Oxidation kinetics of phenol and chlorinated phenols with hydrogen peroxide in a continuous stirred tank reactor

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Abstract- **The degradation of phenolic compounds via hydrogen peroxide (H_2O_2) was investigated using laboratory scale batch reactors. A bench scale continuously stirred tank reactor (CSTR) was used for characterizing the effects of varying experimental concentrations on the degradation rate of phenol as well as 2- and 4-chlorophenols. Results showed that the conversion attained within 15 minutes of reaction accounted for approximately 90% of the total conversion. The drops in pH for phenol, 2-chlorophenol and 4-chlorophenol were 6.6 to 6.38, 5.8 to 4.45 and 5.7 to 4.40 respectively. Concentration of H_2O_2 measured at different time intervals remained almost constant during reaction. The optimum conversion of substrates could be achieved by maintaining pH at 6.0, 4.55 and 4.5 for phenol, 2-chlorophenol and 4-chlorophenol, respectively. The conversion was amplified with increasing initial concentration of substrates and this phenomenon was observed only when the substrate to H_2O_2 molar ratio was kept constant. The total conversion under similar reaction conditions was comparable for all three substrates. Though the conversion was in the order of 4-chlorophenol > 2-chlorophenol > phenol, the conversion varied only within ±30% for substrate initial concentration of 500 mg/L. The pH after degradation was such that it did not require neutralization for its disposal in any body of water.**

Keywords- Conversion; COD; Phenol; 2-chlorophenol; 4-chlorophenol; H_2O_2 Oxidation

I. INTRODUCTION

Most wastewater produced by chemical processing industries contains high concentrations of organic materials that may be difficult to oxidize biologically. Phenol, catechol, chlorophenol and a number of substituted phenolic compounds which are commonly found in industrial wastewater, are toxic to life, hazardous to the environment, and give a disagreeable taste and odor to water, particularly after chlorination.

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 an oxidant, a bleaching agent, and a disinfectant for purification of industrial wastewater, potable water and contaminated groundwater. A number of researchers have reported the application of H_2O_2 for the treatment of various inorganic and organic pollutants (Table 1). It is also useful in the treatment of gaseous pollutants such as sulfur oxides and nitrogen oxides by conversion to the corresponding acids. Hydrogen peroxide does not contain metals or halogens that can lead to undesirable by-products during the organic oxidation process. There are additional advantages of using hydrogen peroxide over ozone for a chemical oxidant. Hydrogen peroxide has infinite solubility in water (as a result, unlike ozone, mass transfer problems are not encountered during the oxidation process), unlimited dosing capability, and it can be easily stored and is readily available. In most advanced oxidation processes, hydrogen peroxide is the basic oxidizing agent. Therefore, the base level study of hydrogen peroxide decolorization rates of organic pollutants is important.

TABLE 1 APPLICATIONS OF H_2O_2 IN DIFFERENT PROCESSES

Application	Main Industries	Problems solved by H_2O_2
Removal of nitrite (NO_2^{-1})	Hardening shops, metal surface treatment, plating shops	High oxygen demand, nitros-amine formation
Removal of cyanide (CN^{-1})	Hardening shops, mining, plating shops, coking plants, waste incinerator plants, steel mills, pyrolysis plants	Extreme toxicity
Removal of sulfide (S^{-2})	Leather producers, textile mills, tanneries, refineries, metallargical processes	Toxicity, odors, oxygen demand
Removal of NOx	Power plants, nitric acid users and producers	Toxicity, acid rain
Removal of chlorine (Cl_2)	Chlorine producers and processors	Toxicity
Removal of hypochlorite (OCl^{-1})	Wastewater treatment, chlorine producers and processors	Fish toxicity, corrosion, formation of chlorinated compounds
Oxygen supply	Sewage treatment, food processing plants	Biological waste Treatment
Aseptic packaging	Food processing plants	Producing and Maintaining sterile Conditions
De-Inking (recycling of waste paper)	Recycling mills	Yellow and low brightness of recycled pulp

Replacement of Cl_2 and ClO_2 in pulp bleaching	Pulp and paper mills	Chlorinated compounds in effluents, low brightness, long bleaching sequences
Removal of fat, oil, grease and suspended solids	Food processing, pulp and paper mills, textile mills	Meeting COD, BOD and other discharge limits
Removal of formaldehyde	HCHO processing, resin plants, disinfection etc.	Toxicity
Removal of phenols	Refinireis, coke and gas plants, resin plants, disinfection operation, aviation	Toxicity
Odor and corrosion control	Sewage treatment, pulp and paper mills, textile mills, food processing plants	Health hazards (H_2S), concrete deterioration
Treatment of photoprocessing effluents	Film and paper (copy) processes	High oxygen demand, silver loss

A few studies very similar to oxidation of phenolic compounds by utilizing hydrogen peroxide as oxidant are tabulated and their major findings are given in the Table 2 below:

