optimum amount of catalyst loading is found to be 75 mg/50 ml of the degradation of 4-nitrophenol. Hence, 75 mg/50 ml was used as the catalyst dosage for the photocatalytic reaction.

3.4. Effect of 4-nitrophenol concentration

The photocatalytic degradation of 4-nitrophenol (pollutant) has been carried out at different initial concentrations of 4-nitrophenol in the range 2×10^{-4} to 8×10^{-4} mol/l. The results
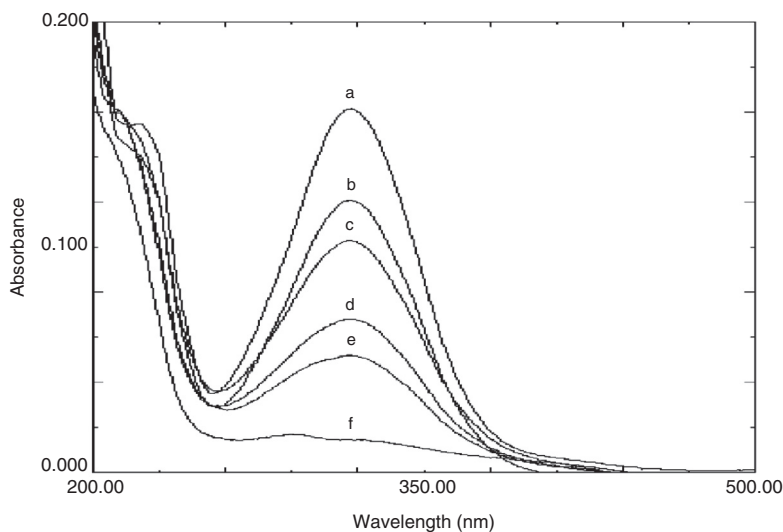

Figure 2 The changes in UV–visible spectrum of 4-nitrophenol on irradiation with Solar-light in the presence of ZnO [4-NP] = 2×10^{-4} mol/l; pH 5.0 ± 0.1; ZnO = 75 mg/50 ml. (a) 0 min; (b) 20 min; (c) 40 min; (d) 60 min; (e) 80 min; (f) 90 min.
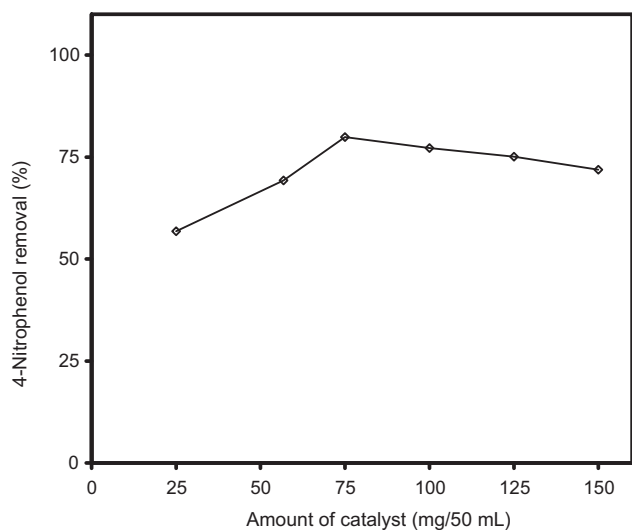
Figure 3 Effect of catalyst loading on the degradation of 4-nitrophenol using solar light 4-Nitrophenol = 2×10^{-4} mol/L; pH 5 ± 0.1; irradiation time = 60 min.

are shown in Fig. 4. Increase in the concentration of 4-nitrophenol decreases the degradation from 97.7% to 42.3% at 90 min. The increase in pollutant concentration decreases the path length of photon entering into the pollutant solution. At high pollutant concentrations, a significant amount of solar light may be absorbed by the pollutant molecules rather than the catalyst and this reduces the catalytic efficiency (Mills et al., 1993).

3.5. Effect of electron acceptors

In the photocatalytic reaction of ZnO the major energy-wasting step is the electron-hole recombination which leads to low quantum yield. Hence, the prevention of electron-hole recombination becomes very important. This can be achieved by adding a proper electron donor (or) acceptor to the system. Usually molecular oxygen is used as an electron acceptor in a heterogeneous photocatalyzed reaction. Besides, the addition
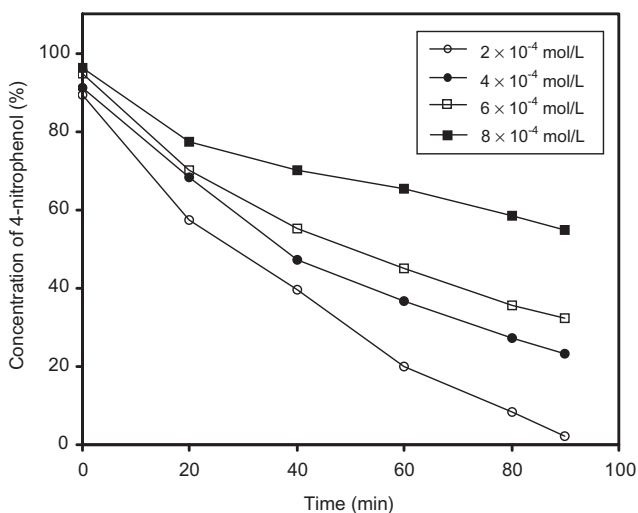
of molecular oxygen, the electron-hole recombination can be reduced by the addition of irreversible electron acceptors such as H_2O_2, $K_2S_2O_8$ and $KBrO_3$. The addition of these electron acceptors enhanced the degradation rate in several ways (i) preventing the electron-hole recombination by accepting the conduction band electron (ii) increasing the hydroxyl radical concentration (iii) generating other oxidizing species (SO_4^{2-}) to accelerate the intermediate compound oxidation rate.

