International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 3 Issue 6, June - 2014

Reaction Rate Constants for Hydrogen Peroxide Oxidation of Phenol and Chlorinated Phenols in a Continuous Stirred Tank Reactor

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***Abstract*-The degradations of phenolic compounds were investigated so far using laboratory scale batch reactors but in the present study, a bench scale continuous stirred tank reactor (CSTR) was used for experiencing the effects of different process parameters like substrate and oxidant concentrations, pH and temperature effects on the degradation rate of phenol as well as 2- and 4-chlorophenols. Experimental results were analyzed to determine oxidation rate constants for substrates mentioned. Oxidation rate constants for phenol, 2-chlorophenol and 4-chlorophenol were found 1.18 × 10^{-6}, 1.35 × 10^{-6} and 1.49 × 10^{-6} m^3 $gmol^{-1}$ s^{-1}, respectively. These results were supported by conversion of individual substrates with the order of 4-chlorophenol > 2-chlorophenol > phenol. Substrate mineralization was found negligible indicating formation of reaction intermediates.**

Key words: conversion, mineralization, phenol, 2-chlorophenol, 4-chlorophenol, H_2O_2 oxidation

1 INTRODUCTION

Oxidation processes remain attractive prospects for wastewater treatment and have become the subject of intense research. Hydrogen peroxide (standard oxidation potential 1.80 V and 0.87 V at pH 0 and 14, respectively) is a strong oxidizing agent which has been used commercially as oxidant, bleaching agent and disinfectant for purification of industrial wastewater, potable water and contaminated groundwater. A number of researchers reported the application of H_2O_2 for the treatment of wastewater. In most of the advanced oxidation processes hydrogen peroxide is the basic oxidizing agent and therefore the base level study of hydrogen peroxide oxidation either alone or with catalyst are important.

Eckenfelder et al. [1] investigated on the oxidation of nitrobenzene, aniline, cresols and monochlorophenols using H_2O_2 as oxidant. They reported that oxidation by H_2O_2 alone was not effective at high concentrations of certain refractory contaminants; such as highly chlorinated aromatic compounds. It was established [2] that perhydroxyl anion (OOH^-) was the active species responsible for the oxidizing property of H_2O_2. They also reported that H_2O_2 oxidation of dilute solutions of wastes containing organic compounds might result in lowering of initial concentration of the pollutant, but substantial reduction of COD required high dosage of H_2O_2 and extended contact time. De et al. [3] reported on the factors affecting H_2O_2 oxidation such as pH, temperature, contact time etc to catechol, phenol and chlorophenol in laboratory scale batch set-up. Cheng and Guo [4] reported that the rate constant for the H_2O_2 oxidation of methyl red intermediate product was 7.44×10^{-4} mol L^{-1} s^{-1}. Goi et al. [5] reported that H_2O_2 treatment was able to remediate chlorophenols, polycyclic aromatic hydrocarbons, diesel and transformer oil contaminated soil at natural soil pH. Cheneviere et al. [6] studied the oxidation reaction of various substituted phenols and reported that product yields depend on the conditions of reaction medium. Gao [7] reported that H_2O_2 alone was not capable of degrading Orange-II dye significantly.

From literature it is revealed that significant parts of studies were made on the degradation of phenol and chlorinated phenols using laboratory scale batch reactors. Again, most of those studies are without estimation of reaction rate constants. Our study was conducted in a bench scale continuous stirred tank reactor (CSTR) for characterizing the effects of different process parameters on the degradation rate of phenol and 2- and 4-chlorophenols. These experimental results have also been analyzed to estimate the reaction rate constants for the oxidation process.

2 EXPERIMENTAL SET UP AND ANALYTICAL PROCEDURE

A stainless steel CSTR with an overall capacity of 0.18 m^3 was used for conducting all the experiments and the same is shown in Fig.1. Outlet port of the reactor was fabricated so as to attain the reactor operating volume of maximum 0.12 m^3. Substrates solution prepared at desired concentrations were placed in a separate storage tank and pumped to the reactor through a rotameter maintaining constant flow rate of 0.002 m^3 per minute (2 lpm). H_2O_2 (30%) solution was continuously introduced into the CSTR by a separate feed line. Reaction mixture in the CSTR was continuously stirred mechanically using an agitator. A digital pH meter was also used for noting pH of the reaction mixture. A thermometer was also placed in the solution for recording the reaction temperature. Reaction samples were withdrawn at different time intervals preferably after 5, 15, 30 and 60 minutes but average residence time of substrates solutions in the CSTR was maintained 60 min. Oxidation experiments were conducted with varied substrate concentrations [100 to 1000 mg/L for phenol, 50 to 1000 mg/L for 2-chlorophenol and 60 to 1000 mg/L for 4-chlorophenol]. The concentration of H_2O_2 on the other hand, was varied between 600 and 30000 mg/L. Reproducibility of results were ascertained by repeating the same experiment twice and excellent match (within ±3%) in results of successive experiments was obtained.