TABLE 2 OXIDATION OF ORGANIC SUBSTRATES BY USING H_2O_2 AS OXIDANT

Reference	Study	Principal observation
Adewuyl and Carmichael [1]	Carbondisulfide oxidation using H_2O_2	The degradation kinetics with respect to both substrate and H_2O_2 is first order
Glaze and Kang [2]; and Aieta et.al.[3]	Chlorinated alkanes, carboxylic acids and polynuclear aromatic hydrocarbons oxidation by H_2O_2.	Refractory to oxidation by H_2O_2
Eckenfelder et al. [4]	Oxidation of nitrobenzene, aniline, cresols and monochlorophenols using H_2O_2 as oxidant.	Oxidation by H_2O_2 alone was not effective at high concentrations of certain refractory contaminants
Venkatadri and Peters [5]	H_2O_2 oxidation of dilute solutions of wastes containing organic compounds	Perhydroxyl anion (OOH^-) is the active species responsible for the oxidizing property of H_2O_2.
De et al. [6]	Oxidation of catechol, phenol and chlorophenol in laboratory scale set-up by H_2O_2	pH, temperature, contact time etc affect the rate of conversion.
Badellino et al. [7]	Electrogenerated H_2O_2 was used to degrade 2,4-dichlorophenoxyacetic acid	First order reaction kinetics
Min et al. [8]	degradation of 4-aminophenol using H_2O_2 as oxidizer	There is an optimum condition for efficient degradation
Shokrolahi et al. [9]	treated tertiary amines and secondary alcohols to the respective oxides by using 30% H_2O_2	Found excellent yield.
Madeira et al. [10]	Dibenzothiophenes (DBT) were treated using different molar ratio of DBT to H_2O_2	At molar ratio of 1:20 with stepwise addition of H_2O_2 produced best results for removal of DBT.
Matta et al. [11]	Oxidation of phenol by H_2O_2	Produced catechol and hydroquinone as two intermediate reaction products.
Li and Gao [12]	Degradation of Orange-II dye	H_2O_2 alone was not capable of degrading the substrate significantly.

Critical appraisal of the existing literature therefore revealed that the investigations carried out on the degradation of phenolic compounds used laboratory scale batch reactors. Furthermore, these studies were not efficient for large scale application. In the present study, a bench scale continuously stirred tank reactor (CSTR) was used for characterizing the kinetics of degradation of phenol and 2- and 4-chlorophenols.

II. EXPERIMENTAL PROCEDURE

A. Materials

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 were used in the study. Distilled water was used for preparing aqueous solutions of phenol and phenol derivatives in all experiments.

B. Experimental set up and Procedure

A CSTR of stainless steel with an overall capacity of 0.2 m^3 was used for conducting the experiments (Fig. 1). The outlet port of the reactor was fabricated so to attain the reactor operating volume of 0.12 m^3. Phenolic solutions prepared at desired concentrations were placed in a separate storage tank and were fed to the reactor at a constant flow rate of 0.12 m^3/h. Provision was made at the inlet of the CSTR for introducing H_2O_2 (30%) continuously to the substrate solutions. The solution in the CSTR was continuously stirred mechanically using an agitator. Average residence time of substrates solutions in the CSTR was maintained for 60 minutes. A digital pH meter was used for recording pH of the reaction mixture at different time intervals. A thermometer was also placed in the solution for recording the reaction temperature. 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 (the range starts from nearly stoichiometric amount of hydrogen peroxide to some higher values required for complete oxidation of substrates). Samples were drawn periodically to estimate the concentration of substrates in the reaction mixture.
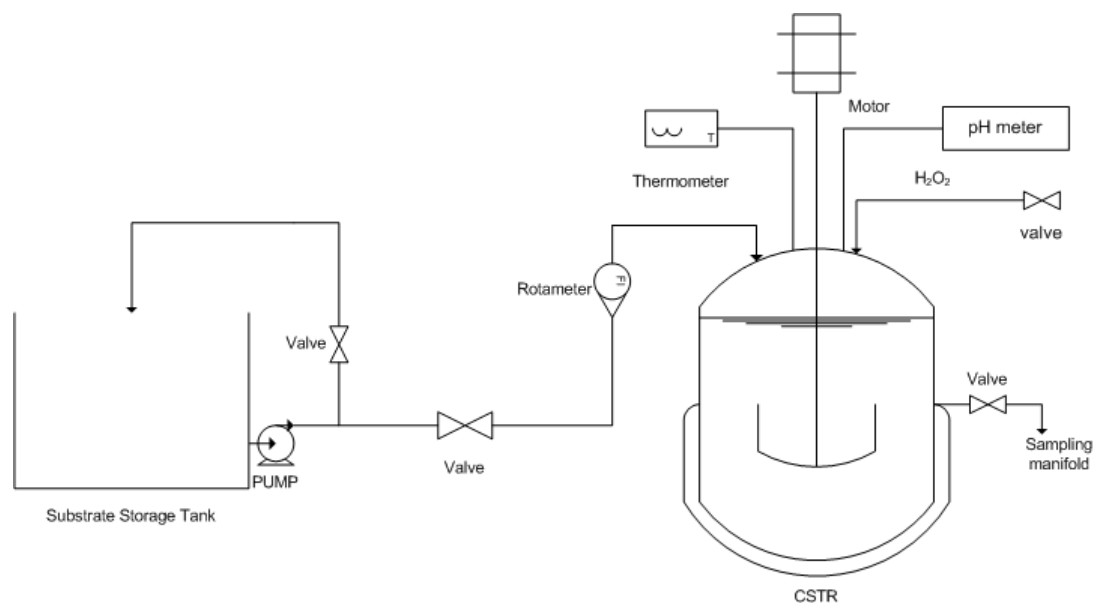