3.6. Effect of addition of H_2O_2

The effect of addition of H_2O_2 (5–20 mmol) on the photocatalytic oxidation has been investigated. The results are given in Fig. 5. The addition of H_2O_2 (5–20 mmol) increases the degradation from 79.9 to 95.5 % at 60 min. A photocatalytic reaction in the presence of hydrogen peroxide increases the concentration of hydroxyl radicals in the solution thereby enhancing the rate of photocatalytic oxidation (Augugliaro et al., 1990). The initial rate of the reaction has been found to increase in the presence of ZnO and hydrogen peroxide thereby confirming the hydroxyl radicals are produced on the surface of ZnO by irradiation. The cleavage of H_2O_2 yields ·OH radical as shown by the following equations.

$$H_2O_2 + e_{(CB)}^- \rightarrow \text{·OH} + OH^- \tag{3}$$

$$H_2O_2 \xrightarrow{h\nu} 2\text{·OH} \tag{4}$$

H_2O_2 also reacts with superoxide anion to form ·OH radical

$$H_2O_2 + O_2^{\cdot-} \rightarrow \text{·OH} + OH^- + O^{2-} \tag{5}$$

3.7. Effect of addition of potassium persulphate ($K_2S_2O_8$)

The effect of addition of $K_2S_2O_8$ on the photocatalytic oxidation of 4-nitrophenol has been investigated by varying the amount of $K_2S_2O_8$ from 10 to 25 mg/50 ml. The results are shown in Table 2. Addition of $K_2S_2O_8$ up to 15 mg/50 ml increases the degradation from 79.9% to 93.8% in 60 min.

Figure 4 Effect of various initial 4-nitrophenol (4-NP) concentrations on the degradation of 4-NP using Solar light ZnO = 75 mg/50 ml; pH 5.0 ± 0.1.

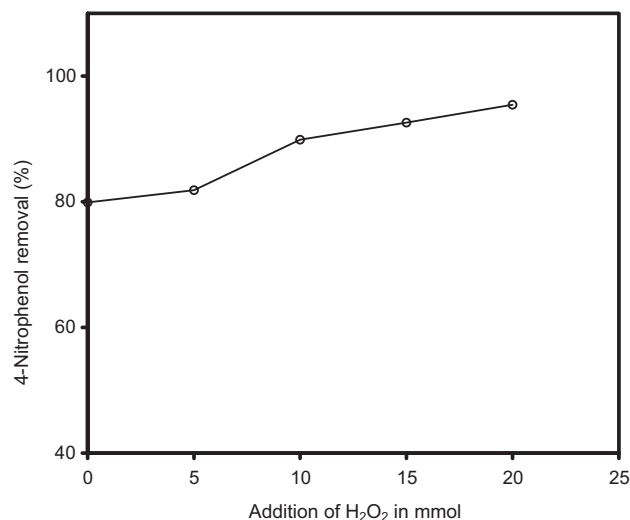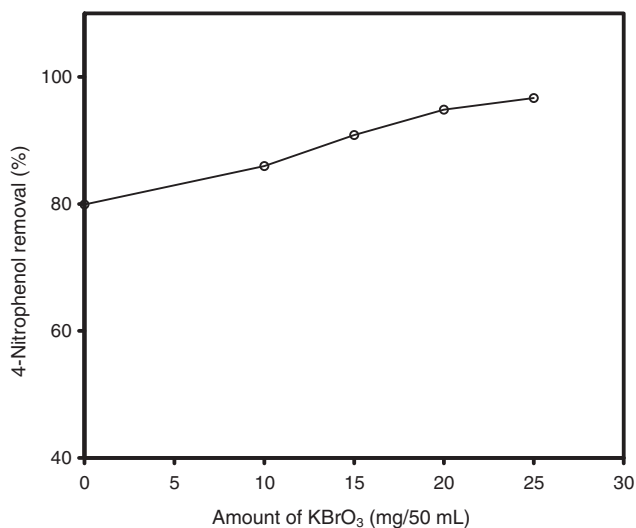**Figure 5** Effect of addition of H_2O_2 concentration on the degradation of 4-nitrophenol using solar light ZnO = 75 mg/50 ml; [4-NP] = 2×10^{-4} mol/l; irradiation time = 60 min.

Table 2 Effect of addition of $K_2S_2O_8$ on the photocatalytic degradation of 4-nitrophenol using solar light.

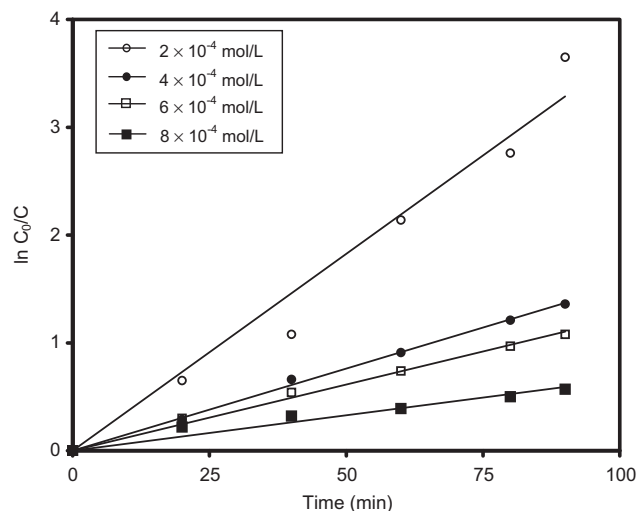| Amount of $K_2S_2O_8$ added in mg/50 ml	Percentage of degradation
0	79.9
10	85.3
15	93.8
20	80.5
25	68.6

4-Nitrophenol = 2×10^{-4} mol/L; pH = 5 ± 0.1; ZnO = 75 mg/50 mL; irradiation time = 60 min.

