Removal of Phenol from Waste Water using Hydrogen Peroxide

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Abstract—*In this study, the photo catalytic degradation of phenol over H_2O_2 was carried out in the presence of UV light. Control experiments were carried out. The Photo catalytic degradation of phenol was done and degradation was studied on UV spectrophotometer. The various parameters like concentration of substrate, amount of catalyst and duration was studied for radicals affecting the kinetics of the degradation process. Photo catalytic experiments were carried out using laboratory photo reactor for degradation of phenol from waste water. Experiments were carried out with 1-5ml/lit of H_2O_2 catalyst for different concentration of phenol waste water ranging from 10, 20, 30, 40 and 50 ppm. It was found that maximum degradation of phenol was possible in a reasonable time (i.e.6hrs) when the dose of catalyst was 5 ml. The results of the photo catalytic activity under UV radiation shows maximum phenol conversion up to 99.5%.*

1. INTRODUCTION

Organic contaminants present in industrial waste water are of major concern with respect to public health. Phenol and phenolic compounds are important organic contaminants frequently found in various industrial effluents and reported in hazardous waste sites. They are released to the environment from effluents discharged by industries such as petroleum refining, coal tar, steel dye stuff, synthetic resins, coal gasification and liquefaction surface runoff from coalmines, by product of agriculture chemicals, paper and pulp mills, tanning, paint stripping and fibre board production operation.

According to environmental protection rules (1992) of control board of India, the discharge limit of phenol in inland water is 1 ml/l. There are several established ways for the removal of such contaminants the most widely used method is adsorption, oxidation, photo catalytic and biological method etc. Other applied method includes adsorption on activated carbon H_2O_2/UV, H_2O_2/UV/O_3, UV/O_3 and photo assisted fenton degradation techniques.[1-3] Advanced oxidation process (AOP$_S$) are near ambient temperature and pressure water treatment process which involve the generation of highly reactive radicals (especially hydroxyl radicals) in sufficient quantity to enhance water purification.[4] Hydroxyl radicals are extra-ordinarily reactive species that attack most of the organic molecules and these treatment processes are considered as very promising method for the remediation of contaminated ground, surface and waste water containing non-biodegradable organic pollutants.

Kinetic of reaction is generally first order with aspect to the concentration of Hydroxyl radicals and to the concentration of the species to be oxidized. Hydroxyl radical is powerful oxidants that can rapidly and non-selectively oxidize organic contaminants into carbon dioxide and water, and hence can degrade pollutants effectively.[5-8]. Matthew has reported that photo catalytic oxidation of aromatic compounds generally takes place through the hydroxylation mechanism involving ·OH radicals.[9]

Among the top priority pollutants, a phenol represents an important class of environmental water pollutants. Most chlorophenolic compounds presents in waste waters mainly arise from chemical intermediates or by product in petrochemicals, paper making, plastics, pesticide industries and also the conventional drinking water disinfection. Recent studies indicate that advance oxidation process such as sonication, ionizing radiation, combination of UV and hydrogen peroxide are able to destroy environmentally persistent pollutants, due to their ability to generate the highly oxidizing species, OH radical.[10] In the natural environment, phenol derivatives are toxic and refractory pollutants. Moreover, phenols are only partly biodegradable and therefore, they are not easily removed in biological waster water treatment plants. That is why there is need to develop effective methods for the degradation of these pollutants, either to less harmful compounds or to their complete mineralization.

Recently the application of AOP for the destruction of phenols has been intensively studied. These studies have been suggested a wide variety of AOP for the destruction of phenols such as the fenton and photofenton treatment, hydrogen peroxide photolysis, combination of ozone with ultraviolet (uv),and also combination of sonolysis and ozonolysis. These studies were mainly devoted to the degradation of phenol.

The degradation was studies mainly in batch reactors and with limited process parameters. In the present study, an attempt was made to degrade the known solution of phenol by UV

light and H_2O_2 as catalyst in a batch reactor and to find the optimal process conditions.

2. MATERIALS AND METHODS

2.1. Experimental Setup and Materials used

To carry out the photocatalytic degradation experiment of synthetic solution of phenol, a phtocatalytic system was used as shown in Fig. 1.1. It was a closed chamber of 3x2.5x2.5 feet[3]. A UV Bulb of 125 watt was used to provide the UV light and a magnetic stirrer was used to provide the continuous stirring to solution. Analytical grade H_2O_2 (30% w/v) was used as catalyst and crystalline Phenol, to prepare the synthetic solution of phenol, phosphate buffer solution, 4-aminoantipyrine ($C_{11}H_{13}N_3O$), potassium ferricyanide (K_3FeCN_6) and ammonium hydroxide (25% w/v) was supplied by Scientific Aid, Kanpur (India). All the solutions were prepared in distilled water. A spectrophotometer (spectronic 20) was used to measure the absorbance of treated solution of phenol.