Fig. 1 Schematic of the experimental set up

C. Analytical Procedure

Concentrations of the phenolic compounds (substrates) present in the reaction mixture were estimated as per the Standard Methods [13] by scanning simultaneously at wavelengths corresponding to the maximum absorption of the colored complex for each individual compound in a Shimadzu (UV-160A) spectrophotometer. To ascertain that the H_2O_2 did not interfere with the estimation process, absorbance at 500 nm and 510 nm for different H_2O_2 concentrations were measured to confirm 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 below 500 mg/L of H_2O_2 during analysis of intermediate reaction samples. Hydrogen peroxide remaining in the final solution was measured by using ceric sulfate method [14]. Chemical oxygen demands (COD) of the initial substrate solution and the final solution were estimated following APHA Methods [13]. The standard method of determining the COD however, is briefly described here for our better understanding. In its determination, the organic matter is oxidized completely by $K_2Cr_2O_7$ in the presence of H_2SO_4 to produce CO_2 and H_2O. The excess $K_2Cr_2O_7$ remaining after the reaction carried out by digesting (refluxing) the reaction mixture for 2 hrs is titrated with $Fe(NH_4)_2(SO_4)_2$ using ferroin as an indicator to obtain a wine red color at the end point. The amount of dichromate consumed in this reaction gives the O_2 required for oxidation of organic matter from which the COD was determined and reported.

Conversion of any substrate is defined as the ratio of difference in initial and final concentration of the substrate divided by initial concentration of the substrate. Thus, conversion is only associated with the concentration of substrate during reaction.

It is reported and proved that during oxidation of any substrate by hydrogen peroxide, a number of intermediate reaction products could be formed. These reaction intermediates themselves are oxygen demanding and may be considered pollutants. Therefore, considering environmental aspects, these intermediates should be further converted to ultimate products. Mineralization of any substrate means converting the substrate and its intermediate reaction products to ultimately benign forms of carbon dioxide and water. Mineralization is measured in terms of COD (Chemical Oxygen Demand) or TOC (Total Organic Carbon).

D. Statistical Analysis

Five samples were taken at uniform time intervals for each set of experiments to study the kinetics and other associated parameters. The average of these five values was used for the purpose of data analysis. Reproducibility of results was ascertained by repeating the same experiment twice and an excellent match (within ±3%) in results of successive experiments was obtained.

III. RESULTS AND DISCUSSION

The kinetics of the oxidative degradation of phenol, 2-chlorophenol and 4-chlorophenol with H_2O_2 after varying initial substrate concentration, initial H_2O_2 concentration, substrate to H_2O_2 molar ratio (R) and reaction temperature on the degradation kinetics were investigated.

A. Effect of Reaction Time on Conversion

The effects of reaction time on the conversion of phenolic compounds for different experiments are shown in Fig. 2 through Fig. 4. It can be seen from these figures that the conversion increased very quickly within 15 minutes (ca.) and thereafter remained almost constant. In an aqueous solution, H_2O_2 dissociates to form the nucleophile HOO^- ion and $^\bullet OH$ free radicals which break the benzene rings of the phenolic substrates and undergo substitution reactions to form oxygenated intermediates. In phenol, the presence of -OH group activates the o- and p- positions in the ring making it susceptible to attack by the nucleophile HOO^- or $^\bullet OH$ radical. In 2-chlorophenol, the -Cl and -OH groups are both ortho- and para- orienting, but since the predominating group is -OH the substitution will depend on the orienting power of -OH group. At the same time, due to the presence of more electronegative -Cl group (-I effect) nucleophilic attack will be more rapid. Therefore, 2-chlorophenol will undergo nucleophilic transformation faster than phenol. Between 2- and 4-chlorophenols, 4-chlorophenol showed relatively better degradation than 2-chlorophenol, possibly due to ease of substitution and elimination reactions of 4-chlorophenol with $^\bullet OH$ and other reactive free radicals.
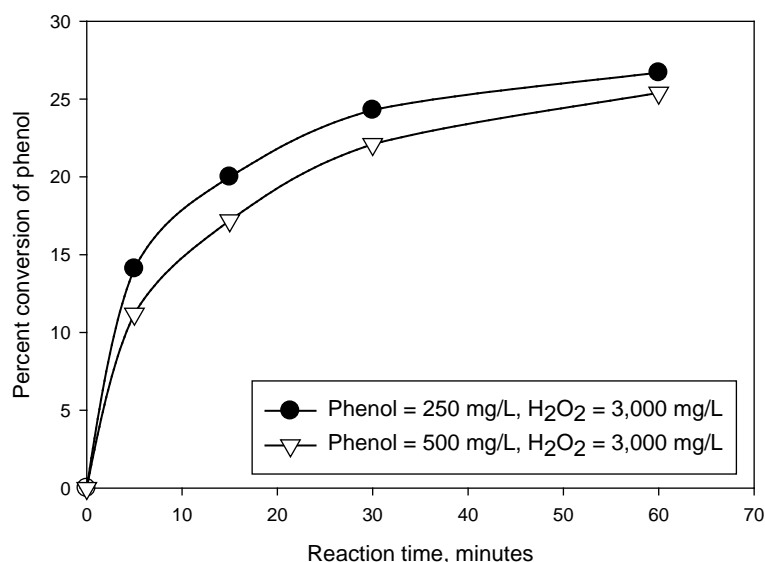

