Photolytic Oxidation of Hazardous Organic Compound: Phenol

Parteek Singh Thind, Swapna Thomas, and Siby John

Abstract—Refractory aromatic compounds like phenols and halogenated derivatives of phenols are highly persistent and exhibit acute toxic effects. These compounds are common constituents in effluents of industries such as dye, petroleum refineries, steel, textile etc. Conventional wastewater treatment technologies generally applied to these refractory compounds do not destroy the pollutants but merely transfer the pollutants from one phase to another leading to attendant problems of disposal. Although biodegradation is considered as a viable option, these organics are highly resistant to biodegradation. Using techniques of advanced oxidation process (AOP), it has been established that these compounds can be transformed into harmless/less harmful compounds.

Considerable amount of work has been done over the past few years using oxidants like \( \text{H}_2\text{O}_2 \), \( \text{O}_3 \) with or without the use of photocatalyst (s). Various designs of photoreactors have also been developed and practised.

In this study, experiments were conducted in a batch mode recirculating falling film reactor system. The cylindrical reactor made of borosilicate glass 60 mm diameter and 210 mm height. A UV lamp, housed in quartz immersion well, served as the UV light source. The feed phenol solution mixed with required volume of \( \text{H}_2\text{O}_2 \) was continuously re-circulated through the reactor using a peristaltic pump. Experimental studies were conducted using phenol concentration range from 50 to 500 mg/L. The operational parameters varied for the study included concentration of \( \text{H}_2\text{O}_2 \), phenol, initial and final temperature and pH.

The combination of \( \text{H}_2\text{O}_2 \) and UV light was much more effective than UV or \( \text{H}_2\text{O}_2 \) alone in destroying phenol. The optimum \( \text{H}_2\text{O}_2/\text{Phenol} \) concentration ratio was found to be 20. Initial pH of the solution ranging from 6.0 to 8.2 yielded the best phenol destruction. Increase in solution temperature exhibited a positive correlation with efficiency of phenol degradation. The presence of bicarbonates in the solution acted as deterrent in the oxidation process due to scavenging of hydroxyl radicals. It warrants that pre-treatment of highly alkaline wastewaters is essential for application of AOP. As the COD or BOD of the samples decreased with irradiation time, it could be suggested that combination of AOP with biodegradation could be viable option for treatment of such difficult to biodegrade compounds. Also, the falling-film reactor proposed herein is a simple design which allows efficient light utilization with good mass transfer characteristics.

Keywords—Waste water treatment, phenol, AOP, UV light, BOD, COD.

I. INTRODUCTION

PHENOL and its derivatives have been contaminating a large part of environment due to various anthropogenic activities. These activities may include their prominent use in the petrochemical, plastic, steel or pharmaceutical industries. Waste water, from such industries, is frequently dumped into nearby water bodies as well as on land. Therefore, our food chains have also been contaminated with phenolic compounds, which can show chronic effects on human health. Keeping this in mind, it has been made mandatory, for all industries, to use efficient technologies to maintain the concentration of phenols in their waste waters below permissible limits.

To meet the environmental regulations, various innovative technologies like adsorption on granular activated carbon (GAC), air stripping and biodegradation are being used, but the present trend in waste water treatment is towards development of destructive technologies i.e. technologies which not only remove the contaminants from waste water but also destroy them in the process. In recent years, advanced oxidation processes (AOP) have emerged as potentially powerful methods which are capable of transforming the pollutants into harmless substances. These methods promote free radicals, such as the hydroxyl (OH) radical, in the reactions which lead to complete oxidation (or mineralization) of the pollutant to yield CO\(_2\), H\(_2\)O and corresponding salts.