Table 3 Rate constants of 4-nitrophenol degradation by solar/ZnO.

Initial concentration of 4-nitrophenol $\times 10^{-4}$ mol/L	Degradation k' (min^{-1})
2	0.0242
4	0.0151
6	0.0119
8	0.0058

Figure 7 Effect of 4-nitrophenol degradation for different initial concentrations by Solar/ZnO. ZnO = 75 mg/50 ml; pH 5.0 ± 0.1.

$$SO_4^{\cdot-} + H_2O \rightarrow {}^{\cdot}OH + SO_4^{2-} + H^+ \quad (8)$$

Further increase in the addition from 20 to 25 mg decreases the degradation. At high dosage of $S_2O_8^{2-}$, the inhibition of reaction occurs due to increase in concentration of SO_4^{2-}. The excess of SO_4^{2-} ions are adsorbed on the ZnO surface and the catalytic activity is reduced. The adsorbed SO_4^{2-} ion also reacts with photogenerated holes and with hydroxyl radicals.

Figure 6 Effect of addition $KBrO_3$ of on the degradation of 4-nitrophenol using Solar light ZnO = 75 mg/50 ml; [4-NP] = 2×10^{-4} mol/l; pH 5.0 ± 0.1; irradiation time = 60 min.
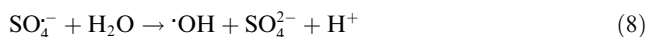
The enhancement of reaction rate is due to the inhibition of electron-hole recombination and production of other oxidizing species namely sulphate radical anion.
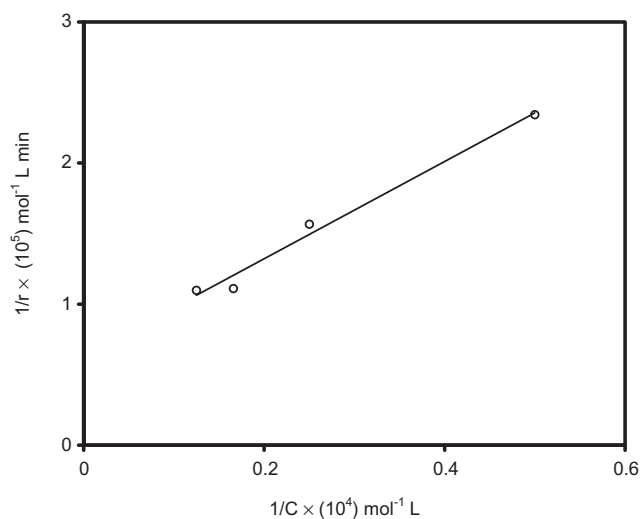
$$S_2O_8^{2-} + e_{(CB)}^- \rightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (6)$$

The sulphate radical anion may react with photogenerated electron and with water molecule producing hydroxyl radical.

$$SO_4^{\cdot-} + e_{(CB)}^- \rightarrow SO_4^{2-} \quad (7)$$
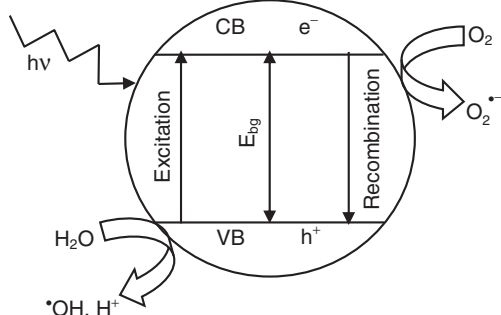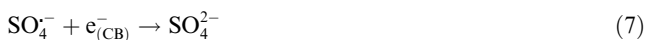
Scheme 1 Mechanism of photodegradation.

Figure 8 Linearized reciprocal kinetic plot of the degradation of 4-nitrophenol by Solar/ZnO.

$$SO_4^{2-} + h^+ \rightarrow SO_4^{\cdot-} \tag{9}$$

$$SO_4^{2-} + \cdot OH \rightarrow SO_4^{\cdot-} + OH^- \tag{10}$$

Since $SO_4^{\cdot-}$ is less reactive than $\cdot OH$ radical, hence the excess SO_4^{2-} reduces the photodegradation of the 4-nitrophenol.

3.8. Effect of addition of potassium bromate (KBrO₃)

KBrO₃ is an efficient electron acceptor and used as an additive to enhance photocatalytic degradation rate (Poulios and Tsachpinis, 1999; San et al., 2001; Saquib and Munner,

2002). The effect of addition of KBrO₃ (10 to 25 mg/50 ml) on the photocatalytic degradation is given in Fig. 6. The addition of KBrO₃ up to 15 mg increases the degradation from 79.9% to 90.9% at the time of 60 min. The enhancement of the removal rate is due to the reaction between BrO_3^- ion and conduction band electron which reduces the recombination of electron-hole.