Fig. 2 Effect of initial concentration of substrate on conversion of phenol at constant concentration of H_2O_2
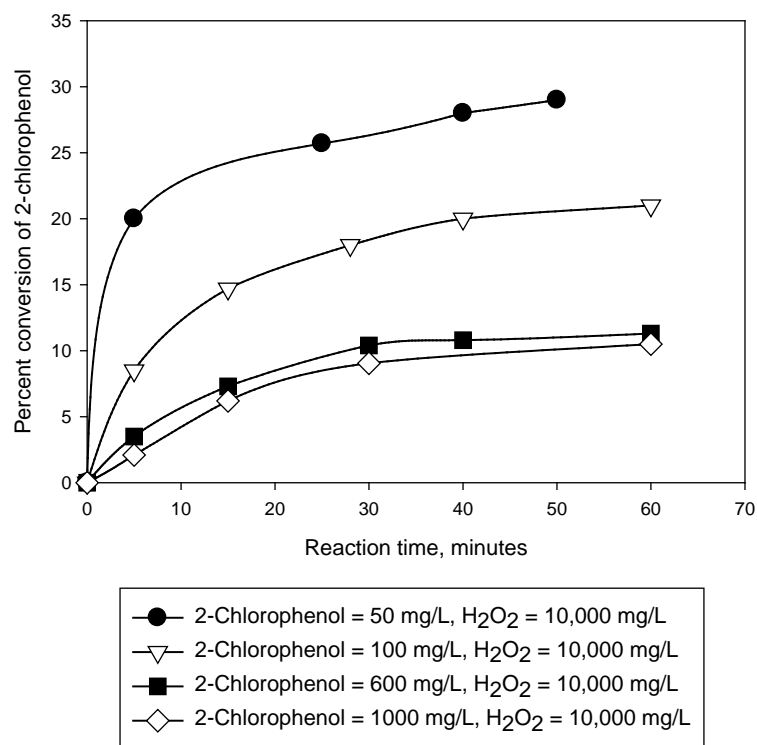
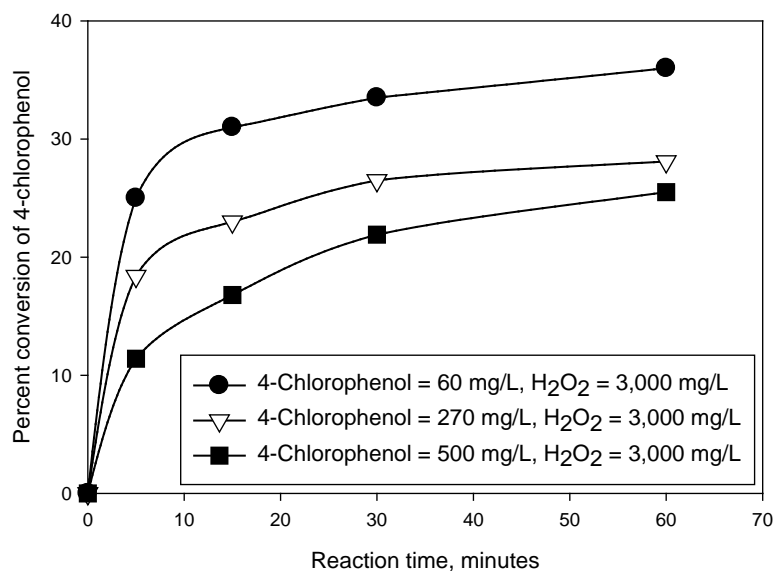Fig. 3 Effect of initial concentration of 2-chlorophenol on conversion at constant concentration of H_2O_2

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

B. Effect of Initial Substrate Concentration

The effects of initial substrate concentration on the conversion (destruction) of phenol, 2- and 4-chlorophenols are shown in Fig. 2 through 4 at constant concentration of H_2O_2. It can be seen from these figures that the conversion decreased with the increase in initial substrate concentration. It could possibly be due to the fact that the concentration of available reactive

oxidizing agent (H_2O_2) for degradation was lesser in the case of higher substrate concentration than in the case of lower values of substrate concentration.

C. Effect of Initial H2O2 Concentration

The effect of initial H_2O_2 concentration, the reactive oxidizing species, on the conversion of phenol, 2-chlorophenol and 4-chlorophenol at constant initial substrate concentration are shown in Fig. 5 through Fig. 7. It can be seen from these figures that H_2O_2 played an important role in the extent of degradation of substrates. As expected, increased conversion of all three substrates were observed after increase in H_2O_2 concentration. The tendency of increasing conversion was observed for all substrate concentrations, even at high concentration of 1000 mg/L. The extent of conversion, however, was not increased linearly with the rate of increase of H_2O_2 concentration. Clearly, this observation demonstrated that there could be an optimum H_2O_2 concentration for which the substrate conversion would become effective based on economic (cost of treatment) and environmental (percentage removal of substrates) aspects.
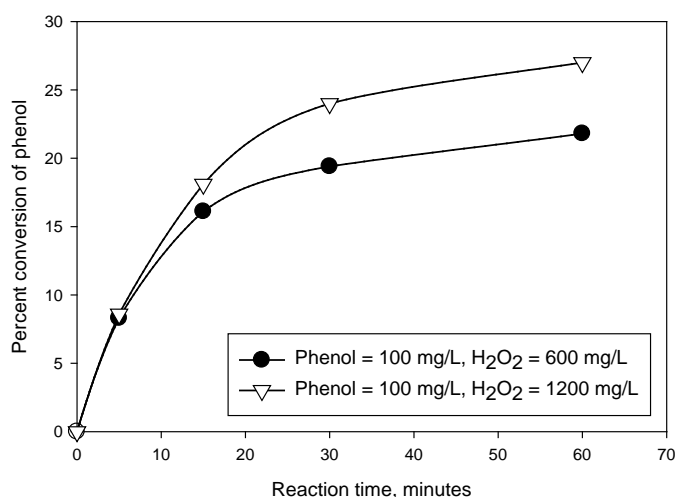

