PHOTOCHEMICAL DEGRADATION OF CHLOROBENZENE BY PHOTO–FENTON'S REAGENT

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ABSTRACT

The photochemical degradation of chlorobenzene on titanium dioxide was carried out in the presence of Fenton's reagent and the progress of the reaction was observed spectrophotometrically. The effect of the variation of various parameters such as pH, concentration of chlorobenzene, Fe^{2+} ion concentration, amount of photocatalyst, amount of hydrogen peroxide, light intensity etc. on the photodegradation of chlorobenzene was observed. A tentative mechanism for this degradation has also been proposed.

Key words : Photochemical degradation, Fenton's reagent, Chlorobenzene, Titanium dioxide

INTRODUCTION

Fenton's reagent[1] 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. Sedlak[2] investigated the effect of $FeCl_3$, $K_3[Fe(CN_6)]$ and $Na_2[Fe(CN)_5NO]$ on photochemical reactions of H_2O_2 with benzene. Photocatalytic degradation of trinitrotoluene and trinitrobenzene influenced by H_2O_2 was observed by Dillert et al.[3].

Polszynska et al.[4] studied the reactivity of substituted benzenes towards reactive species formed in the $Fe(II)/H_2O_2$ aqueous system. Jacob et al.[5] investigated the mechanism of reaction between benzene and H_2O_2 in the presence of dioxygen with added Fe^{3+} or Cu^{2+} ions. Three reaction products phenol, 2–hydroxy–2,4–hexadiendial and 3–hydroxy–2,4–hexadiendial have been obtained. Nedoloujko and Kiwi[6] 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.[7] described the photo–Fenton reaction as an effective photochemical wastewater treatment process. Prousek et al.[8] reported the utilization of Fenton reaction for the degradation of conventionally used dyes and coloured wastewater. Prousek and Duriskova[9] 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^{3+}/H_2O_2 under visible irradiation has been observed by Wu et al.[10]. Sanchez[11] et al.[11] reported the degradation of 2,

4–dichlorophenoxy acetic acid by *in situ* photogenerated Fenton reagent. Hydroxylation of benzoic acid by H_2O_2 using the photochemical formation of Fenton's reagent intiated by 589 nm radiation and in presence of sensitized methylene blue has been reported by Lunak *et al.*[12] New evidences against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reaction has been given by Bassmann *et al.*[13]. Walling[14] reported intermediates in the reaction of Fenton's type reagents. It was observed that organic dyes were effective in degrading some of pesticides whereas iron compounds especially in combination with H_2O_2 as the oxidising agent proved to be more effective for degrading all the target pesticides. Yasmin[15] has reported photochemical degradation of phenoxy derivatives using photo–Fenton's reagent. Recently, photochemical degradation of p–dichlorobenzene by photo–Fenton's reagent hás been reported by Mogra *et al.*[16]. The present study describes the photodegradation of chlorobenzene using photo–Fenton's reagent.

EXPERIMENTAL

The photochemical degradation of chlorobenzene (Merck) was studied in the presence of titanium dioxide, Fenton's reagent and light. Stock solution of chlorobenzene (1.0×10^{-2} M) was prepared in doubly distilled water. The photochemical degradation of chlorobenzene was observed by taking 4.0×10^{-4} M of its solution, 3.2×10^{-6} M ferric ions, 0.70 mL hydrogen peroxide and 0.06 g semiconductor was added. It was irradiated with a 200 W tungsten lamp (Philips; light intensity 60.0 mWcm^{-2}). The intensity of light at various distances from the lamp was measured using solarimeter (SM CEL 201). A water filter was used to cut off thermal radiation. The pH of the solution was measured using digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductor particles and other impurities; a centrifuge (Remi 1258) was used to remove these species. A.U.V.–Visible spectrophotometer (JASCO 7800) was used to measure the optical density at regular time intervals. The progress of the reaction was observed at $\lambda_{max} = 350$ nm.

RESULTS AND DISCUSSION

An aliquot of 4.0 mL was taken out from the reaction mixture and the optical density was measured. It was observed that the optical density of the solution decreases with increasing time intervals. This indicates that the concentration of chlorobenzene decreases with increasing time of exposure. A plot of 1 + log O.D. against time was linear and follows pseudo–first order kinetics. The rate constant was measured with the expression.