$$BrO_3^- + 6e_{(CB)}^- + 6H^+ \rightarrow Br^- + 3H_2O \tag{11}$$
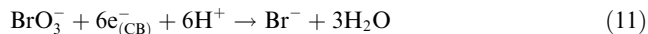
On further increase of KBrO₃ addition, only small enhancement was observed.
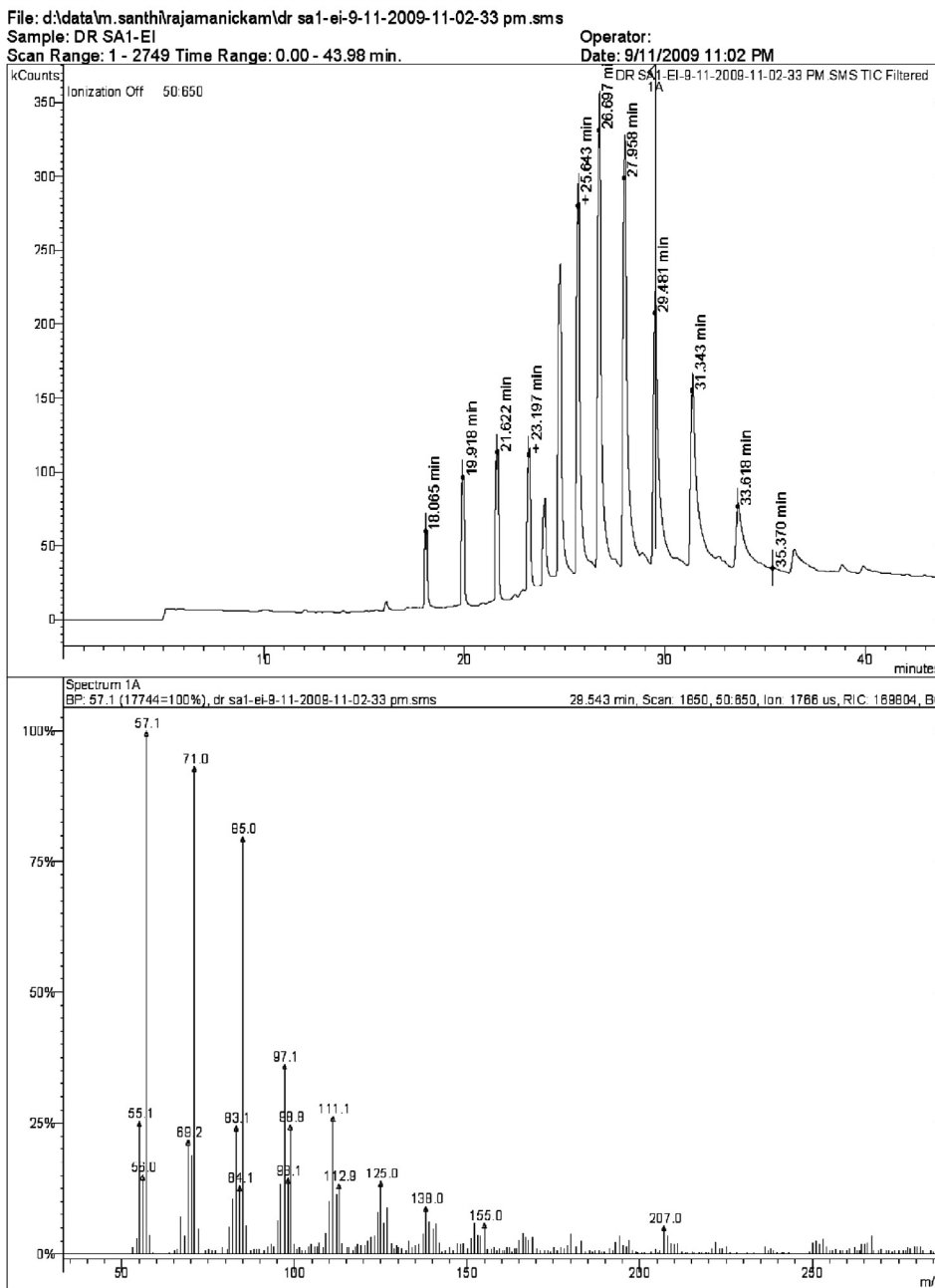
Figure 9   GC-MS spectra of 4-nitrophenol (Ret. Time 29.481 min).
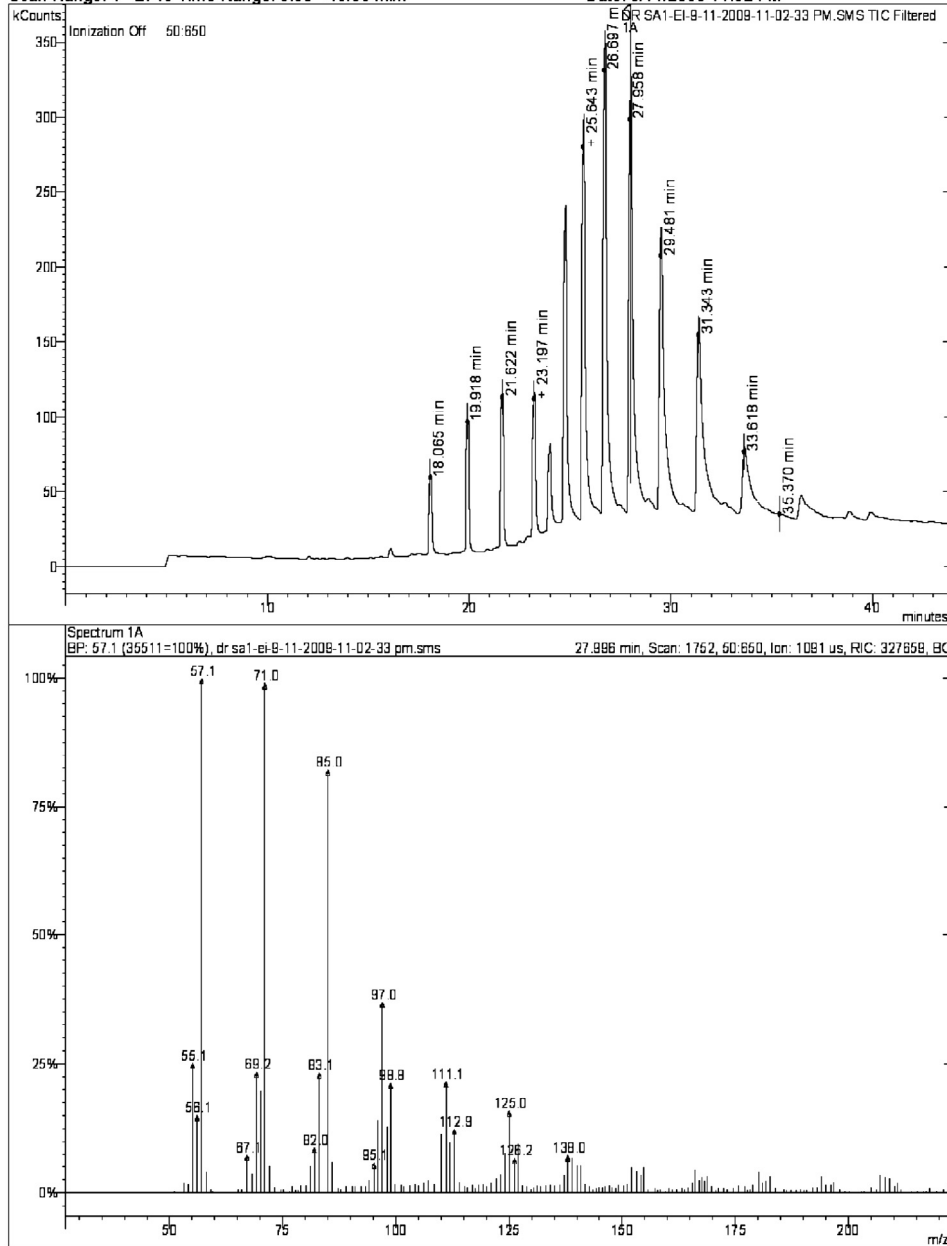
Figure 10   GC-MS spectra of 4-nitrophenol (Ret. Time 27.958 min).