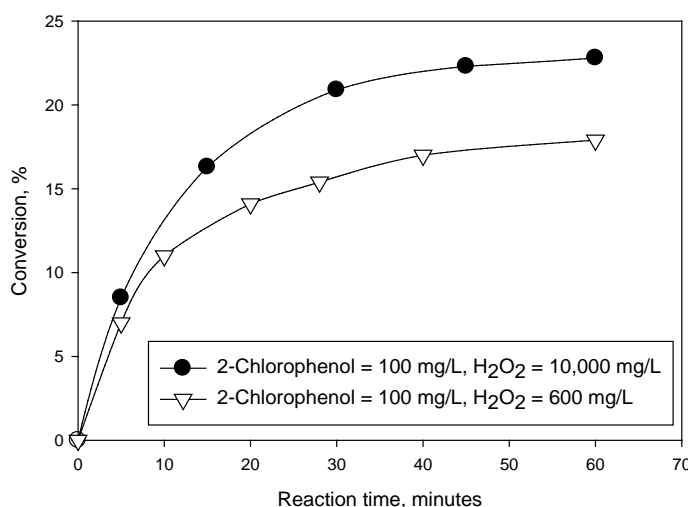Fig. 5 Effect of initial concentration of H_2O_2 on conversion at constant concentration of phenol

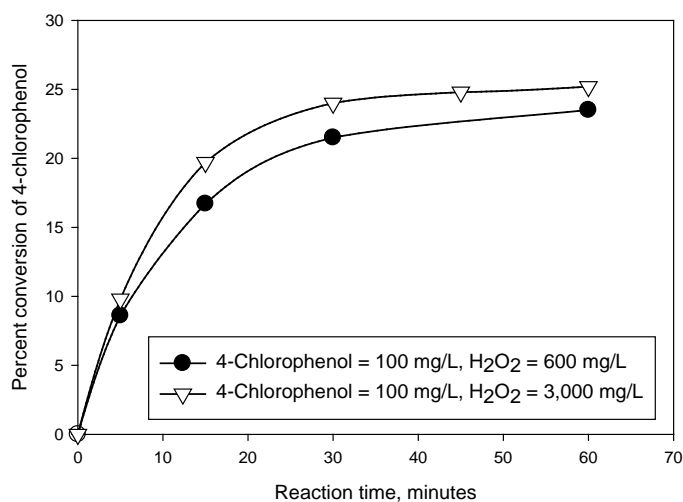Fig. 6 Effect of initial concentration of H_2O_2 on conversion at constant concentration of 2-chlorophenol

Fig. 7 Effect of initial concentration of H_2O_2 on conversion at constant concentration of 4-chlorophenol

D. Effect of Substrate to H2O2 Mole Ratio

From looking at the earlier studies it is conceivable that the ratio of substrate concentration to H_2O_2 concentration (substrate to H_2O_2 mole ratio) played an important role in assessing the performance of the system both in terms of economic as well as environmental aspects. Therefore, the effect of substrate to H_2O_2 mole ratio on the percentage conversion of substrate was studied and is shown in Fig. 8. The trends of variation were similar for all the substrates. It can be seen from the illustration that the conversion of the substrate was generally enhanced with the increase in the initial substrate concentrations while keeping the substrate to H_2O_2 mole ratio constant. But at tremendously higher substrate concentrations (i.e., at higher H_2O_2 concentration for constant substrate to H_2O_2 mole ratio), the percentage of conversion decreased. It might possibly be due to the interaction of the highly populated reaction intermediates (these intermediates are produced by way of different reactions to produce the ultimate goal of carbon dioxide) generated from the substrate degradation by H_2O_2 that impaired the original substrates to react with the reactive species, the H_2O_2 and as a result the percentage conversion was reduced. The presence of intermediates was confirmed by COD analysis of the reaction mixture from time to time.
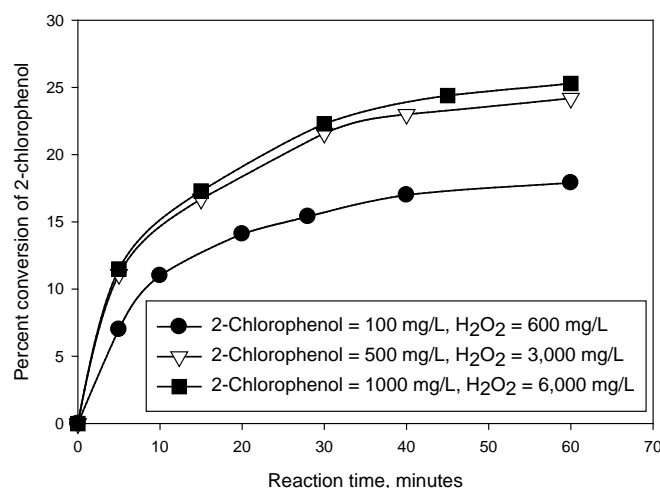

Fig. 8 Effect of substrate to H_2O_2 mole ratios on conversion (initial concentrations varied but ratio remains constant)

