

Determination of Reaction Rate constant for p-Chlorophenol and Nitrobenzene reacting with $\cdot\text{OH}$ during oxidation by Fe(II)/ H_2O_2 system

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Abstract: Fenton's oxidation process (using a mixture of hydrogen peroxide and ferrous ion) rapidly oxidizes these organic compounds under acidic conditions. Different molar ratios of H_2O_2 to the organic compound were used. This study describes oxidation of 4-chlorophenol and nitrobenzene, in aqueous solutions, as individual pollutant. A ratio of $[\text{H}_2\text{O}_2] / [\text{Fe}^{2+}]$ of 8.2 was kept constant for all the experiments based on typical ratios reported in literature. Maximum 99.29% degradation for p-chlorophenol and 96.32% degradation for nitrobenzene were achieved at $[\text{H}_2\text{O}_2] / [\text{organic}]$ molar ratio of 7.55 and 3.60 respectively. In this work, the experimental initial rate data is fitted to a kinetic model for determination of rate constant values between organic compound and hydroxyl radicals for individual compounds. The second order absolute rate constant for reaction between hydroxyl radical and p-chlorophenol is found to be $2.144 \times 10^6 / \text{M}\cdot\text{s}$, and the same in case of nitrobenzene is: $1.102 \times 10^6 / \text{M}\cdot\text{s}$.

Keywords: Kinetic model; Initial degradation rate; Rate constant estimation, Fenton's reaction.

1. INTRODUCTION

Chlorophenols (CP) are introduced into the environment due to several man-made activities, such as water disinfection, waste incineration and also as byproducts in the bleaching of paper pulp with chlorine¹ and have become one of the major contaminants in water and air due to their carcinogenicity and non-biodegradability.^{2,3} All chlorophenols possess bactericidal activities, phytotoxicity and have ability to bioaccumulate in organisms and these properties tend to increase with increasing chlorination.⁴ Parachlorophenol / 4-chlorophenol is a solvent for extraction of sulfur and nitrogen from coal, as an intermediate in the synthesis of dyes and drugs or solvent in the refining of oils. It is found in industrial wastewaters from oil refineries,

iron smelting, resin, manufacturing etc and it is also listed among the 65 priority pollutants by the USEPA.⁵ p-chlorophenol was therefore chosen as a model compound in this study because of its high toxicity and being largely non-biodegradable, posing serious risks to the environment.⁶

Nitrobenzene, an organic compound, consisting of a benzene ring and a 'nitro' functional group has been categorized as hazardous waste by USEPA.⁷ It is widely used in the production of products, such as dyes,⁸ explosives and pesticides⁹ and for preparation of textiles and papers. Consequently, this compound is a common water pollutant due to its presence in industrial wastewater.^{10,11} It affects the central nervous systems, causes fatigue, headache, vomiting and coma.

In this work, nitrobenzene (NB), which is also listed as a priority pollutant by USEPA was also chosen as a model pollutant.

The conventional technologies for the removal of both p-chlorophenol and nitrobenzene include biological treatment, incineration, adsorption over activated carbon, air stripping, etc.¹² Remediation of wastewaters containing these pollutants is very difficult by biological treatment because activities of microorganisms are affected by toxicity; incinerations may cause substantial emission of other hazardous compounds; adsorption or air stripping requires a post-treatment to remove the pollutants from the newly contaminated environment. Although these methods are effective, there are some difficulties in using these processes: high cost, formation of hazardous by-products and applicability to only a limited concentration range.¹³⁻¹⁵

Among the various methods available, the advanced oxidation processes (AOPs) appear to be a promising technology which have been reported to be effective at ambient condition in the degradation of wide variety of soluble organic contaminants from wastewaters.¹⁶⁻¹⁹

