

Removal of catechol from aqueous solution by advanced photo-oxidation process

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Abstract

A comprehensive experimental investigation has been made on removal of catechol from aqueous solution by advanced photo-oxidation with hydrogen peroxide in presence of UV light. The effect of different process parameters, such as initial substrate concentration, H₂O₂ to substrate concentration ratio, addition of a solid catalyst (ferrous sulfate) has been studied. It was found that initial rate of conversion of catechol was extremely high compared to the later part of the reaction. Conversion attained within around 10 min of reaction accounted for approximately 90–95% of the conversion attained within 60 min of reaction. A kinetic model for degradation of catechol has been developed, which shows that the degradation reaction of catechol with UV/H₂O₂ follows a pseudo second-order pathway.

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1. Introduction

Wastewater discharged from a number of process industries, such as oil refineries, petrochemical industries, and coke plants, contain dissolved organic pollutions such as phenol and substituted phenolic compounds, which are toxic and hazardous to the environment. Wastewater containing such chemical ingredients is extremely toxic to the aquatic life and environment unless they are treated properly. Maximum allowable concentration of phenolic compounds in treated wastewater varies between 1 and 5 mg/l.

The biological oxidation processes (BOPs) are the common methods used worldwide for the treatment of industrial wastewater. BOP requires a lot of space and hence, it is difficult to maintain a consistent effluent quality, and finally it produces activated sludge residue, which is a hazardous waste. It is also to be mentioned here that there are a number of persistent pollutants which are non-biodegradable even at very low concentration in wastewater. Therefore, for the degradation of these refractory pollutants tertiary wastewater treatment or advanced wastewater treatment is essential. Chemical oxidation of the dissolved organics present in in-

dustrial effluents or concentrated in aqueous waste streams is an alternative technology that can be successfully applied to a broad spectrum of organic compounds. The process converts the dissolved organics to CO₂ and H₂O. On the other hand, photo-degradation of such chemical compounds using H₂O₂ or ozone in presence of UV light enables enhanced degradation [1–4]. Oxygen cannot be directly used for oxidation of the dissolved organics in wastewater. The cleavage of the oxygen–oxygen bond requires high energy and therefore oxidation kinetics of organic compounds with molecular oxygen is extremely slow. Fluorine, the strongest oxidant (oxidation potential, E^0 : 3.06 V) cannot be used for wastewater treatment because of its high toxicity. Hydrogen peroxide (E^0 : 1.77 V) and ozone (E^0 : 2.07 V) are also strong oxidizing agents. Hydrogen peroxide is commercially available and can be conveniently stored at a site. In contrast, ozone may be generated at the site and is toxic to the environment (TLV 0.1 ppm). Hydroxyl radical is also a strong oxidizing agent (E^0 : 2.80 V) second only to fluorine. Preis et al. [5] reported that the photo-oxidation process is more efficient for degradation of phenolic compounds at lower concentration compared to biological treatment. Prengle and William [6] described the oxidation characteristics of organic molecules by OH• in three steps. The hydroxyl radical can be generated by UV-irradiation of the wastewater containing hydrogen peroxide or dissolved ozone.

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Nomenclature

BOD	biochemical oxygen demand (mg/l)
C_A	concentration of catechol at any time in solution (ppm)
C_B	concentration of hydrogen peroxide at any time in solution (ppm)
C_A^0	initial concentration of catechol in the solution (ppm)
C_B^0	initial concentration of hydrogen peroxide in the solution (ppm)
E^0	oxidation potential (V)
k	rate constant for overall reaction
k'	rate constant for pseudo m th order reaction ($\text{min}^{-1} (\text{mg/l})^{1-m}$)
m, n	exponent of the concentration term in the rate equation
P	intermediate compound for degradation of substrate
r	regression coefficient
$-r_A$	rate of degradation of catechol
R	ratio of initial concentration of hydrogen peroxide to catechol (C_B^0/C_A^0)
S	substrate (catechol solution)
t	time of reaction after addition of hydrogen peroxide to the UV irradiated catechol solution, minute
TCE	trichloro ethane

The processes which generate high energy hydroxyl free radicals in reaction medium and then degrade organic contaminants in wastewater, take place due to oxidation of pollutants in a series of reactions to the ultimate product of mainly CO_2 and H_2O , and are known as advanced oxidation processes. The generation of highly effective hydroxyl free radical might possibly be by the use of UV, UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$, $\text{Fe}^{+2}/\text{H}_2\text{O}_2$, $\text{TiO}_2/\text{H}_2\text{O}_2$ and a number of other processes.