To investigate the efficiency of UV/H_2O_2 process, three obvious variables of photo catalytic process were chosen namely concentration of phenolic solution (C), dose of photocatalyst H_2O_2 and reaction time (t).

The classical approach of experimental design was formulated as one variable at a time (OVAT). Table (1) shows the design matrix of input variables that were carried out.
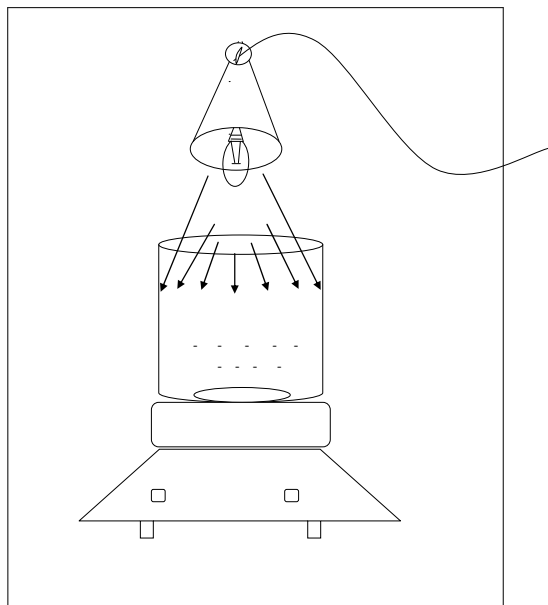

Fig. 1.1: Schematic diagram of photcatalytic system.

2.2. Method

A synthetic solution of phenol was prepared in distilled water and a measured volume of photocatalyst Hydrogen peroxide (H_2O_2; 30%) was added in the phenolic solution as the source of hydroxyl radicals. Before treating the blank solution with UV light, Absorbance of solution was measured and then blank mixture was placed in photocatalytic reactor to proceed the degradation reaction. During the experiments, sample of the reaction mixture were withdrawn at different reaction times to measure the absorbance of phenolic solution.

Analysis of treated solution was carried out by chemical method followed by the measurement of UV light absorbance with spectrophotometer. In chemical analysis step, phosphate buffer solution was added in the treated solution to adjust the pH and a quenching solution containing 4-aminoantipyrine ($C_{11}H_{13}N_3O$: 1ml) and potassium ferricynide (K_3FeCN_6:1ml) was added to stop the reaction. All reagents were analytical grade.

2.3. Photo Catalytic Reactor

Photo catalytic degradation was carried out in a specially designed Batch type reactor. All experiment were carried out in batch reactor (with dimensions of height=19.68cm, diameter=12.5cm and capacity= 2lit.) in the uv chamber equipped with one uv Bulb of 125W having wave length 500nm (Fig.1) measurement of uv light intensity was done by chemical method. Constant stirring of solution was ensured by using magnetic stirrer. The temperature was maintained constant through out the reaction time. The absorbance of the sample was recorded at 500 nm using uv- spectrophotometer (spectronic 20) while pH of the solution and analyzed by pH meter.

2.4. Analysis

Phenol was monitored spectrophotometrically by the antipyrine method. The method is based on the reaction of phenol with 4-aminoantipyrine in the presence of potassium ferricyanide at pH 7.9 to form a colored (AMPH) as shown below:
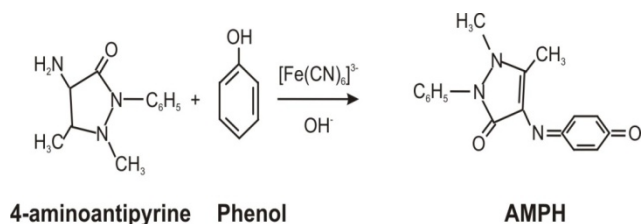

Fig. 2.1: Suggested PCD pathway of Phenol

Concentration of phenol in AMPH was estimated from the absorbance of the solution at 500nm using spectronic 20, spectrophotometer.

2.5. Procedure

The degradation experiments were carried out in uv light with fixed amount of catalyst H_2O_2 added to 100ppm of phenol solution in each trial. At different time intervals, aliquot was taken out with the help of pipette and then analysis with chemicals. For the determination of concentration of phenol,Shimazu, spectronic 20, spectrometer was used. The pH of the solution was varied by adding NH_4OH solution and measured using Naina, India NIG-333 pH meter hydroxide ion was determined by titrating with standard 4aminoantipyrine solution using potassium ferricynide as indicator. The rate of degradation was studied in terms of changes in absorbance. The percentage degradation was calculated as

$$\% \text{ Degradation} = \frac{100 (C_o - C)}{C_o}$$

Where C_o is initial concentration of phenol and C is the concentration after photo radiation.