3.9. Chemical oxygen demand (COD)

To confirm the mineralization of 4-NP, the degradation was also analyzed by COD values. It is observed that the solutions obtained after photodegradation show a significant COD removal from 40.7% to 81.7% after 30 and 90 min. irradiation, respectively. This indicates mineralization of 4-NP. Mineralization of 4-NP was also revealed by the formation of carbon dioxide during photodegradation. Carbon dioxide formation

was tested by passing the evolved gas during photodegradation into lime water.

3.10. Mechanism of photodegradation

The photocatalytic process is initiated by the illumination of a semiconductor catalyst with radiation of energy higher than the band gap energy of the semiconductor. This irradiation generates electrons (e^-) and holes (h^+) in the conduction band
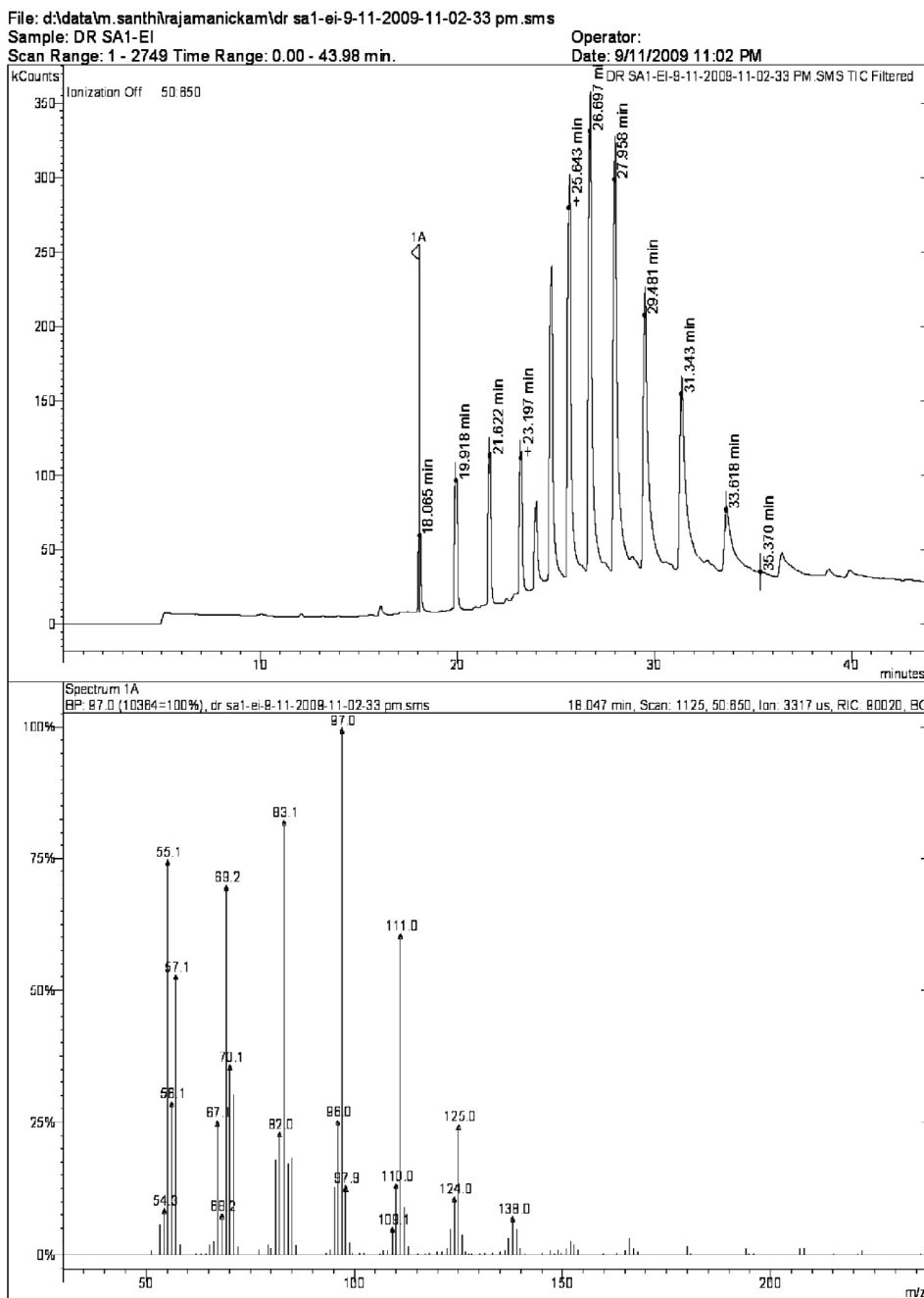
Figure 11   GC-MS spectra of 4-nitrophenol (Ret. Time 18.065 min).