The literature review reveals that significant works have been made on degradation of phenol [7] and other substituted phenolic compounds [8,9] using advanced oxidation processes. However, comparatively little attention has been paid on removal of catechol [10,11] though it is reported to one of the important substituted phenolic compounds present in different industrial effluent. The objective of the work was preliminary to characterize the oxidative degradation of dilute aqueous solution of catechol by using hydrogen peroxide in presence of UV light. In the study, the effect of different process parameters like initial substrate concentration, hydrogen peroxide concentration, pH, ratio of hydrogen peroxide to substrate has been observed. Based on these experimental results, a kinetic model of the degradation reaction has been developed. A number of experiments have also been performed by adding ferrous sulfate as a solid cat-

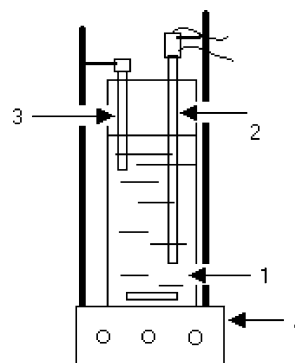


Fig. 1. Experimental setup. Legends: (1) solutions of catechol + H_2O_2 ; (2) UV-lamp; (3) pH meter; (4) magnetic stirrer.

alyst in the reaction medium and a comparison of degradation reported in the paper.

2. Experimental procedure

Fig. 1 shows the schematic diagram of the experimental setup. Catechol solution of different concentrations (50–1200 ppm) was taken batch wise in a 300 ml cylindrical reactor placed on a magnetic stirrer for constant stirring. Low pressure mercury vapor UV-lamp of 6W (Sankyo Denki, Japan) with 1.3 cm diameter and 20 cm effective length was introduced centrally inside the reactor. The lamp was positioned vertically to the reactor. The UV-lamp used in the study had wavelengths ranging from 250 to 273 nm. However, it was specified that maximum fraction of radiation would be at wavelength of 254 nm and, therefore, studies were made based on 254 nm UV-irradiation. The temperature of the reaction mixture was maintained at 27°C . The temperature inside the reactor was controlled using a thermostatic temperature control bath. A digital pH meter was used for continuous monitoring of pH of the solution. To start each experimental run, a sample solution was taken, UV-lamp was switched on and then hydrogen peroxide was added to the solution after 2–3 min. Samples of reaction medium were withdrawn time to time from the reactor for analysis. Reaction time was considered immediately after addition of hydrogen peroxide to the solution.

Some experiments were also conducted by adding ferrous sulfate to the reaction mixture as it is well known that the compounds of certain metal such as sulfate of iron [12,13], oxides of molybdenum and titanium [14] accelerates the decomposition of hydrogen peroxide. Increasing decomposition of hydrogen peroxide increases the availability of hydroxyl radical, which in turn gives increasing degradation of catechol. Concentrations of catechol in the solution were measured by colorimetric methods [15] using a Shimadzu (UV-160A) spectrophotometer. The color complex for analysis of catechol was formed by using 4-aminoantpyrine [15] and absorbance was measured at 510 nm in the spectrophotometer.

3. Results and discussion

The experimental programs were designed to study the time–concentration profile for oxidative degradation of catechol with hydrogen peroxide in presence of UV light. The effects of initial concentration of catechol, initial concentration of hydrogen peroxides to catechol ratio and addition of solid catalyst on degradation of catechol have been studied in detail.

In general, the concentration of catechol versus time profile for each experiment shows identical behavior. It is shown in Fig. 2 that a sudden substantial drop in the concentration of catechol was observed within few minutes after the addition of hydrogen peroxide to the UV-irradiated aqueous solution of catechol. The conversion attained within 5 min of adding of hydrogen peroxide in presence of UV light accounted for almost 90% of the total conversion achieved within a period of 1–2 h. In a number of experimental runs, particularly at low initial concentrations of catechol, conversion achieved within 5 min was more than 90% of the overall conversion, and in all test runs degradation of catechol at the initial period was very high compared to later part of reaction.

Fig. 3 shows the variation of conversion of catechol and pH of the reaction mixture with time. Experimental results show that almost 80–90% of the catechol present in the solution can be removed by the use of present process. The pH of the reaction mixture shows a similar trend. After addition of hydrogen peroxide, the pH of the reaction mixture dropped from 5–6 to 2–3 and remained almost constant at this value for the rest of the period of duration of experiment. The drop in pH values in the earlier part of reaction is rapid compared to the later part of the reaction. From Figs. 2 and 3 it is clear that within around 20–30 min rate of pH drop is very high (from 5.20 to 2.80 within first 30 min and then 2.80–2.72 in the last 30 min, Fig. 3) and then the rate of pH drop is negligible.