3. RESULT AND DISCUSSION

Photo catalytic degradation of phenol has been studied under different concentration of phenol and doses of catalyst (H_2O_2) 1-5ml/l. The degradation experiments were performed with 100 ppm of phenol by using 1-5ml of catalyst and at pH 7.9.
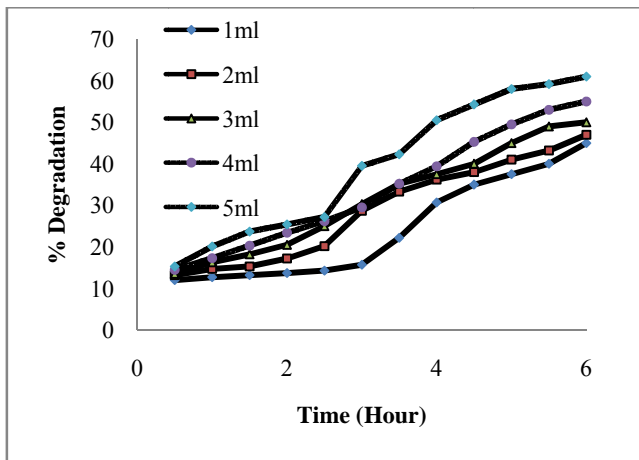

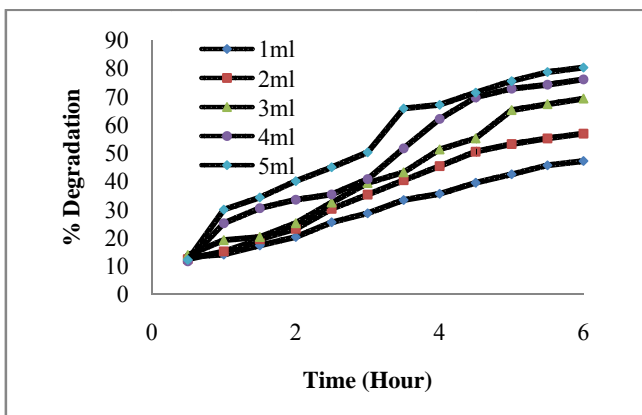**Fig. 3.1: Phenol degradation curve (50 ppm)**
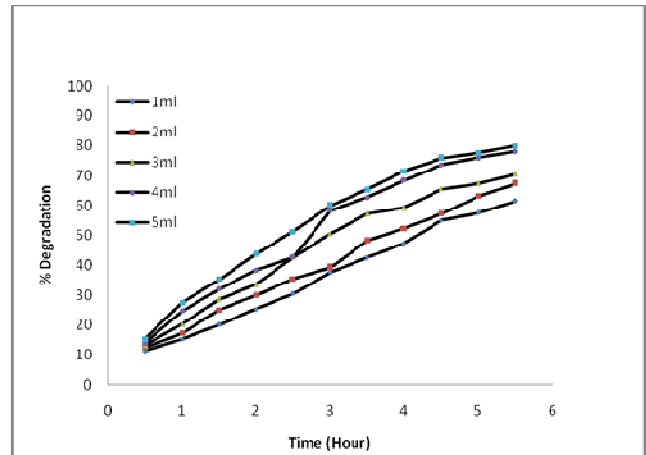

Fig. 3..2: Phenol degradation curve (40 ppm)

Fig. 3.3: Phenol degradation curve (30ppm)
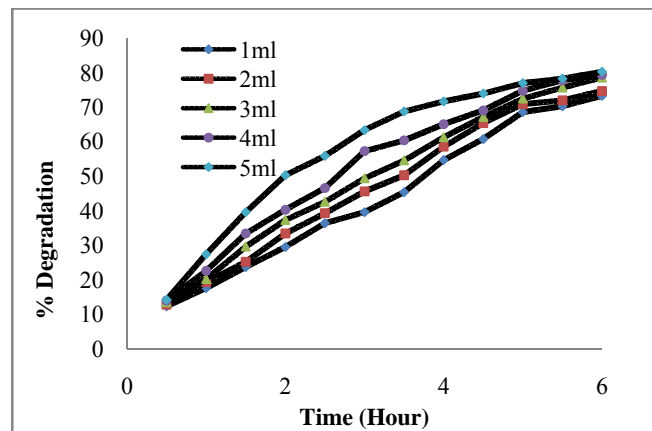

