

## Photochemical degradation of *p*-dichlorobenzene by photo-Fenton's reagent

Deepika Mogra, Mukesh Mehta, Ramesh Ameta and Suresh C. Ameta\*

Department of Chemistry, M. L. Sukhadia University, Udaipur-313 002, India

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The photochemical degradation of *p*-dichlorobenzene on titanium dioxide was carried out in the presence of Fenton's reagent, and progress of the reaction was observed spectrophotometrically. The effects of the variation of various parameters, such as pH, concentration of *p*-dichlorobenzene, Fe<sup>3+</sup> ion concentration, amount of photocatalyst, amount of hydrogen peroxide, light intensity etc. on the photodegradation of *p*-dichlorobenzene were observed. A tentative mechanism for this degradation has also been proposed.

Fenton's reagent<sup>1</sup> is used to treat a variety of industrial wastes containing a range of toxic organic compounds. The process may be applied to wastewaters, sludges or contaminated soils. Fenton<sup>1</sup> discovered that the addition of ferrous salt initiated the rapid oxidation by hydrogen peroxide of  $\alpha$ -hydroxy acids, such as tartaric acid. Fenton's reagent is one of the most powerful inorganic oxidizing reagents. Sedlak<sup>2</sup> investigated the effect of FeCl<sub>3</sub>, K<sub>3</sub>[Fe(CN)<sub>6</sub>] and Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO] on photochemical reactions of H<sub>2</sub>O<sub>2</sub> with benzene. FeCl<sub>3</sub> markedly raises the phenol content in the product in the reaction initiated by UV radiation, i.e. it catalyzes hydroxylation, while the cyano complexes catalyze photodestruction of the benzene ring. Photocatalytic degradation of trinitrotoluene and trinitro-benzene influenced by H<sub>2</sub>O<sub>2</sub> was observed by Dillert *et al.*<sup>3</sup>

Polszynska *et al.*<sup>4</sup> studied the reactivity of substituted benzenes towards reactive species formed in the Fe<sup>II</sup>/H<sub>2</sub>O<sub>2</sub> aqueous system. Sawyer *et al.*<sup>5</sup> studied metal (ML<sub>x</sub>; M = Fe, Co, Mn)/hydroperoxide induced activation of dioxygen for the oxygenation of hydrocarbons. Jacob *et al.*<sup>6</sup> investigated the mechanism of reaction between benzene and H<sub>2</sub>O<sub>2</sub> in the presence of dioxygen with added Fe<sup>3+</sup> or Cu<sup>2+</sup> ions. Nedoloujko and Kiwi<sup>7</sup> reported that transient intermediate species are active during the Fenton's mediated degradation of quinoline in oxidative media by pulsed laser spectroscopy. Ruppert *et al.*<sup>8</sup> described the photo-Fenton reaction as an effective photochemical wastewater treatment process. Prousek *et al.*<sup>9</sup> reported the utilization of Fenton reaction for the degradation of conventionally used dyes and coloured wastewater. Prousek and Duriskova<sup>10</sup> studied the oxidative degradation of poly(ethylene glycol) by the Fenton and photo-Fenton's reactions. Photodegradation of malachite green in the presence of Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> under visible irradiation was observed by Wu *et al.*<sup>11</sup>. Sanchez *et al.*<sup>12</sup> reported the degradation of 2,4-dichlorophenoxyacetic acid by *in situ* photogenerated Fenton reagent. Hydroxylation of benzoic

acid by H<sub>2</sub>O<sub>2</sub> using the photochemical formation of Fenton's reagent initiated by 589 nm radiation and in presence of sensitized methylene blue was reported by Lunak *et al.*<sup>13</sup>. New evidences against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reaction were furnished by Bassman *et al.*<sup>14</sup>. Walling<sup>15</sup> studied intermediates in the reaction of Fenton type reagents. It was observed that organic dyes were effective in degrading some of pesticides whereas iron compounds especially in combination with H<sub>2</sub>O<sub>2</sub> as the oxidising agent proved to be more effective for degrading all the target pesticides. Recently, Yasmin<sup>16</sup> has also reported photochemical degradation of phenoxy derivatives using photo-Fenton's reagent. The present study discusses the photodegradation of *p*-dichlorobenzene using photo-Fenton's reagent.