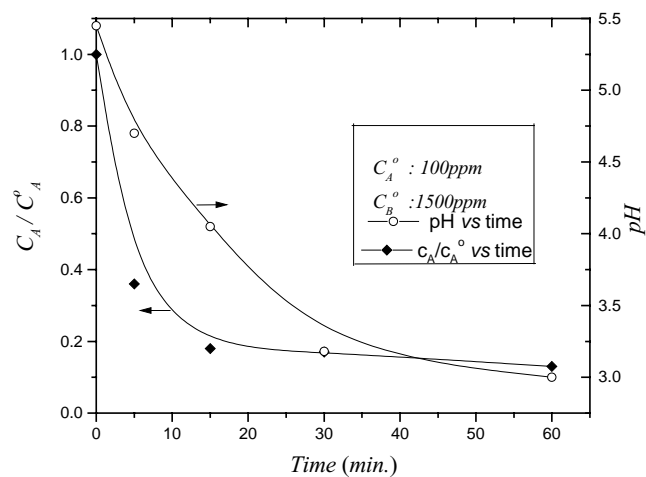


Fig. 2. Variation of concentration of catechol and pH of the reaction mixture with time.

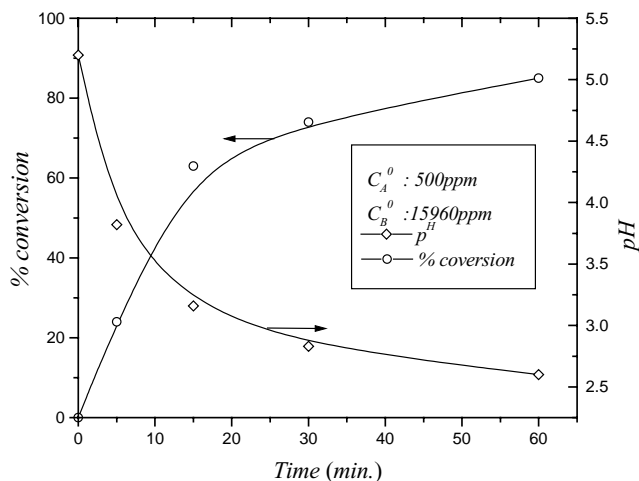


Fig. 3. Variation of conversion of catechol and pH of the reaction mixture with time.

In the present study, the time–concentration data for oxidative degradation of catechol were collected for various initial concentration of catechol, keeping the ratio of hydrogen peroxide to catechol constant. Fig. 4 shows a typical plot of conversion of catechol versus initial concentration of catechol. It was found that for the same hydrogen peroxide to catechol concentration ratio (R) the conversion gradually decreases with an increase of initial catechol concentration. For the same hydrogen peroxide to catechol concentration ratio (R), an increase in initial catechol concentration means an increase in hydrogen peroxide concentration also. For a particular initial substrate concentration, increased hydrogen peroxide concentration in the reaction medium normally will result in more and more of hydroxyl radical generation in presence of UV radiation and the effect will be increased percentage degradation of substrate as shown in Fig. 4. It was also observed that a huge increase of hydrogen perox-

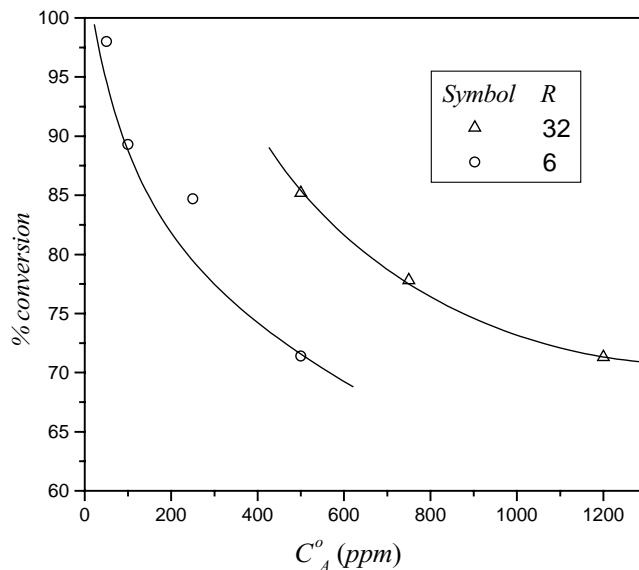


Fig. 4. Effect of initial concentration of catechol on conversion.