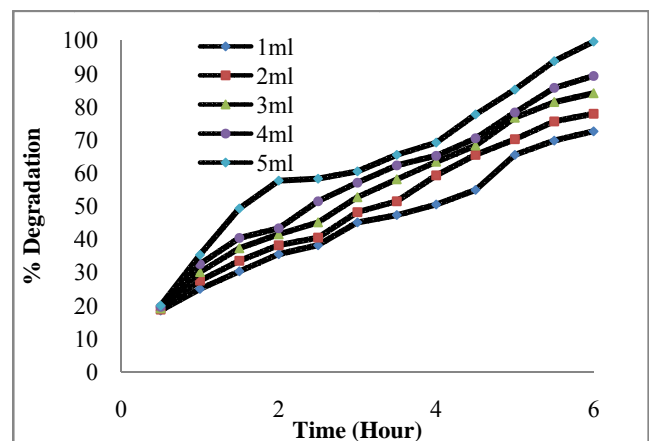**Fig. 3.4: Phenol degradation curve (20ppm)**

Fig. 3.5: Phenol degration curve (10 ppm)

The result shows that increases the concentration of H_2O_2 then the degradation is increasing as increases the doses of $H_2O_2.$ By the taking the time and temperature constant then can find in the graph.1 that the values of phenol degradation is changing with the values of $H_2O_2.$ If see all the graphs at different values of phenol (10, 20, 30, 40,50ppm) the value s

of degradation % is vary as the concentration of phenol increasing the concentration of H_2O_2, also the degradation % is increasing by taking phenol concentration constant. In graph 1,2,3,4 and 5degradation is minimum 10ppm of phenol and 1ml of H_2O_2 at constant time for 6hr and constant temperature (50 ^oC). Degradation is maximum 50ppm of phenol and 5ml of H_2O_2. If taking the concentration of H_2O_2 greater than 5ml then there is no changes occur in %degradation.

3.1. Effect of catalyst dose

The photo degradation of phenol was studied by varying the amount of H_2O_2 from 1-5ml. Fig. 3.1 to 3.5 shows the variation of initial rate of photo degradation of phenol as function of catalyst dose.

$$-(dx/dt) \; \alpha$$

The initial rate value indicates that the degradation rate increased with an increase in catalyst dose up to an optimum loading of 2-3ml. Therefore, increase in the catalyst dose showed no further increase in % degradation. This may be attributed to the fact that as the weight of the catalyst increased, the number of organic molecules adsorbed was increased, owing to an increase in number of (OH) hydroxyl radicals, there by enhancing the rate of photo degradation. Hydrogen peroxide is unstable as shown by the following equation:

$$H_2O_2 \longrightarrow H_2O \; (l) + ½ \; O_2 \; (g)$$

The reaction from left to right is a spontaneous process and is accompanied by a decrease of free energy. Hydrogen peroxide is a weak acid. For the equibrium,

$$H_2O_2 \longrightarrow H^+ + HO_2^-$$
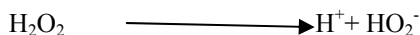
(Its dissociation constant is 1.5×10^{-12} at 20 ^0C)

3.2. Effect of concentration of oxidant

The rate of photo catalytic degradation was significantly improved by the addition of oxidant concentration in range 1m to 5ml, the rate constant enhanced up to concentration of 4ml. Beyond that the rate of degradation remained almost the same. Blank experiments were carried out by irradiating the aqueous solution of phenol in absence of photo catalyst using optimum concentration of oxidant. No observable loss of compound was noticed during irradiation.

3.3. Effect of concentration of phenol

The photo catalytic degradation of phenol at different concentration in the range 100ppm investigated under optimized conditions (catalyst dose: 1-5ml, pH 7.9). The time required for complete degradation increased from 3-6 hr. when the initial concentration was increased from 1-5ml. A decrease in the initial rate was observed with further increase in the initial concentration. A plausible explanation can be that since the initial concentration increases, more and more organic substances are adsorbed on the surface of H_2O_2, but the intensity of light and illumination time are constant. Fig.5 reported similar findings for the degradation of phenol.

4. CONCLUSIONS

The experimental results presented in this work showed that the application of this new photochemical reactor for the treatment of waste waters containing phenol was well succeeded. This reactor showed to be very promising for industrial applications because of its easy operational procedure and simple design. Further more, the use of uv lamp (violet light) result in an important advantage in the economical point of view in relation to usual uv radiation sources. The experiment results obtained in this work showed that the new photo chemical reactor developed (single lamp reactor) presented a satisfactory performance for the phenol photo degradation by batch process.

The study of the effect of the uv radiation, on the degradation increase with increase in catalyst dose up to an optimum loading. Further increase in catalyst dose show no effect. Also, the initial rate of photo degradation was high at low concentration and it increase with increase in initial concentration of phenol. The degradation of phenol was found to follow pseudo-first order kinetics. The apparent rate constant values obtained were found to decrease with increase in the initial concentration.

5. ACKNOWLEDGEMENT

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