E. Effect of Conversion on Ph And Effect of Ph on Conversion

The effect of conversion (degradation) on the pH of the reaction mixture is shown in Fig. 9. It can be seen from the figure that with the increase in the conversion, the pH of the reaction mixture was decreased slowly and eventually reached a constant value after nearly 20 minutes. This trend of variation was similar to that observed while studying the effect of initial substrate

concentration on the conversion. It can also be seen from the figure that the pH of the reaction mixture was dropped substantially from 6.60 to 6.40 in the acidic range immediately upon the addition of H_2O_2 (see Fig. 9) and remained almost constant at 6.38 until the completion of the reaction. The drop in the pH for 2-chlorophenol (from 5.8 to 4.45) was more pronounced than what was observed for phenol (from 6.6 to 6.38). This observation supports the observation made by Pintar and Levec [15]. They further reported that oxygenated intermediates such as p-benzoquinone, 1,2-benzenediole, and 1,4-benzenediole were formed as reaction products during liquid phase oxidation of phenol and chlorophenol by molecular oxygen. Most of these intermediates were more acidic than their parent organic substrates and thus their existence in solution would inevitably result in a sharp drop in the pH of the reaction mixture. The possible mechanistic approach leading to the conversion into the oxygenated intermediates could therefore, be due to the very rapid nucleophilic substitution reaction after addition of H_2O_2 to the diluted solutions of phenol and phenolic compounds.
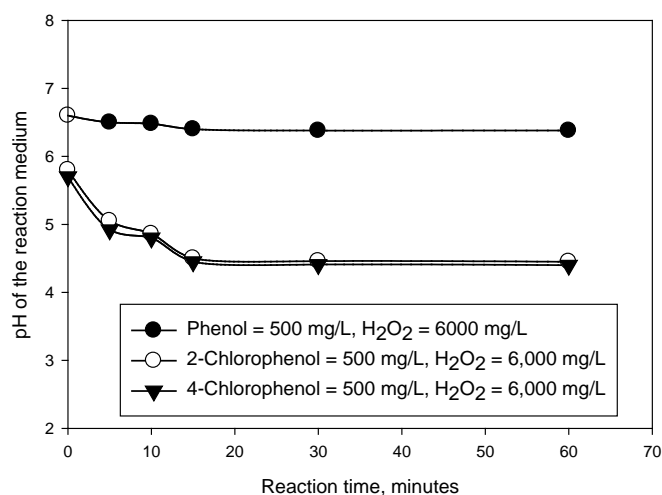

Fig. 9 Effect of time of degradation of phenol, 2-chlorophenol and 4-chlorophenol on the pH of reaction mixture

To determine the optimal pH for the maximum conversion of the phenolic substrates, reactions were carried out at a constant pH by adding acid/alkali solution to the reaction mixture continuously. The acidity or alkalinity of the reaction medium was monitored continuously to keep the pH at a consistent desired level throughout the experimentation. The effect of pH of the reaction medium on the conversion is shown in Fig. 10. It can be seen from the figure that the optimum conversion of phenol was attained at a reaction medium with a pH level of approximately 6.0. On the other hand, the optimum conversion of chlorophenols was observed when the pH of the reaction medium was maintained around 4.5 and beyond which (on either side, i.e., for pH<4.5 and pH>4.5) the conversion decreased substantially with the pH of the reaction mixture (Fig. 10). It can also be seen from the figure that the conversion in all cases was lowered when the solution pH > 7.0. Therefore, the operating pH of the present investigation does not require any additional treatment when disposing of the waste into any body of water since the standard for pH of Organic Chemical Manufacturing Industry in India is stipulated between 6.5 and 8.0 [16].
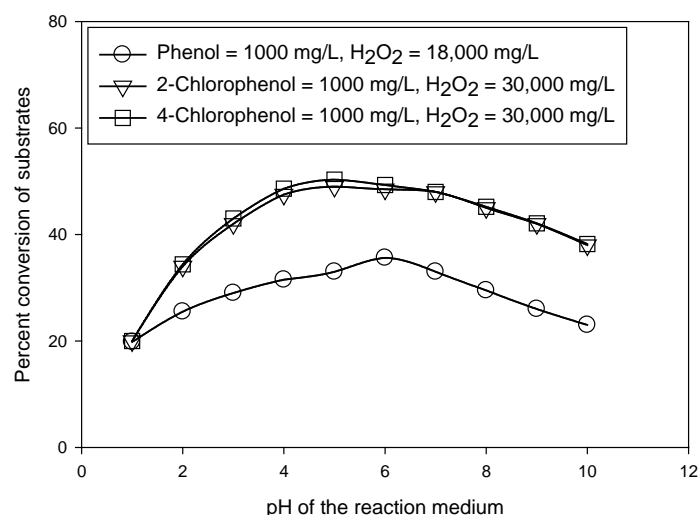

Fig. 10 Effect of reaction medium pH in the reactor on conversion of phenol, 2-chlorophenol and 4-chlorophenol for reaction time of 60 minutes

The mechanism in support of this observation can be explained as follows: Hydrogen peroxide is regarded as an equilibrium mixture of two isomers as illustrated below.

$$H - O - O - H \leftrightarrow \overset{H}{O^+} \to O^- \qquad 1$$

$$(1) \qquad\qquad H \quad (2)$$

Structure (2) represents H_2O_2 as a molecule of water linked to an oxygen atom by a co-ordinate linkage. Being a very weak acid, H_2O_2 ionizes in alkaline solution (acids are used as inhibitors to decomposition) and liberates molecular oxygen in the presence of traces of alkali. Due to this decomposition of H_2O_2 in alkaline solution, the availability of HOO^- or $^{\bullet}OH$ is reduced in the reaction mixture. Therefore, the conversion of substrates was decreased when the pH levels of the reaction mixtures were adjusted in the alkaline range.