(CB) and valence band (VB) respectively shown in Scheme 1 and as given by Eq. (12)

$$ZnO \xrightarrow{h\nu} e^-_{(CB)} + h^+_{(VB)} \qquad (12)$$

The electron-hole pair formed may recombine in the bulk lattice (or) migrate to the surface where they can react with the adsorbents (Turichi and Ollis, 1990). Holes are trapping reaction proceeds with the formation of hydroxyl radicals as given by equation.

$$h^+ + OH^- \rightarrow \cdot OH \qquad (13)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \qquad (14)$$

The electrons are trapped by dissolved oxygen resulting in the formation of superoxide ion.

$$e^- + O_2 \rightarrow O_2^{\cdot-} \qquad (15)$$

The photocatalytic degradability by ZnO involved the hydroxy radical and holes for oxidation of organic molecules (OM). The reactions are given below.

$$h^+ + OM \rightarrow OM^+ \qquad (16)$$
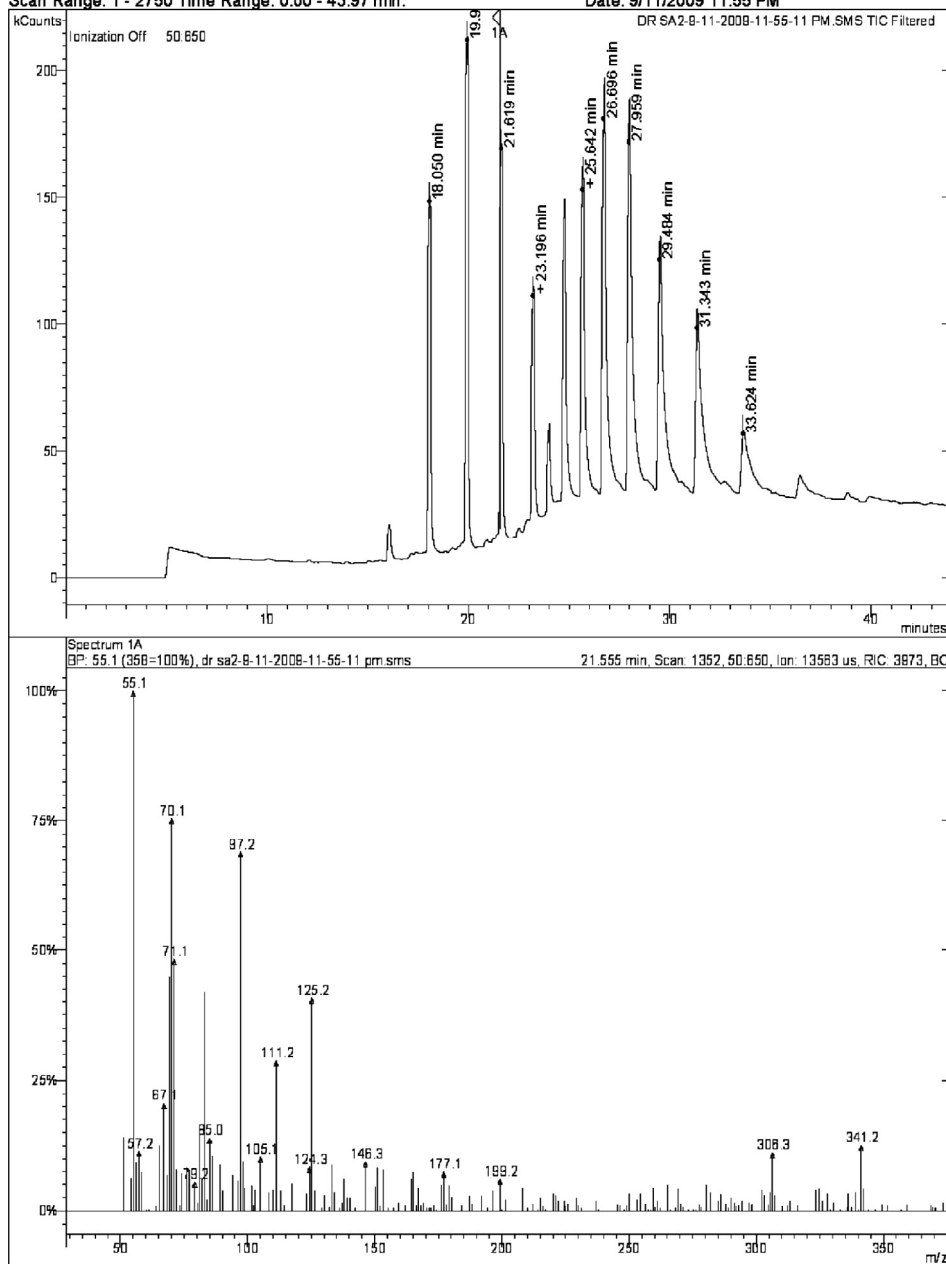
Figure 12   GC-MS spectra of 4-nitrophenol (Ret. Time 21.619 min).