Fenton's oxidation, one of the AOPs that involve the generation of the highly reactive hydroxyl radical ($\bullet\text{OH}$) having stronger oxidation potential (2.80 V) than ozone (2.07 V), is of current interest for the destruction of organic pollutants in synthetic wastewaters. Fenton's reagent (hydrogen peroxide in presence of ferrous salt) involves homogenous reaction and is environmentally acceptable. The Fenton's reactions at acidic pH lead to the production of ferric ion (Fe^{3+}) and of the hydroxyl radicals ($\bullet\text{OH}$).²⁰

The thrust in study regarding oxidation of organic compounds by Fenton's reagent has mostly been on studying the effects of concentration (substrate and oxidant) and catalyst (FeSO_4) on the degradation rates. In this present work, a kinetic model from fundamentals is fitted. Reaction rate constants between individual organic compounds (B) and $\bullet\text{OH}$ are determined by fitting the model to the experimental data. Proper kinetic data would enable modeling, design and optimization of reactors for these systems. The main objective of the present work is to study the degradation kinetics of p-chlorophenol and nitrobenzene by Fenton's reaction, when they are present separately and evaluate the hitherto unreported

kinetic constants for degradation of the said organics by hydroxyl radicals.

2. MATERIALS AND METHODS

2.1. REAGENTS

P-chlorophenol and nitrobenzene (both GR grade), Hydrogen peroxide solution (50%, v/v), Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were procured from M/s Merck, India. NaOH and H_2SO_4 were used to adjust the pH of the solution. Distilled water was used for preparing aqueous solutions throughout.

2.2. EXPERIMENTAL PROCEDURE

All experiments were carried out in batch mode in beakers of 1000 ml capacity with 500 ml of pollutant solution. Appropriate amount of FeSO_4 was dissolved using part of the liquid in the beaker and then the same was transferred back to beaker. To start each experiment, appropriate amount of H_2O_2 were added into the beaker being stirred with a magnetic stirrer at a fixed high (250) rpm. Initial pH of the reaction solution was adjusted by using 1M H_2SO_4 , as and when necessary. Small volumes of samples were withdrawn at interval of 5 minutes using a pipette. 0.1 ml of 4 N NaOH per ml of sample was added to arrest the reaction and then the sample was filtered through Whatman No. 42 filter paper. The filtrate was analyzed by gas chromatography.

2.3 ANALYTICAL METHODS

pH was recorded using a digital pH meter (Model: CL-46, Toshniwal Instruments, India). P-chlorophenol and nitrobenzene concentrations were determined using a gas chromatograph (Chemito India Ltd. GC 8610 with a Chemito 10% OV17 column, 8' x 0.125") with Flame Ionization Detector (FID). Carrier gas (Nitrogen) flow was kept at 25 ml/min and the sample volume being injected was 0.5 μl . Other operating conditions were: Injector temperature 230°C, Column temperature 120-220 °C and Detector temperature 280°C. P-chlorophenol and nitrobenzene peaks were observed at a retention time of 3.8 minutes and 3.2 minutes.

3. RESULTS AND DISCUSSION

The results of two sets of experiments are presented in this section.

Table 1: Initial conditions for the degradation of p-chlorophenol (B₁) for [H₂O₂]/[Fe²⁺] molar ratio 8.2

Exp. No.	[B ₁] x 10 ⁻³ gmol/l	[H ₂ O ₂] gmol/l	[Fe ²⁺] x 10 ⁻⁴ gmol/l	R=[H ₂ O ₂] / [B ₁] mol/mol	-(d[B ₁] /dt) ₀ x 10 ⁴ (gmol/l-s)
E-1	3.889	0.0220	26.78	5.65	0.354
E-2	5.445	0.0308	37.50	5.65	0.559
E-3	7.778	0.044	53.57	5.65	1.04
E-4	3.889	0.0294	35.71	7.55	0.227
E-5	5.445	0.04116	50	7.55	0.698
E-6	7.778	0.0588	71.42	7.55	1.390