$$k \quad = \quad 2.303 \times slope \qquad\qquad ....(1)$$

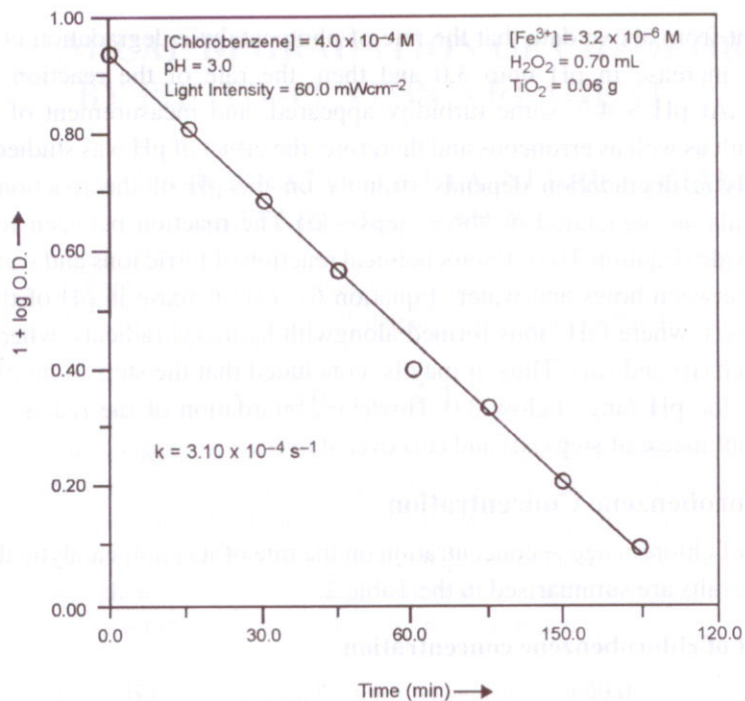The results are presented graphically shown in Figure 1.

Figure 1. A Typical Run

Effect of pH

The effect of pH on photocatalytic degradation was investigated. The results are reported in Table 1.

Table 1. Effect of pH

[Chlorobenzene]	=	4.0×10^{-4} M		[Fe³⁺]	=	3.2×10^{-6} M
TiO₂	=	0.06 g		H₂O₂	=	0.70 mL
Light Intensity	=	60.0 mWcm⁻²				

pH	$k \times 10^4$ (s⁻¹)
1.0	0.49
1.5	0.68
2.0	0.78
2.5	1.66
3.0	3.10
3.5	2.59
4.0	2.03

It is evident from above data that the rate of photocatalytic degradation of chlorobenzene increases with increase in pH upto 3.0 and then, the rate of the reaction decreases with increasing pH. At pH > 4.0, some turbidity appeared, and measurement of optical density becomes difficult as well as erroneous and therefore, the effect of pH was studied up to 4.0 only. The photocatalytic degradation depends strongly on the pH of the reaction medium. The hydroxyl radicals are generated by three steps – (i) The reaction between ferrous ions and hydrogen peroxide (Eqation 3) (ii) Photochemical reaction of ferric ions and water (Equation 2) (iii) Reaction between holes and water (Equation 6). The increase in pH of the medium will favour the step (i), where OH^- ions formed alongwith hydroxyl radicals, whereas protons are generated in step (ii) and (iii). Thus, it may be concluded that the step (i) dominates over step (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 Chlorobenzene Concentration

The effect of chlorobenzene concentration on the rate of its photocatalytic degradation was observed and results are summarised in the Table 2.

Table 2. Effect of chlorobenzene concentration

TiO_2	=	0.06 g		pH	=	3.0
Light Intensity	=	60.0 mWcm^{-2}		$[Fe^{3+}]$	=	3.2×10^{-6} M
H_2O_2	=	0.70 mL				

[Chlorobenzene] $\times 10^4$ M	$k \times 10^4$ (s^{-1})
1.0	1.20
1.5	1.27
2.0	1.39
2.5	1.72
3.0	2.02
3.5	2.76
4.0	3.10
4.5	2.92
5.0	2.70
5.5	2.42
6.0	2.18

The rate of photocatalytic degradation was found to increase with increasing concentration of chlorobenzene upto 4.0×10^{-4} M. On further increase, a sudden decrease in the rate of

degradation was observed. This may be explained on the basis that on increasing the concentration of chlorobenzene, the reaction rate increases as more molecules of chlorobenzene are available for degradation. However, on increasing the concentration above 4.0×10^{-4} M, the movement of chlorobenzene molecules towards semiconductor surface is hindered because of its larger concentration, and hence, a decrease in the rate of degradation was observed.

Effect of Ferric Ion Concentration

The effect of concentration of Fe^{3+} ions on the rate of photocatalytic degradation of chlorobenzene was observed by keeping all other factors identical. The results are summarised in Table 3.