A considerable amount of work has been done over the past few years using oxidants e.g., hydrogen peroxide, ozone and photocatalyst simultaneously coupled with ultraviolet light in treating wide variety of hazardous organics in water. Despite all these processes, studies have also been conducted for the treatment of phenol contaminated water, using heterogeneous photocatalysis [1, 2, 3, 4, 5, 6]. Though this technology has wide applications, the separation of fine TiO\(_2\) particles is slow, expensive and also depth of penetration of UV light is limited because of strong absorption by TiO\(_2\) and dissolved organic species. The combination of ozone and UV light has proven effective with many types of aliphatic and aromatic compounds. But ozone is an unstable gas that must be generated on site and transferred into the liquid phase which is quite expensive at low production levels. To avoid these difficulties, hydrogen peroxide in combination with UV-light is most suitable and has enjoyed considerable success in photolytic oxidation. Hydrogen peroxide is also an effective oxidizing agent for UV catalysed reactions. It can be stored for use according to process demand, is readily miscible with water.

The effectiveness of UV – catalyzed oxidation by hydrogen peroxide process was determined for typical aromatic compounds including phenol and chlorinated phenols[7].
Similar studies were performed on destruction of phenol and chlorophenols in the presence of different oxidants like sodium hypochlorite (NaOCl), hydrogen peroxide (H₂O₂) and oxygen (O₂) [8]. These studies indicate that the combination of ultraviolet (UV) radiation with H₂O₂ is very effective and achieved nearly complete oxidation of refractory organics present in waste waters under proper operational conditions. Various other contaminants such as trichloroethylene (TCE), phenol, 4-chlorophenol and catechol have also been degraded using this process. In these studies the effectiveness of the process is determined by estimating the total organic carbon (TOC) removal [9, 10].

In this study all experiments were conducted in a photo-chemical reactor, for the treatment of phenol, using UV light and hydrogen peroxide. After analyzing the related researches, the reactor configurations, employed for photo-degradation studies in this research, have included a recirculating flow reactor, annular immersion photoreactor, continuous annular photoreactor, open-upflow slurry reactor etc. most often in laboratory experiments, well mixed heterogeneous or homogenous batch reactors have been used [7, 11, 12, 2]. In a similar study, researchers modeled simple reactors (falling film reactor, plug flow reactor and slit flow reactor) and concluded that falling film or slit flow reactor could have superior performance [13]. Yatmaz et al., used falling film reactor for different types of TiO₂-catalysed and organic effluents. The reactor is a simple design which allows efficient light utilization to be combined with good mass transfer characteristics [14].

II. METHODOLOGY

The experiments were conducted in a batch mode re-circulating falling film reactor system as shown in figure 1. The reactor made of borosilicate glass, in a 2 mm thick cylindrical glass tube of length 21 cm and 6 cm diameter lined with aluminum foil on the outside to minimize stray radiation and acts as a reflector. A circular trough of 9 cm diameter is attached at top of the cylinder. The UV lamp, housed in quartz immersion well, is a low pressure mercury vapour lamp which emits predominantly radiation at a wavelength 253.7 nm. The feed phenol solution mixed with required volume of H₂O₂ is continuously re-circulated through the reactor using a peristaltic pump. The flow rate is maintained to ensure a uniform thickness over the whole of the reactor surface. The samples were withdrawn at different intervals of time for phenol estimations. All experiments were conducted at ambient temperature (27 – 30°C). Analysis of phenol, BOD and COD were done according to procedure given standard methods and initial concentration of hydrogen peroxide was estimated by iodometry[15, 16].

III. RESULTS AND DISCUSSION

Experimental studies were conducted for the phenol concentrations ranging from 50 to 500 mg/L., the operational parameters investigated include the concentration of hydrogen peroxide, concentration of phenol, initial pH and temperature. The effect of interferences on the degradation efficiency of phenol was also studied.