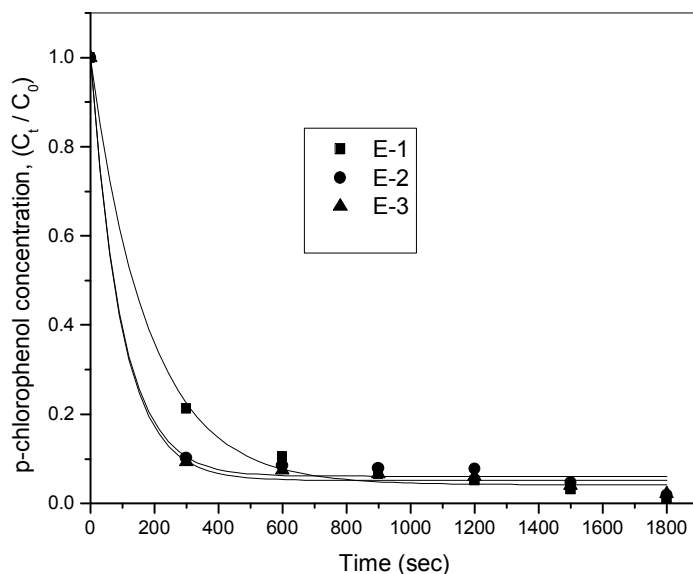
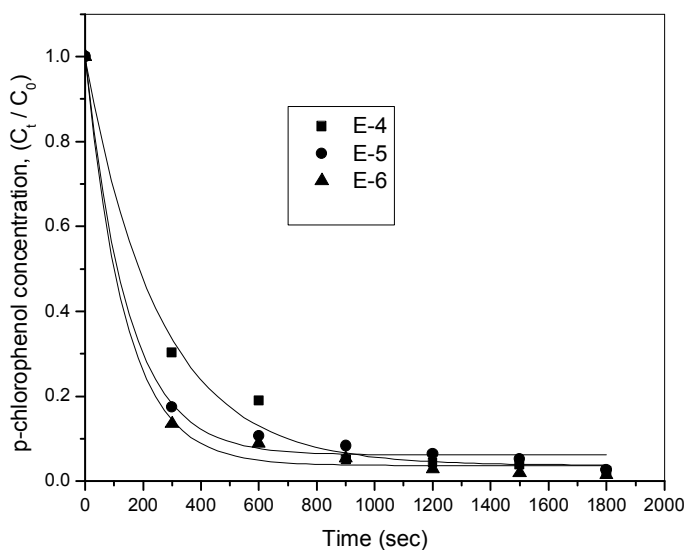
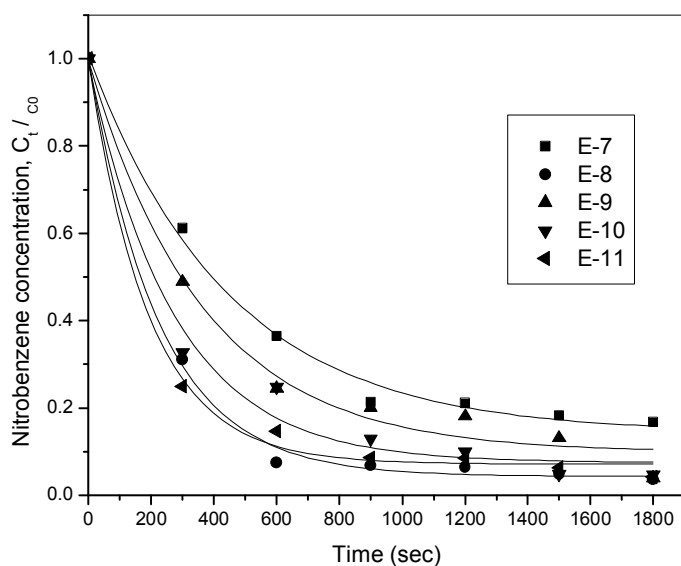
**Figure 1. Fall in p-Chlorophenol concentration with time for different initial organic concentrations and same ratio (5.65) of hydrogen peroxide to p-Chlorophenol****Figure 2. Fall in p-Chlorophenol concentration with time for different initial organic concentrations and same ratio (7.55) of hydrogen peroxide to p-Chlorophenol**