$$OM^+ + O_2 \rightarrow Products \tag{17}$$

$$^{\cdot}OH + OM \rightarrow Products \tag{18}$$
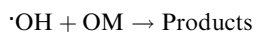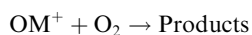
3.11. Kinetic analysis

The heterogeneous photocatalytic degradation of 4-nitrophenol containing ZnO obeys apparently pseudo-first order kinetics. At low initial substrate (4-nitrophenol) concentrations the rate expression is given by equation.

$$\frac{-\mathrm{d}[C]}{\mathrm{d}t} = k'[C] \tag{19}$$

where k' is the pseudo-first order rate constant. The rate constant of degradation is given in Table 3. 4-Nitrophenol is adsorbed on to ZnO surface and the adsorption–desorption equilibrium is reached. After adsorption, the equilibrium concentration of 4-nitrophenol solution is determined and it is taken as the initial 4-nitrophenol concentration for kinetic analysis. Integration of the above equation with the limit of $C = C_0$ at $t = 0$ with C_0 being the equilibrium

concentration of the bulk solution gives the following equation

$$\ln\left[\frac{C_o}{C}\right] = k't \tag{20}$$

where C_0 is the equilibrium concentration of 4-nitrophenol and C is the concentration at time 't'

A plot of $\ln C_0/C$ versus time for degradation is shown in Fig. 7. A linear relation between 4-nitrophenol concentration
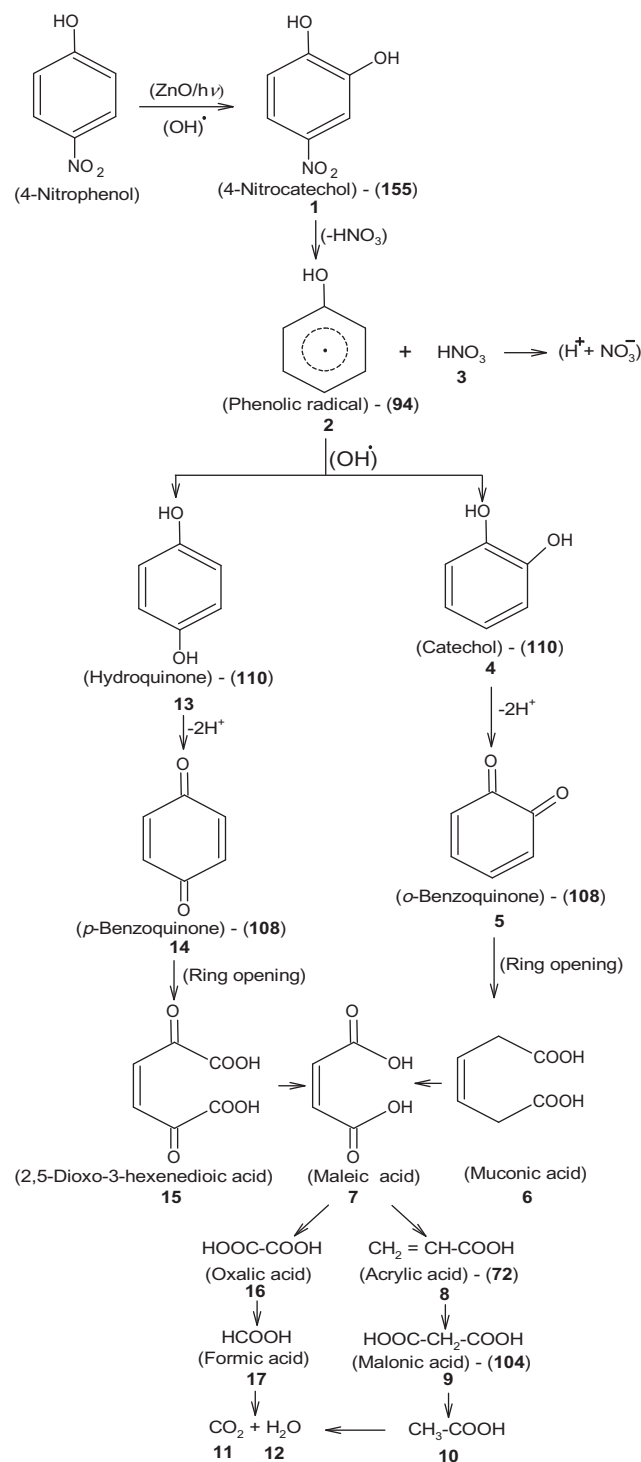
and irradiation time has been observed. Many authors (Chen and Chou, 1993; Wenhua et al., 2000) have used the Langmuir–Hinshelwood (L–H) kinetic expression to analyze the heterogeneous photocatalytic reaction successfully. The experimental data have been rationalized in terms of the modified form of L–H kinetic model to describe the solid–liquid reaction (Alaton and Balcioglu, 2001). The rate of oxidation of 4-nitrophenol at the surface reaction is proportional to the surface coverage of 4-nitrophenol on ZnO assuming that 4-nitrophenol is strongly adsorbed on the catalytic surface than the intermediate products (Sharma et al., 1995). The effect of 4-nitrophenol concentration on the rate of degradation is given in the form of equations (Matthews, 1987).