### Results and Discussion

The optical density of the solution was found to decrease with increasing time intervals, which indicates that the concentration of *p*-dichlorobenzene decreases with increasing time of exposure. A plot of  $1 + \log$  O.D. against time was linear and followed pseudo-first order kinetics. The rate constant was calculated from the expression,  $k = 2.303 \times \text{slope}$ .

**Effect of pH :** The effect of pH on the photocatalytic degradation was investigated in the pH range 1.0–3.5. The data reveal that the rate of photocatalytic degradation of *p*-dichlorobenzene increases with increase in pH upto 3.0 and then, the rate decreases with increasing pH. At pH >3.5, some turbidity appeared, therefore, the effect of pH was studied up to 3.5 only. The photocatalytic degradation depends strongly on the pH of the reaction medium. The hydroxyl radicals are generated by three steps : (i) reaction between ferrous ions and hydrogen peroxide, (ii) photochemical reaction of ferric ions and water, (iii) reaction be-

tween holes and water. The increase in pH of the medium will favor step (i) where  $\text{OH}^-$  ions are formed along with hydroxyl radicals, whereas protons are generated in steps (ii) and (iii). Thus it may be concluded that step (i) dominates over steps (ii) and (iii) in the pH range below 3.0. However, retardation of the reaction above pH 3.0 suggests the dominance of steps (ii) and (iii) over step (i).

*Effect of p-dichlorobenzene concentration* : The effect of *p*-dichlorobenzene concentration [in the range (1.0–7.0)  $\times 10^5 M$ ] on the rate of its photocatalytic degradation was studied. The rate of photocatalytic degradation was found to increase with increasing concentration of *p*-dichlorobenzene upto  $5.0 \times 10^{-5} M$  ( $k = 2.50 \times 10^4 \text{ s}^{-1}$ ). On further increase, a sudden decrease in the rate was observed. This may be explained on the basis that on increasing the concentration of *p*-dichlorobenzene, the reaction rate increases as more molecules of *p*-dichlorobenzene are available for degradation. However, on increasing the concentration above  $5.0 \times 10^{-5} M$ , the movement of *p*-dichlorobenzene molecules towards semiconductor surface is hindered because of its large concentration, and hence, a decrease in the rate of degradation was observed.

*Effect of ferric ion concentration* : The effect of concentration of  $\text{Fe}^{3+}$  ion [in the concentration range (3.0–11.0)  $\times 10^5 M$ ] on the rate of photocatalytic degradation of *p*-dichlorobenzene was observed by keeping all other factors identical.

The results reveal that the rate of photodegradation increases on increasing concentration of  $\text{Fe}^{3+}$  ions upto  $9.0 \times 10^{-5} M$  ( $k = 2.50 \times 10^4 \text{ s}^{-1}$ ), while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the  $\text{Fe}^{3+}$  ions in the reaction mixture, the concentration of  $\text{Fe}^{2+}$  ions also increases accompanied by enhanced generation of the active species  $\text{OH}^\bullet$  radicals and as a consequence, the rate of photocatalytic degradation also increases. However, on increasing the concentration of  $\text{Fe}^{3+}$  ions further, the rate was found to decrease. This is because of the fact that the increasing concentration of  $\text{Fe}^{3+}$  ions imparts a yellow colour to the solution, and at larger concentrations, it may act as a filter to the incident light and the desired light intensity will not reach the surface of the semiconductor and, therefore, a decrease in the rate of reaction was observed.

*Effect of hydrogen peroxide* : The effect of amount (0.10–1.30 ml) of hydrogen peroxide on the photocatalytic degradation of *p*-dichlorobenzene was also investigated. It was observed that the rate of the reaction increases as the amount of  $\text{H}_2\text{O}_2$  is increased and it attained an optimum value at 1.1 ml ( $k = 2.51 \times 10^4 \text{ s}^{-1}$ ). Thereafter, the rate of

degradation becomes virtually constant. This saturation like behavior can be explained on the basis that the surface of semiconductor titanium dioxide is completely covered by hydrogen peroxide molecules. Any further amount of hydrogen peroxide will remain in the bulk of the solution and in turn, will not add to the rate of the reaction.