Chemical used for the study were: A.R grade phenol (Loba Chemie), 2- and 4-chlorophenols (Loba Chemie), hydrogen peroxide (MERCK), 4-aminoantipyrene (Aldrich Chemie), potassium dichromate, potassium Ferro cyanide and ceric sulfate.

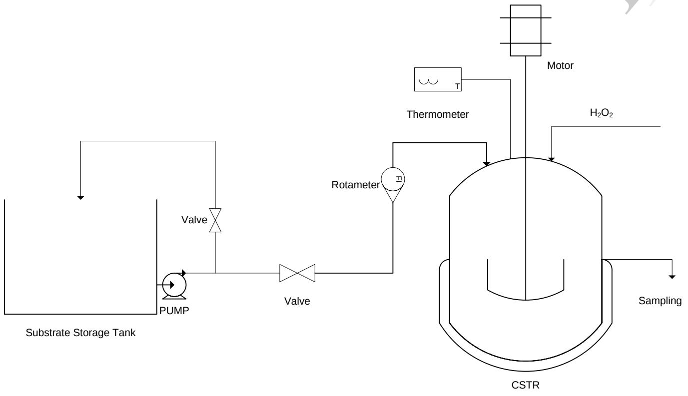

Fig. 1. Schematic of the experimental set up

Concentrations of the substrates present in the reaction mixture were estimated following the Standard Methods [8] by scanning simultaneously at wavelengths corresponding to the maximum absorption of the colored complex for each individual compound in a Shimadzu (UV-160A) spectrophotometer. Interference of H_2O_2 during estimation was also studied. Absorbance of hydrogen peroxide solution at 500 nm and 510 nm were measured and found that the absorbance of H_2O_2 was close to zero for H_2O_2 concentration below 500 mg/L. Therefore, the reaction mixtures were diluted in such a way that concentration of hydrogen peroxide dropped down below 500 mg/L of H_2O_2 during analysis of sample. Hydrogen peroxide remaining in the final solution was measured by using ceric sulfate method [9]. Mineralizations of substrates were measured by determining Chemical oxygen demands (COD) of the initial substrate solution and the final solution as per the Standard Methods [8].

3 RESULTS AND DISCUSSION

3.1 Effect of reaction time, initial substrates and hydrogen peroxide concentration on conversion

In each experimental run of average 1 hour duration, it was observed that for all substrates conversion increased initially very rapidly within 15 minutes and thereafter improvement in conversion achieved poorly. It was perhaps due to a sudden substantial drop in the concentration within 15 minutes of adding H_2O_2 to the aqueous solutions [10]. The effect of reaction time on the conversion of substrates for different experiments is shown in Fig.2.

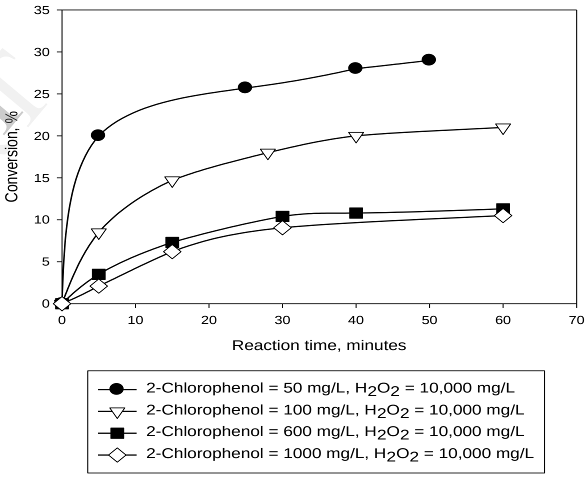

Fig.2.Effect of initial substrate (2-chlorophenol) concentration on conversion at constant concentration of H_2O_2

Based on average residence time of reaction (1 h) mixture in the CSTR, the effects of initial substrate concentration on the conversion of phenol, 2- and 4-chlorophenols were studied and result of set of reaction is shown in Fig.3 when concentration of H_2O_2 remained constant. It can be seen from the figure that the conversion was decreased with the increase in initial substrate concentration. If concentration of available reactive oxidizing agent (H_2O_2) for degradation remains constant, availability of oxidative species per mole of substrate would be lesser in the case of higher substrate concentration and therefore, percent conversion will be lesser.