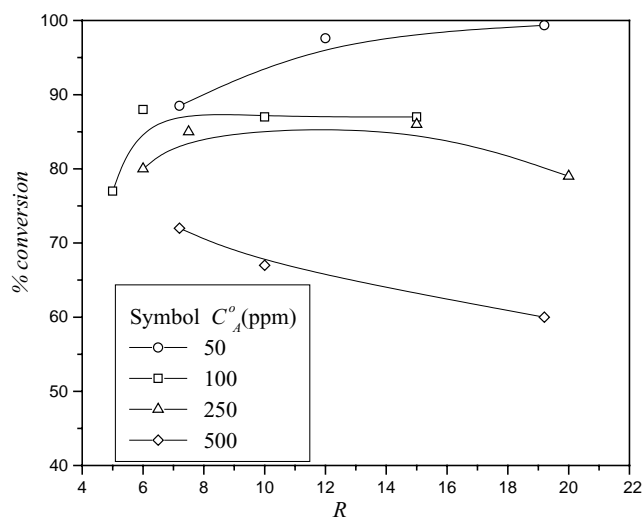


Fig. 5. Effect of hydrogen peroxide to catechol concentration ratio (R) on conversion of catechol.

ide resulted in a decrease in percentage degradation instead of an increase (Fig. 5). It was reported [19,20] that a large excess of hydrogen peroxide adversely affect the oxidation kinetics probably because of perhydroxyl radical generation in the reaction medium. They also reported that if hydrogen peroxide concentration exceeds a critical value, the rate reaches a maximum and then becomes independent of hydrogen peroxide concentration. The scavenging effect of hydrogen peroxide, which consumes highly reactive hydroxyl free radicals is according to the reaction given below:



The reaction scheme revealed that highly reactive hydroxyl radicals are consumed and converted to less reactive perhydroxyl radical. Thus the degradation of substrate will reduce after an increase of hydrogen peroxide concentration when the critical hydrogen peroxide concentration present in reaction medium is reached. Moreover, for a fixed UV-radiation intensity, the number of photons emitted is fixed and therefore, for a given lamp intensity, capability of generating hydroxyl free radical remains fixed and independent of the total amount of hydrogen peroxide in reaction medium. This result indicates that the incident UV-photon concentration in the reaction medium is rate limiting. We observed an effective concentration of hydrogen peroxide for an initial substrate concentration for which degradation was a maximum and beyond that point degradations were less in either conditions and these observations are valid only for UV-irradiation of 6 W/300 mL of substrate solution. It may be possible that other UV dosages will produce different maximum ratios of hydrogen peroxide to catechol for effective degradation of substrate. We lack those data because we conducted experiments only by using 6 W UV sources for irradiation. The observed result is shown in Fig. 5.

Fig. 5 shows the effect of increasing ratio of hydrogen peroxide to catechol concentration on conversion. Four sets of

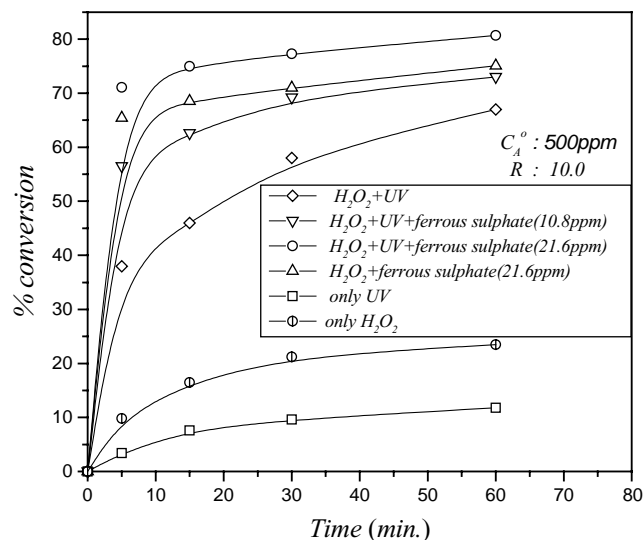


Fig. 6. Effect of different operating conditions on conversion of catechol.

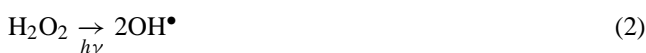
data are shown in the figure. It was observed that for a very dilute solution (50 ppm) of catechol conversion increased with an increase in R . For a moderate concentration of catechol solution (100–250 ppm) conversion first increased and then decreased or remain constant. From observation it was found that for a high initial concentration of catechol conversion decreased with an increased ratio of hydrogen peroxide to catechol [16].