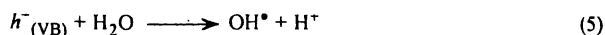
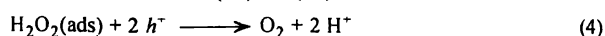
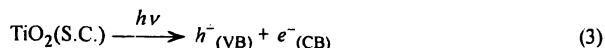
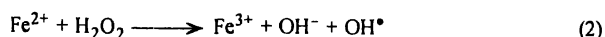
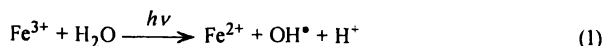
*Effect of amount of semiconductor* : The effect of amount (0.01–0.08 g) of semiconductor on the photocatalytic degradation of *p*-dichlorobenzene was investigated. The rate of photodegradation of *p*-dichlorobenzene increases with an increase in the amount of semiconductor upto 0.06 g ( $k = 2.51 \times 10^4 \text{ s}^{-1}$ ), and on further increase of amount, the rate of reaction becomes almost constant. This may be attributed to the fact that the number of exposed semiconducting particles will increase as the amount of semiconductor powder was increased and as a result, the number of electron-hole pairs will also increase. This will result into a corresponding increase in the rate of the reaction. On further increasing the amount of semiconductor, the number of exposed semiconducting particles will not increase as the exposed surface area will limit the number of particles directly exposed to the light source and the reaction rate remains almost constant after this limit.

*Effect of light intensity* : The effect of light intensity (in the range 20.0–80.0  $\text{mW cm}^{-2}$ ) on the photocatalytic degradation of *p*-dichlorobenzene was investigated. A linear plot between the rate constant and light intensity was observed, which indicates that an increase in the light intensity will increase the rate of reaction. This may be attributed to the increased number of photons striking  $\text{TiO}_2$  particles per unit area per second and as a result, more electron-hole pairs are generated. This, in turn, will increase the number of active species, the hydroxyl radicals. As a consequence, an overall increase in the rate of the reaction has been observed.

#### *Mechanism* :

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the photocatalytic degradation of chlorobenzene with photo-Fenton's reagent in the presence of semiconducting  $\text{TiO}_2$  powder (Scheme 1).

The aqueous solution of ferric ions on exposure to light dissociates water molecule into a proton and  $\text{OH}^\bullet$  radical and itself reduces to ferrous ions. These ferrous ions will decompose  $\text{H}_2\text{O}_2$  into hydroxyl ion and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions.  $\text{TiO}_2$  on exposure generates an electron-hole pair. This hole may dissociate the  $\text{H}_2\text{O}_2$  adsorbed on the semiconductor surface into oxygen and proton whereas a hole may decompose water



Scheme 1

into a proton and a hydroxyl radical. The hydroxyl radical will degrade the chlorobenzene adsorbed on semiconductor surface into products.

### Experimental

The photochemical degradation of *p*-dichlorobenzene (SDS) was studied in the presence of titanium dioxide, Fenton's reagent and light. Stock solution of *p*-dichlorobenzene ( $1.0 \times 10^{-2} \text{ M}$ ) was prepared in double-distilled water. The photochemical degradation of *p*-dichlorobenzene was observed by taking  $5.0 \times 10^{-5} \text{ M}$  of solution,  $9.0 \times 10^{-5} \text{ M}$  ferric ions, 1.10 ml hydrogen peroxide, and 0.06 g semiconductor was added and irradiated with a 200 W tungsten lamp (Philips; light intensity  $60 \text{ mW cm}^{-2}$ ). The intensity of light at various distances from the lamp was measured using a solarimeter (SM CEL 201). A water filter was used to cut off thermal radiation. pH of the solution was measured using a Systronics 324 pH meter. pH of the solution was adjusted by adding  $\text{H}_2\text{SO}_4$  and NaOH solutions. The necessary condition for the correct measurement of the optical density was that the solution was free from semiconductor particles and other impurities, and a centrifuge (Remi

1258) was used to remove these species. A Jasco 7800 spectrophotometer was used to measure the optical density.

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