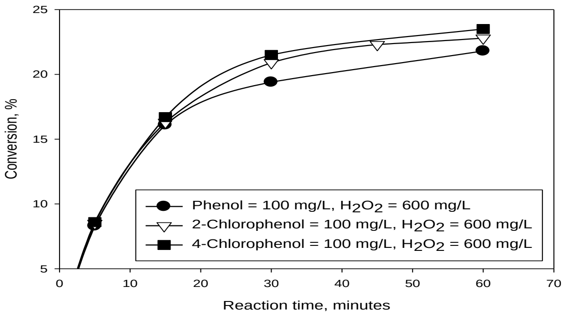

Fig.3. Conversion of phenol, 2-chlorophenol and 4-chlorophenol by H_2O_2 at constant substrate to H_2O_2 mole ratio; a comparison.

The effect of initial H_2O_2 concentration which is the source of supplying the reactive oxidizing species, on the conversion of substrates at constant initial substrate concentration is shown in Fig.4. It was observed that H_2O_2 had played a vital role on the level of degradation of substrates. As the concentration of reactive oxidizing species was increased (increase in H_2O_2 concentration), the conversion of all three substrates were increased.

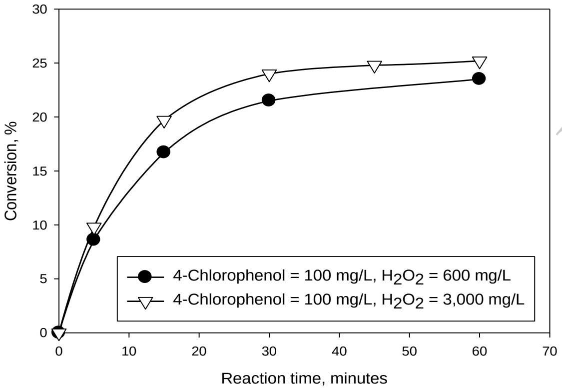

Fig.4. Effect of initial H_2O_2 concentration on conversion at constant concentration of substrate (4-chlorophenol)

3.2 Effect of solution pH and reaction temperature on substrates conversion

In general, when there was no control on reaction pH, it was observed that in all cases of studies pH of the reaction mixture were dropped substantially to acidic range and finally reached a constant value almost after 20 minutes [10]. This observation supports the observation made by Pintar and Levec [11] where they have reported formation of oxygenated intermediates such as p-benzoquinone, 1,2-benzenediole, 1,4-benzenediole during liquid phase oxidation of phenol and chlorophenol by molecular oxygen.

Experiments were carried out at different pH, particularly in the acidic range to observe oxidation rates of substrates. The acidity of the reaction medium was monitored continuously to keep the pH constant at a desired level throughout the experimentation. The effect of pH of the reaction medium on the conversion is shown in Fig.5.

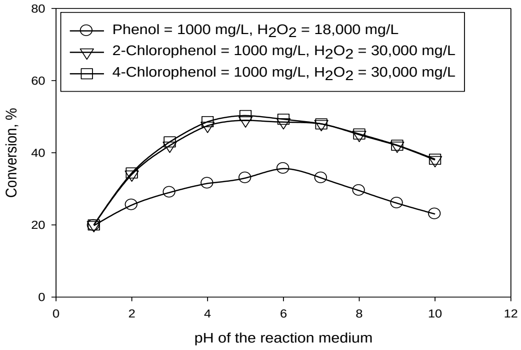

Fig.5. Effect of controlled reaction medium pH in the reactor on conversion of phenol, 2-chlorophenol and 4-chlorophenol, after 60 minutes of residence time.

Effect of temperature on conversion of substrates was studied by maintaining constant temperature of the mixture using constant bath. In general, it was observed that there is no change in temperature of the reaction mixture during reaction. But in the study, we carried out experiments at elevated temperatures, to observe whether there is any change in oxidation rates. From experimental results (Fig.6), it was observed that at high temperature oxidation rates decreased. This might be due to decomposition of hydrogen peroxide, at elevated temperature, into molecular oxygen instead of forming reactive hydroxyl radicals and/or perhydroxyl ions. In fact, from experimental run, we observe optimum conversion at about 303 K.

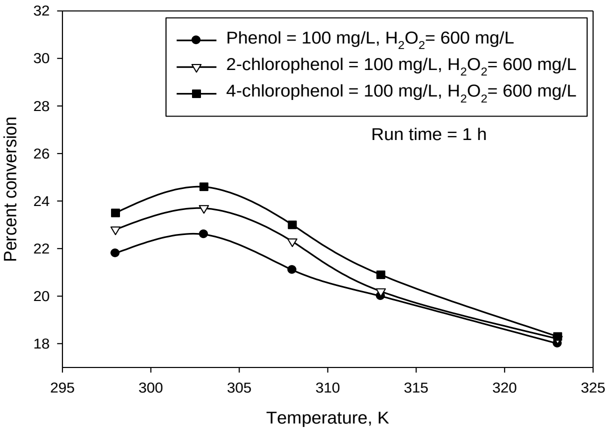

Fig.6. Effect of reaction medium temperature on conversion of phenol, 2-chlorophenol and 4-chlorophenol, after 60 minutes of experimental run.