A. Effect of hydrogen peroxide dosage on phenol degradation

The effect of hydrogen peroxide to phenol concentration ratio on phenol removal rate is illustrated in Fig. 2 and 3. With UV alone, a moderate rate of reaction was observed for all concentrations of phenol. The combination of hydrogen peroxide and UV light was much more effective than UV alone in destroying the compound. The rate of phenol removal increase with increase in hydrogen peroxide to phenol concentration ratio and this pattern is observed for all concentrations of phenol. At lower concentration of phenol = 50 mg/L (Fig.2), higher ratio of peroxide to phenol yielded the faster rates of phenol destruction. The initial rate of removal is faster i.e. upto two hours of irradiation when compared to later part of reaction. This is due to formation of

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Fig. 1 Schematic of experimental set-up
intermediates during the course of reaction which also compete for hydroxyl radicals and UV light. At higher concentration of phenol = 100 mg/l (Fig.3), though the rates of phenol removal increases with increase in peroxide dosage, there was not significant increase in the rate of reactions beyond the ratio 20. At higher dosages, hydrogen peroxide itself acts as inhibitor and scavengers hydroxyl radicals thereby decreasing the rate of reaction.

C. Effect of initial pH on phenol degradation

The effect of initial pH on phenol (50, 100 and 300 mg/l) removal was examined at four pH values ranging from 4 to 12. The pH of the solution was adjusted using conc. H$_2$SO$_4$ and NaOH. The percentage removal of phenol at different initial after two hours of irradiation is shown in Fig.5.

D. Effect of temperature on phenol degradation

The effect of temperature (27 and 40°C) on phenol (500 mg/l) removal is shown in Fig.6. The rate of phenol removal increased with increase in temperature.

For lower concentrations of phenol, rate of removal is faster than for higher concentrations due to availability of sufficient amount of hydroxyl radicals. However, the amount of phenol destroyed per unit time was higher in the solutions containing higher phenol concentrations. Thus the effect of initial phenol concentration on phenol destruction depends on hydrogen peroxide to phenol concentration ratio.
E. Effect of interferences on degradation of phenol

The principal hydroxyl radical scavengers like bicarbonate and carbonate ions are ubiquitous in natural water and waste water which effect the efficiency of phenol \( \text{H}_2\text{O}_2/\text{UV} \) oxidation process. The effect of sodium bicarbonate concentration ranging 0-5 g/l on degradation of phenol concentration (50 mg/l) is shown in Fig. 7.

It is observed that the rate of phenol removal decreases with increase in initial concentration of bicarbonate. This is similarly observed for other concentrations also. Bicarbonate or carbonate present in water scavenges the hydroxyl radical to form carbonate radical. This carbonate radical reacts with excess hydrogen peroxide to produce bicarbonate ions again.

F. Effect on COD and BOD with irradiation time

COD (Chemical oxygen demand) and BOD (Biochemical oxygen demand) were found at different intervals of irradiation time and are plotted in graph as shown in Fig. 8 and 9.

COD and BOD values decrease with increase in time of irradiation. Though the pollutant phenol is totally removed by the end of eight hours, we observe from graphs that COD and BOD values still persist which indicates some of the intermediates formed during the course of reaction are not degraded completely.

IV. CONCLUSIONS

Based on the experimental studies following conclusions are drawn:

1. The combination of hydrogen peroxide and UV light was much more effective than UV alone in destroying phenol.
2. Phenol is converted to chemical intermediates and which are destroyed by further irradiation.
3. The optimum \( \text{H}_2\text{O}_2/\text{phenol} \) concentration ratio is 20 beyond which there was no significant increase in the degradation rate.
4. The initial solution pH is an important operational parameter the optimum range occurred at pH 6.0 – 8.2. The fastest rates of phenol destruction occurred at approximately at initial pH 8.0. proper control of solution pH can increase the removal efficiency of phenols.
5. Solution temperature greatly increases the removal efficiency with increase in the temperature.
6. In the presence of bicarbonates in the solution, the rate of oxidation has negative effect due to scavenging of hydroxyl radicals. This suggests that pretreatment of high-alkalinity ground water or waste water may be required in AOPs.
7. COD and BOD values decrease with irradiation time. This suggests that the combination of biodegradation with AOPs may be cost effective in treatment of highly toxic pollutants like phenol.
8. The falling film reactor is a simple design which allows efficient light utilization to be combined with good mass transfer characteristics.

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