$$r = \frac{K_1 K_2 C}{1 + K_1 C} \tag{21}$$

$$\frac{1}{r} = \frac{1}{K_2 K_1 C} + \frac{1}{K_2} \tag{22}$$

Where 'C' is the concentration of 4-nitrophenol at time 't', K_1 is the constant related to adsorption and K_2 is related to the reaction properties of the substrate (4-nitrophenol). The applicability of L–H equation for the degradation has been confirmed by the linear plot obtained by plotting the reciprocal of initial rate $(1/r)$ against reciprocal of initial concentration of 4-nitrophenol $(1/C)$ as shown in Fig. 8. The values of K_1 and K_2 have been determined from the slope and intercept of these plots. The values of K_1 and K_2 are found to be $1.83 \times 10^3 \, M^{-1}$, $1.59 \times 10^{-5} \, Mm^{-1}$, for degradation respectively.

3.12. GC–MS analysis

The photodegradation reactions of organic pollutants may take place through the formation of harmful intermediates that are more toxic than the original compounds. Therefore, the knowledge on the identities of the intermediates is a necessity in photocatalytic degradation processes.

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of 4-nitrophenol through GC–MS analysis. The GC–MS analysis of the solution was performed after 30 and 60 min irradiation. We get four predominant peaks for retention times of 18.0, 21.6, 27.9 and 29.4 min. Eight products were identified based on their molecular ions and mass spectrometric fragmentation peaks. Some representative GC–MS spectra are given in Figs. 9–12. The formation of eight compounds from the photocatalytic degradation of 4-nitrophenol is shown in the Scheme 2. The data are given below.

Scheme 2 Proposed degradation pathway of 4-NP with ZnO.

Compound	Retention time (min)	m/e values
1	29.481	207.0, 155.0, 138.0, 125.0, 112.9, 111.1, 98.8, 98.1, 97.1, 85.0, 84.1, 83.1, 71.0, 69.2, 57.1, 55.1, 56.0
2	27.958	138.0, 126.2, 125.0, 112.9, 111.1, 98.8, 95.1, 97.0, 85.1, 83.1, 82.0, 71.0, 69.2, 57.1, 56.1, 55.1
4, 5, 13, 14	18.065	138.0, 125.0, 124.0, 111.0, 110.0, 109.1, 97.9, 97.0, 96.0, 83.1, 82.0, 70.1, 69.2, 68.2, 67.1, 57.1, 55.1, 56.1, 54.3
8, 9	21.619	341.2, 306.3, 199.2, 177.1, 146.3, 125.2, 111.2, 105.1, 97.2, 95.0, 79.2, 71.1, 70.1, 67.1, 57.2, 55.1

The formation of 4-nitrocatechol might be explained by the electrophilic attack of ˙OH radical on the *ortho* position of 4-nitrophenol. Attack of the electrophilic radical ˙OH occurred at the ring positions activated by the presence of the two substituents. The phenolic –OH group was electron donating for the electrophilic aromatic substitution, while the –NO$_2$ group was electron-withdrawing. The electron-donating substituents increased the electron density at the *ortho* and *para* positions while the electron-withdrawing substituents were strongly deactivating and *meta* directing. When both the substituents (-OH and –NO$_2$) were present, the electrophilic attack would occur preferentially in *ortho* and *para* positions with respect to the –OH group (Goi et al., 2004; Di Paola et al., 2003). In the case of 4-nitrophenol only 4-nitrocatechol could be obtained.

Simultaneously, if ˙OH attacked the carbon carrying a nitro group, phenol radicals and/or its derivatives, such as hydroquinone (quinol), catechol and quinones, would be generated and nitrate ions are released by the radical addition-elimination. Furthermore, reactions of the primary intermediates mentioned above with ˙OH led to benzene ring cleavage and formation of oxygenated aliphatic compounds such as muconic acid, maleic acid, malonic acid, 2,5-dioxo-3-hexenedioic acid, oxalic acid, acrylic acid, formic acid and acetic acid. The fact is that these organic diacids were not detected under photocatalytic compounds (Brillas et al., 1998). Maleic acid was directly mineralized to CO$_2$ *via* oxalic acid, being accelerated by reaction of such diacids and its intermediates with ˙OH (Sauleda and Brillas, 2001). Moreover, malonic acid would be converted into acetic acid by further oxidation initiated by ˙OH. Finally, these aliphatic by-products would be mineralized to CO$_2$ and H$_2$O (Zhao et al., 2008).

4. Conclusions

4-Nitrophenol (an organic pollutant) is successfully degraded by ZnO assisted photocatalysis in aqueous dispersion under irradiation by Solar light. The adsorption of 4-nitrophenol on ZnO was found to be favorable by the langmuir approach. The adsorption was maximum at pH 5. Increase in initial dye concentration decreases the removal rate. The optimum concentrations of oxidants H$_2$O$_2$, K$_2$S$_2$O$_8$ and KBrO$_3$ for enhanced degradation are 10 mM, 15 mg and 15 mg/ 50 ml respectively. All processes follow pseudo-first order kinetics. Degradation of 4-nitrophenol has been confirmed by decreasing COD values and the intermediate products separated and confirmed by GC–MS analysis.

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