3.3 Mineralization of substrates

A few samples were analyzed for observation of complete oxidation of substrates to carbon dioxide and water (and acids for chlorophenols). It was done by COD analysis following standard methods [10]. From analysis of results (Table 1), it was observed that mineralization was not complete supporting formation of stable oxygenated reaction products which are refractory to further oxidation by H_2O_2 only.

Table 1. Mineralization of phenol, 2-chlorophenol and 4-chlorophenol when treated with hydrogen peroxide (at different time intervals and 303 K).

Substrate 100 mg/L	Initial H_2O_2 conc. mg/L	COD Reduction, %				
		Time, min				
		5	15	30	60	90
Phenol	1200	5.10	7.20	8.60	9.44	9.77
2-chlorophenol		6.52	8.67	9.21	9.61	9.80
4-chlorophenol		6.58	8.76	9.40	9.92	10.1

3.4 Reaction rates and rate constants

Long days back, oxidizing characteristics particularly, dissociation constant of hydrogen peroxide and reaction with donor particles were investigated [12, 13]. Adewuyl and Carmichael [14] reported that whether the reactive species is $^{\bullet}OH$ radical or HOO^{-} ion, the rate of addition of these species to the aromatic ring depends on the stabilization of σ-complex or benzonium carbanion formed during transformation. They observed that the kinetics of carbondisulfide oxidation using H_2O_2 with respect to both substrate and H_2O_2 was first order. H_2O_2 was used to degrade 2,4-dichlorophenoxyacetic acid of initial concentration of 100 mg L^{-1} by Badellino et al. [15] and reported that H_2O_2 the substrate showing a first order reaction kinetics. The value of the reported rate constant was 0.9 to 6.3×10^{-5} $m^3 gmole^{-1} s^{-1}$.

Following reported informations, overall rate of degradation of substrate in solution could be represented as:

$$-\frac{dC_S}{dt} = kC_S C_{H_2O_2} \qquad (1)$$

Equation (1) is analyzed further considering initial rate of reaction, in order to estimate the rate constant ‘k’ using experimental data sets obtained from the continuous stirred tank reactor (CSTR). From data analysis, it was observed that at 303 K ($30^{O}C$) reaction temperature, rate constants are as follows:

Table 2. Oxidation rate constants of phenol, 2-chlorophenol and 4-chlorohenol when reacted with hydrogen peroxide at 303 K.

Substrate	**Rate constant, k (m^3 $gmol^{-1}$ s^{-1})**
Phenol	1.18×10^{-6}
2-chlorophenol	1.35×10^{-6}
4-chlorophenol	1.49×10^{-6}

Though the halide group present in 2-chlorophenol and 4-chlorophenol at the ortho and the para position of -OH group, respectively, it deactivates the benzene ring and retards the initial attack but the activation effect of -OH group and the resonance effect (two canonical forms of resonance hybrid) due to the presence of -OH and -Cl groups at the ortho and para position counterbalances the deactivation of the benzene ring and for the reason conversion of 2-chlorophenol as well as 4-chlorophenol were found higher than that of phenol. In case of phenol on the other hand, owing to the presence of only one group (-OH group) the σ-complex is much less stable through resonance. Therefore, the conversion of the phenolic substrates was expected in the order: chlorophenols > phenol which confirms the estimation of reaction rate constant determined on the basis of our experimental results. Between two chlorophenols, the conversion of 4-chlorophenol was more pronounced compared to the ortho isomer. This might be due to the para position of the two substituted groups (-OH and –Cl) in the benzene ring.

4 CONCLUSIONS

Oxidation of phenol and two chlorophenols are function of substrate concentration as well as concentration of oxidant (hydrogen peroxide). Control of solution pH showed optimum conversion if pH maintained in the acidic range. Rate of oxidation is also depends on temperature of reaction mixture. At higher temperature rate of reaction is lower. Mineralization of substrates was found negligible indicating formation of refractory reaction intermediate when degraded using only hydrogen peroxide as oxidant.

Oxidation rate constant for degradation of substrates by using hydrogen peroxide solution (30%) was calculated by analyzing the data obtained during study of the reaction in the CSTR. It was observed that reaction rates constant for chlorophenols are higher than that of phenol. Between 2- and 4-chlorophenol, oxidation rate constant for 4-chlorophenol is higher than that of 2-chlorophenol.

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