F. COD reduction

It was observed from the analysis that the CODs of the reaction mixtures at different time intervals reduced marginally (Table 3) for all three phenolic compounds studied. This observation supports formation of stable oxygenated reaction products which are refractory to further oxidation by H_2O_2 only. A detailed profile of reduction of COD stemming from the destruction of 100 mg/L phenolic substrates with 1200 mg/L H_2O_2 is shown in Fig. 11. It can be seen in the figure that there was a marginal reduction in the COD in all the cases studied. Clearly, this marginal reduction in the values of COD indicated substantially lower mineralization of original substrates to carbon dioxide and water. From the measured values of COD before and after H_2O_2 treatment, it could be concluded that H_2O_2 oxidation of these substrates was not an effective process of mineralization to these types of refractory organic compounds.

TABLE 3 COD REDUCTION DUE TO H_2O_2 OXIDATION OF PHENOL, 2-CHLOROPHENOL AND 4-CHLOROPHENOL AT DIFFERENT TIME INTERVALS AT 303 K

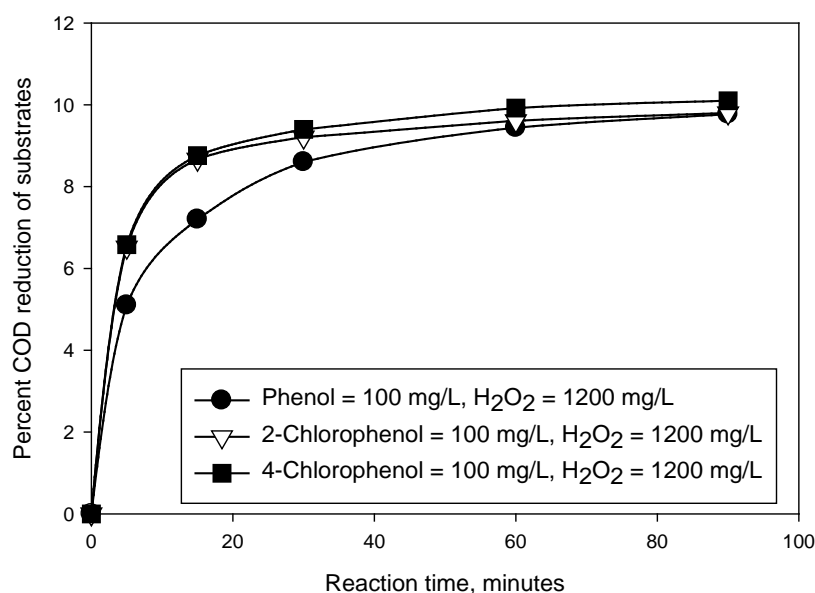| Initial substrate concentration (mg/L)	Initial H₂O₂ concentration (mg/L)	Time (min)	COD reduction (%)		
			Phenol	2-Chlorophenol	4-chlorophenol
Phenol: 100 2-chlorophenol:100 4-chlorophenol:100 (degraded separately)	1200	0	0	0	0
		5	5.10	6.52	6.58
		15	7.20	8.67	8.76
		30	8.60	9.21	9.40
		60	9.44	9.61	9.92
		90	9.77	9.80	10.10

Fig. 11 Reduction of Chemical Oxygen Demand (COD) during H_2O_2 oxidation of phenol, 2-chlorophenol and 4-chlorophenol

G. Probable mechanism of destruction of phenolic substrates

According to Glaze and Kang [17], for photo oxidation, hydroxyl radicals are the most important reactive free radicals that take part in the degradation reaction. In the absence of photolytic activation, literature data on oxidation of phenolic compounds by hydrogen peroxide are scarce. An aqueous solution of H_2O_2 is acidic because H_2O_2 dissociates releasing proton as follows:

$$H_2O_2 \;\rightarrow\; H^+ \;+\; HOO^-, \qquad K = 1.55 \times 10^{-12} \tag{2}$$
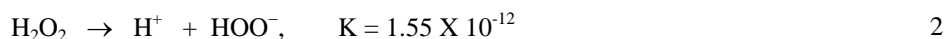
Hydrogen peroxide can also form free radicals by homolytic division of either an O-H bond or the O-O bond [18] as follows:

$$HOOH \;\rightarrow\; {}^\bullet OOH \;+\; {}^\bullet H \,, \quad \Delta H = 380 \text{ kJ/mol} \tag{3}$$

$$HOOH \rightarrow 2\,{}^\bullet OH \,, \qquad \Delta H = 210 \text{ kJ/mol} \tag{4}$$
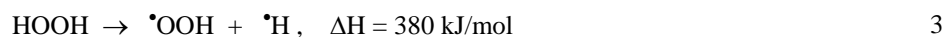
Reaction (3) predominates in uncatalysed vapor-phase decomposition and photo-chemically initiated reactions. In aqueous solution, the nature of the reactant determines which reaction is predominant.