Table 2: pH of solution with time during p-chlorophenol degradation

Time (min)	E-1 pH	E-2 pH	E-3 pH	E-4 pH	E-5 pH	E-6 pH
0	3.12	3.17	3.10	3.09	2.98	2.97
5	2.92	2.81	2.75	2.80	2.76	2.62
10	2.77	2.75	2.63	2.73	2.63	2.54
15	2.56	2.71	2.61	2.68	2.60	2.52
20	2.44	2.69	2.57	2.67	2.58	2.50
25	2.41	2.64	2.56	2.66	2.57	2.49
30	2.38	2.62	2.55	2.66	2.57	2.48

Table 3: Initial conditions for the degradation of nitrobenzene (B₂) for [H₂O₂] / [Fe²⁺] molar ratio 8.2

Exp.No.	[B ₂] x 10 ⁻³ gmol/l	[H ₂ O ₂] gmol/l	[Fe ²⁺] x 10 ⁻⁴ gmol/l	[H ₂ O ₂]/[B ₂] = R mol/mol	-(d[B ₂]/dt) ₀ x 10 ⁵ (gmol/l-s)
E-7	3.25	0.0117	14.28	3.6	0.731
E-8	4.87	0.0176	21.42	3.6	1.26
E-9	3.25	0.0235	28.57	7.2	1.05
E-10	4.06	0.044	53.57	10.8	2.25
E-11	4.87	0.0529	64.28	10.8	4.63

**Figure 3. Fall in Nitrobenzene concentration with time for different initial organic concentrations****Table 4: pH of solution with time during nitrobenzene degradation**

Time(min)	E-7 pH	E-8 pH	E-9 pH	E-10 pH	E-11 pH
0	3.11	3.02	3.02	3.06	3.10
5	3.07	3.0	3.02	3.02	3.05
10	3.07	2.96	2.98	3.02	3.0
15	3.02	2.95	2.98	3.0	3.0
20	3.01	2.94	2.98	2.99	3.0
25	2.96	2.94	2.98	2.95	2.95
30	2.96	2.93	2.97	2.95	2.94

3. RESULTS AND DISCUSSION

The results of two sets of experiments are presented in this section.

3.1. DEGRADATION OF AQUEOUS p-CHLOROPHENOL

Six experiments were conducted for degradation of aqueous p-chlorophenol by varying the (1) initial concentration of organic compound (3.889×10^{-3} gmol/l to 7.778×10^{-3} gmol/l), (2) molar ratio of H_2O_2 to organic component (5.65 to 7.55). The molar ratio of H_2O_2 to Fe^{2+} was kept constant at 8.2, based on typical range of this parameter reported in literature.²¹ Initial conditions of all six experiments are summarized in Table 1. It also reports the rate of degradation of the organic compound determined from initial slope of its concentration-time profile.

Fig. 1 & 2 shows the fall in p-chlorophenol concentration (expressed as a fraction of initial concentration) with time. The change in pH of solution with time is presented in Table 2.

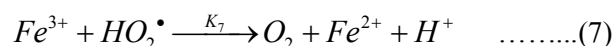
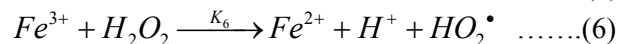
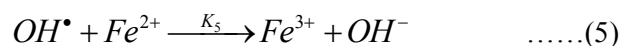
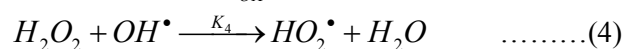
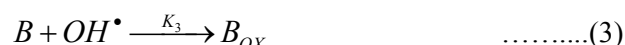
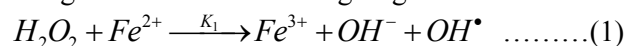
3.2. DEGRADATION OF NITROBENZENE

Five experiments were conducted for degradation of aqueous nitrobenzene by varying the (1) initial concentration of organic species (3.25×10^{-3} gmol/l to 4.87×10^{-3} gmol/l), (2) molar ratio of H_2O_2 to organic component (3.6 to 10.8). Molar ratios of H_2O_2 to Fe^{2+} in these experiments were kept constant. Initial conditions of all five experiments are presented in Table 3 along with the rate of degradation of the organic compound determined from initial slope of its concentration-time profile.