Table 3. Effect of Fe^{3+} concentration

[Chlorobenzene]	=	4.0×10^{-4} M		H_2O_2	=	0.70 mL
pH	=	3.0		TiO_2	=	0.06 g
Light Intensity	=	60.0 mWcm^{-2}				

$[Fe^{3+}] \times 10^6$ M	$k \times 10^4$ (s^{-1})
1.2	1.00
1.6	1.42
2.0	1.96
2.4	2.44
2.8	2.75
3.2	3.10
3.6	2.99
4.0	2.66
4.4	2.31
4.8	1.95

It is clear from the data that the rate of photodegradation increases on increasing concentration of Fe^{3+} ions upto 3.2×10^{-6} M, while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the Fe^{3+} ions in the reaction mixture, the concentration of Fe^{2+} ions also increases. This is accompanied by enhanced generation of the active species OH• radicals and as a consequence, the rate of photocatalytic degradation also increases. However, on increasing the concentration of Fe^{3+} ions further, the rate of the reaction was found to decrease. This is because of the fact that the 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 of hydrogen peroxide on the photocatalytic degradation of chlorobenzene was also investigated. The results are tabulated in Table 4.

Table 4. Effect of hydrogen peroxide

[Chlorobenzene]	=	4.0×10^{-4} M		[Fe^{3+}]	=	3.2×10^{-6} M
pH	=	3.0		TiO$_2$	=	0.06 g
Light Intensity	=	$60.0 \, mWcm^{-2}$				

H$_2$O$_2$ (mL)	$k \times 10^4$ (s^{-1})
0.10	0.50
0.20	0.94
0.30	1.41
0.40	1.79
0.50	2.18
0.60	2.87
0.70	3.10
0.80	3.09
0.90	3.10
1.00	3.11
1.10	3.09

It was observed that the rate of the reaction increases as the amount of H$_2$O$_2$ was increased and it attained an optimum value at 0.70 mL. Thereafter, the rate of degradation becomes virtually constant. This saturation like behaviour 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 of semiconductor on the photocatalytic degradation of chlorobenzene was investigated. It was found that the rate of photodegradation of chlorobenzene increases with an increase in the amount of semiconductor upto 0.06 g and on further increase, the rate of reaction becomes almost constant. This may be attributed to the fact that the number of exposed
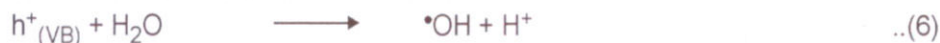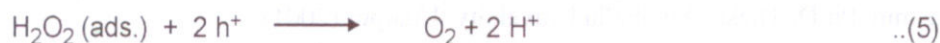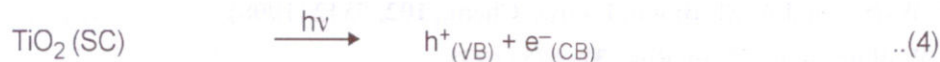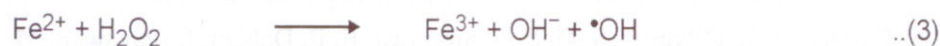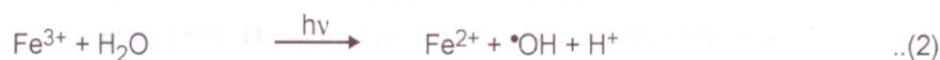
semiconducting particles will increase as the amount of semiconductor powder was increased and as a result, the number of electron–hole pairs will also increase. This will result into a corresponding increase in the rate of the reaction. On further increasing the amount of semiconductor, the number of 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 on the photocatalytic degradation of chlorobenzene was investigated. A linear behaviour 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 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 TiO_2 powder.

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH + H^+ \quad\quad ..(2)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad\quad ..(3)$$

$$TiO_2\ (SC) \xrightarrow{h\nu} h^+_{(VB)} + e^-_{(CB)} \quad\quad ..(4)$$

$$H_2O_2\ (ads.) + 2\ h^+ \longrightarrow O_2 + 2\ H^+ \quad\quad ..(5)$$

$$h^+_{(VB)} + H_2O \longrightarrow {}^{\bullet}OH + H^+ \quad\quad ..(6)$$

$$\text{(chlorobenzene)} + {}^{\bullet}OH \longrightarrow \text{Products} \quad\quad ..(7)$$

The aqueous solution of ferric ions on exposure to light dissociates water molecule into a proton and OH$^{\bullet}$ radical and is reduced to ferrous ions. These ferrous ions will decompose H_2O_2 into hydroxyl ion and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. TiO_2 on exposure generates an electron–hole pair. This hole may dissociate the H_2O_2 adsorbed on the

semiconductor surface into oxygen and proton whereas a hole may decompose water into a proton and a hydroxyl radical. The hydroxyl radical will degrade the chlorobenzene adsorbed on semiconductor surface into products. The participation of hydroxyl radicals as an active oxidising species was confirmed using hydroxyl radical scavangers, where the rate of photodegradation was drastically reduced.

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