From the experimental results of the oxidation of di-nitrotoluene (DNT) with H_2O_2 alone, Ho [19] suggested that the predominant oxidizing species was hydroxyl radicals and the initial step was the attack of hydroxyl radicals to the benzene ring. 2-chlorophenol (pKa = 8.48) is more acidic than phenol (pKa = 9.98) i.e., the acidity is in the order chlorophenols > phenol. Results of the present study showed that the conversion of phenolic substrates was in the order of chlorophenols > phenol. The reasons in support of our findings are explained as follows. Whether the reactive species was ${}^\bullet OH$ 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. Though the halide group present in 2-chlorophenol at the ortho and in 4-chlorophenol at 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/para position counterbalances the deactivation of the ring. Therefore, the conversion for 2-chlorophenol as well as 4-chlorophenol is expected to be 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 by resonance. Therefore, the conversion of the phenolic compounds is expected to be in the order: chlorophenols > phenol, which conforms to our experimental results. The conversions of phenol, 2- and 4-chlorophenols are compared and shown in Fig. 12. It can be seen from the figure that initially the conversion of chlorophenols were almost the same as in phenol but after nearly 15 minutes, the conversion of chlorophenols were more rapid than that of phenol. 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.
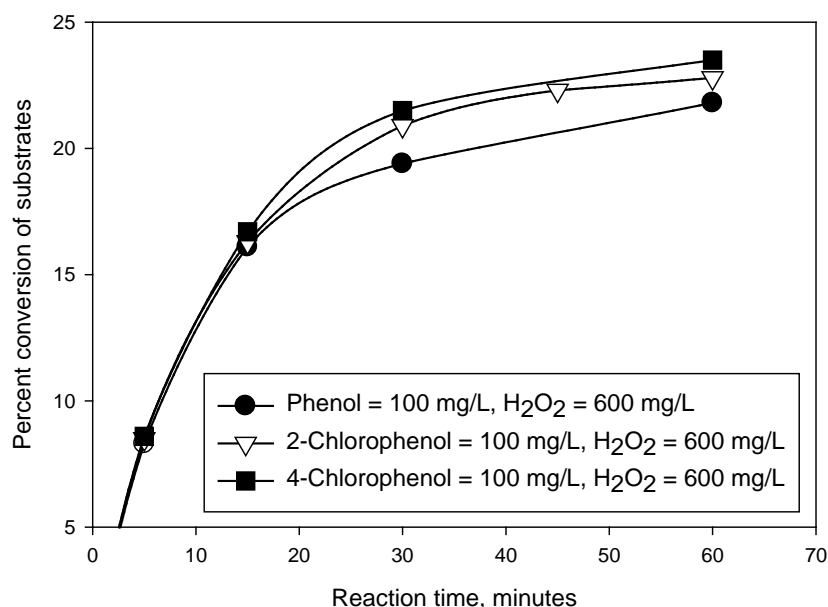

Fig. 12 Comparison of degradation of phenol, 2-chlorophenol and 4-chlorophenol by H_2O_2 at a constant substrate to H_2O_2 mole ratio

The breaking of the peroxide bond is a very slow process in an alkaline or uncatalysed medium. An acid can act as catalyst to enhance the electron shift of the peroxide oxygen by donating a proton to the oxygen, facilitating the formation of hydroxyl ion in the reaction medium [20]. This hydroxyl ion can also take part in the nucleophilic substitution reaction. Hydrogen peroxide in acid solution produces the conjugate acid $H_3O_2^{+}$ which can donate OH^- ion [21] to a nucleophile faster and easier than neutral or alkaline H_2O_2 solution in the rate determining step:

$$H^+ + HOOH \;\rightarrow\; HOO^+H_2 \tag{5}$$

(equilibrium constant = in the order of 10^{-3} M)

In strong alkaline solution H_2O_2 produces hydroperoxide ion [22] as,

$$HOOH + OH^- \rightarrow HOO^- + H_2O \tag{6}$$

Wilson and Harris [23] reported the reactivity of the electrophilic substitution of H_2O_2 to be in the order of $H_3O_2^+ > H_2O_2 > HOO^-$. Therefore, acid catalysed reaction or reaction in an acidic medium increases the reactivity of H_2O_2 to degrade contaminants to a lower level.

IV. CONCLUSIONS

The kinetics of degradation of three phenolic substrates by H_2O_2 was studied in a stirred tank reactor. Conversion attained within 15 minutes of reaction accounted for roughly 90% of conversions that can be achieved within approximately 60 minutes of reaction. The pH of the reaction mixture also showed an identical trend. The drops in pH for phenol, 2-chlorophenol and 4-chlorophenol were 6.6 to 6.38, 5.8 to 4.45 and 5.7 to 4.40 respectively. Concentration of H_2O_2 measured at different time intervals revealed that the concentration remained almost constant during reaction.

Effects of various parameters like the initial concentration of substrates, the initial concentration of H_2O_2 and the pH of the reaction medium were studied. The conversion was increased with raising the initial concentration of substrates, and this phenomenon was observed only when the substrate to H_2O_2 molar ratio was kept constant. Results further showed that the optimum conversion of substrates could be achieved by maintaining pH at certain value beyond (below or above) which the conversion would be lower. In the present study, these pH values were found to be 6.0, 4.55 and 4.5 for phenol, 2-chlorophenol and 4-chlorophenol, respectively. Therefore, the operating pH of the present investigation did not require any additional treatment when disposing the treated effluent to any receiving body of water since the standard for pH of Organic Chemical Manufacturing Industry in India is stipulated between 6.5 and 8.0. The total conversion under similar reaction conditions (e.g., same initial substrate concentration and same substrate to H_2O_2 molar ratio) was comparable for all the substrates studied. Though the conversion was in the order of 4-chlorophenol > 2-chlorophenol > phenol, following the chemistry of reactivity and formation of stable intermediate compounds, the conversion was however, varied within ±30% for substrate initial concentration of 500 mg/L. Mineralization of substrates was found negligible indicating non-suitability of only the hydrogen peroxide oxidation technique for degradation of phenolic substrates.

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