Fig. 3 shows the fall in concentration of nitrobenzene (expressed as a fraction of initial concentration), with time and the change in pH of solution with time is presented in Table 4.

3.3. KINETIC MODELING

The oxidation mechanism of organic compound in a single step mineralization by Fenton's reagent is thought to occur in following stages.²²



3.4. RATE CONSTANT DETERMINATION

As it is observed, $\bullet OH$ are generated or consumed in equations (1), (3), (4) and (5). Therefore, the net rate of generation can be expressed as follows:

$$\frac{d[\bullet OH]}{dt} = k_1[H_2O_2][Fe^{2+}] - k_3[B][\bullet OH] - k_4[H_2O_2][OH] - k_5[\bullet OH][Fe^{2+}] \quad \dots\dots(8)$$

Considering the concentration of the highly reactive $\bullet OH$ radical remains stationary, the left hand side of Equation (7) is 'zero'. Rearrangement of the terms of Equation (8) gives the concentration of hydroxyl radicals.

$$[\bullet OH] = \frac{k_1[H_2O_2][Fe^{2+}]}{k_3[B] + k_4[H_2O_2] + k_5[Fe^{2+}]} \quad \dots\dots(9)$$

As the organic compound is degraded by reactions (2) and (3), the rate of degradation of organic compound (B) may be expressed as

$$-\frac{d[B]}{dt} = k_2[B][H_2O_2] + k_3[B][\bullet OH] \quad \dots\dots(10)$$

On substitution the expression for $\bullet OH$ radicals in equation (9), it becomes

$$-\frac{d[B]}{dt} = k_2[B][H_2O_2] + k_3[B] \frac{k_1[H_2O_2][Fe^{2+}]}{k_3[B] + k_4[H_2O_2] + k_5[Fe^{2+}]} \quad \dots\dots(11)$$

This is the rate expression for the oxidation of organic compound which includes five reaction rate constants. Experiments with only H_2O_2 were conducted. Practically no degradation of the organic species was observed in presence of H_2O_2 alone. So k_2 was considered negligible in this model. Among the other rate constants, the literature²³⁻²⁵ reported value of rate constant k_1 is $76 /M\cdot s$, k_4 is ($3 \times 10^7 /M\cdot s$) and the k_5 value is ($3 \times 10^8 /M\cdot s$). Our present study aims at evaluation of the rate constants (k_3) for the organic compounds and hydroxyl radicals.

Eq. (11) is rewritten in the form

$$\left(-\frac{d[B]}{dt}\right)_0 = \frac{k_1 k_3 [B]_0 [H_2O_2]_0 [Fe^{2+}]_0}{k_3 [B]_0 + k_4 R [B]_0 + k_5 [Fe^{2+}]_0} \quad \dots\dots(12)$$

Where R is the ratio $[H_2O_2]_0 / [B]_0$

The rate constant k_3 for the two compounds were determined by minimizing the sum of square of deviation of the experimental initial rate and the model

predicted rate for all the experiments in Table 1 for p-chlorophenol and in table 3 for nitrobenzene respectively.

MATLAB routine 'LSQNONLIN' was used to solve this non-linear least square fitting problem. Fig. 4 & 5

shows the experimental and model predicted initial degradation rate for p-chlorophenol and nitrobenzene respectively. Average % deviation is below +/- 15% as evidenced by the error limit lines of Fig. 4 & 5.