Fig. 6 gives comparisons for degradation of catechol at different experimental conditions. Conversion of catechol is insignificantly small with UV radiation only and also with H_2O_2 (in the absence of UV radiation), but the synergistic effect of UV/ H_2O_2 results in a marked enhancement of the rates of degradation. It has been seen that addition of ferrous sulfate as a solid catalyst increases the conversion further. This is due to catalytic effect of ferrous sulfate on dissociation of H_2O_2 , and hence, higher availability of hydroxyl radical, which results in improved conversion. According to Kim et al. [17], in the photo-Fenton reaction, hydroxyl radical is generated by the reaction of Fe^{2+} with H_2O_2 , and the Fe^{3+} is reduced by UV light. However the degradation reaction for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system is very much sensitive to pH, reaching an optimum around pH 2.7 [12].

4. Reaction mechanism and kinetics

The concentration of hydrogen peroxide added in the reaction mixture decreases during the progress of the reaction. A possible reaction mechanism by which the catechol is oxidized by dilute solution of hydrogen peroxide and UV light system is given below.

UV light causes direct and hemolytic cleavage of H_2O_2 affording two moles of OH^\bullet for every mole of H_2O_2 by the following pathways [18]:



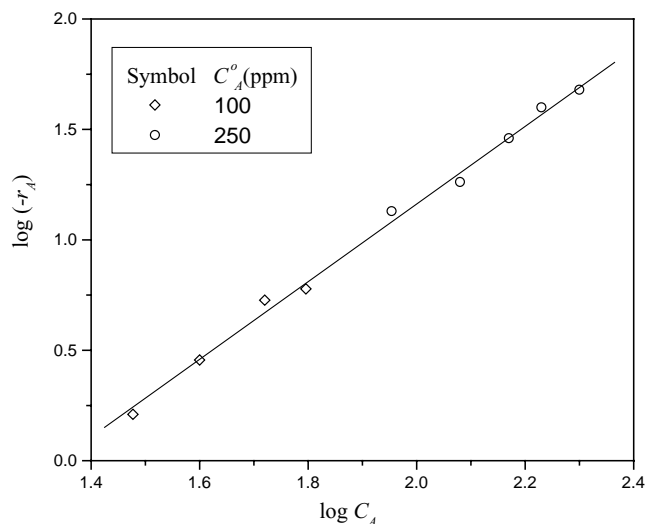
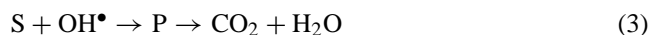


Fig. 7. The log–log plot of the rate vs. concentration of the catechol solutions.

This OH^\bullet radical then undergoes oxidative degradation reaction with catechol present in the solution with nearly complete conversion to CO_2 and H_2O :



The rate equation of the degradation of catechol can be written as

$$\text{Rate} = -\frac{dC_A}{dt} = kC_A^m C_B^n \quad (4)$$

where C_A to C_B represents concentration of catechol and hydrogen peroxide, respectively. Yue and Legrini [20] mentioned that for UV/ H_2O_2 photo-oxidation of phenol, catechol, 4-chlorophenol and TCE, power-law kinetics of the following form were observed:

$$\text{Rate} = -\frac{dC_A}{dt} = k[\text{TOC}]^{1.3-1.5} \text{ at large excess of } \text{H}_2\text{O}_2 \quad (5)$$

In our experiments, a higher ratio (R) of C_B to C_A than the stoichiometric amount was maintained, hence concentration of hydrogen peroxide is assumed to be remaining unchanged. Thus a pseudo m th order type reaction can be written as

$$\text{Rate} = -\frac{dC_A}{dt} = k' C_A^m \quad (6)$$

Using Eq. (6), a log–log plot of rate versus concentration of substrate will give the value of k' and m . Fig. 7 shows the plot of Eq. (6). From Fig. 7, value of rate constant, $k' = 0.0042$; and the order, m , obtained was 1.77. The linear regression analysis showed ($r > 0.99$) that the experimental data fit the kinetic equation satisfactorily.

5. Conclusion

The experimental results obtained in the present system are highly encouraging in regard to the removal of cate-

chol from aqueous solution. It has been found that initial rate of conversion of catechol is extremely high compared to the later part of the reaction. Excellent conversions are observed at lower concentrations of catechol and conversion increases with increase in concentration of hydrogen peroxide. A kinetic model has been developed, which shows that a pseudo second-order type reaction with respect to substrate concentration fits well with the experimental data. Addition of ferrous sulfate as a solid catalyst resulted in an improved degradation of catechol. However, for photolytic process, an important limitation and efficiency factor is penetration of UV light through the wastewater stream. Under certain condition, due to opaqueness of wastewater and the high maintenance cost of VU lamps, non-photo $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process is encouraging.

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