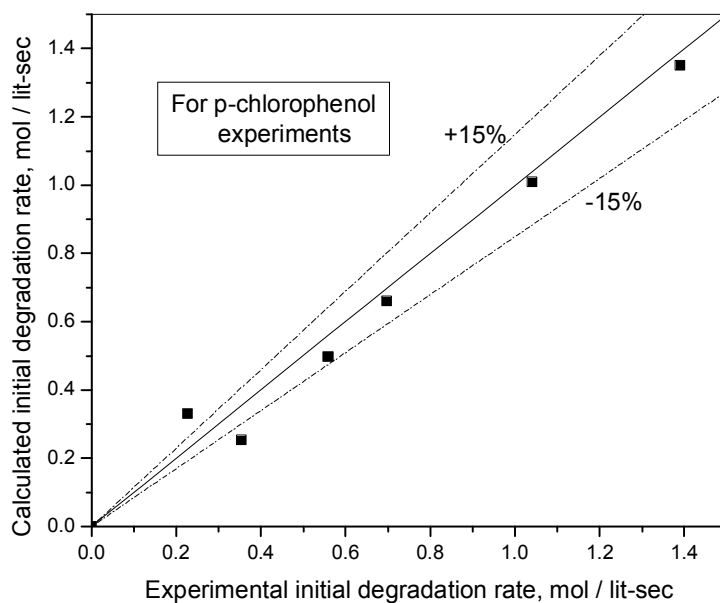


Figure 4. Experimental and model predicted initial degradation rate for p- chlorophenol

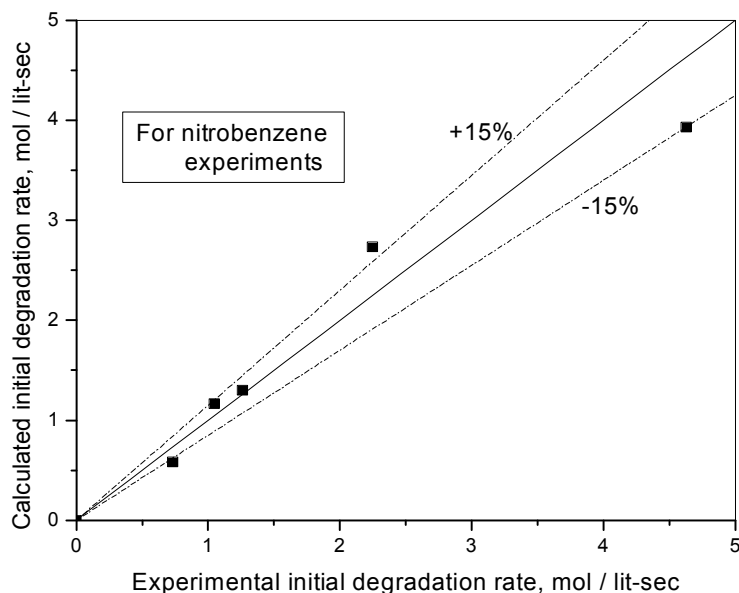


Figure 5. Experimental and model predicted initial degradation rate for nitrobenzene

4. CONCLUSION

The results obtained in this work demonstrate that aqueous solutions containing p-chlorophenol or nitrobenzene can be effectively degraded by Fenton oxidation process. The reasonably high values of rate constants for reaction of $\cdot\text{OH}$ with p-chlorophenol (2.144×10^6 /M-s) and with nitrobenzene (1.102×10^6 /M-s) suggest Fenton's reaction to be a fast and efficient method for degrading these organic pollutants in low concentration. Experimental results show

reduction of p-chlorophenol concentration from 7.77×10^{-3} gmol/l to 1.232×10^{-3} gmol/l and concentration of nitrobenzene falling from 4.87×10^{-3} gmol/l to 0.179×10^{-4} gmol/l within half an hour. Good fit of the experimental results and the theoretical model justifies the assumption that degradation of organics by H_2O_2 is negligible compared to the same by $\cdot\text{OH}$ during Fenton's process. The kinetic study indicated that the degradation of these compounds followed the second order kinetics.

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