

Advanced Oxidation Process to Enhance Removal Efficiency of Phenol Using a Combined Catalyst (TiO₂ and ZnO)

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Abstract: Batch study was done for finding certain parameters using advanced oxidation process which is one of the methods for the removal of pollutants without generating secondary pollutants. Main parameters needed were optimum initial adsorption time, optimum time, optimum dosage required for degradation of phenol. Optimum time was done for varying time. Optimum dosage was done for varying catalyst dosage to get the amount of catalyst needed for maximum removal efficiency of phenol. Along with these parameters removal efficiency was found with varying initial concentration of phenol. Optimum initial adsorption time was found to be 20 min for 10mg/L with 1g/L if catalyst, optimum time for removal of 10mg/L conc. phenol was found to be 420 min, optimum dosage was found to be 1.5g/L, efficiency of removal of phenol was observed to be 86%. Kinetic of the reaction gave the data about order of reaction as one and specific reaction rate constant as 0.24h⁻¹. It was also observed that the removal efficiency of phenol is very high with combined catalyst compared to TiO₂.

Keywords: Phenol Advanced oxidation process; optimum initial adsorption time; optimum time; optimum dosage; Kinetics.

I. INTRODUCTION

Environmental pollution, especially with the hazardous and recalcitrant chemicals, is one of the major problems faced by the developing countries like India.¹ Phenol is one of hazardous pollutant that is released from industries. It is released mainly from petroleum refineries and pharmaceutical industries. In petroleum refineries phenol is released from various stage of refining of crude oil. Phenol is generated from vacuum distillation, catalytic hydro treating, catalytic cracking and various treating and solvent processes. The average phenol content in the untreated effluent from a refinery is found to be 12-30mg/L. The effluent standards allow only 0.35mg/L (Central Pollution Control Board) of phenol to be discharged. Aquatic life is affected because of release of phenol into the river streams. According to GHS (Globally Harmonized System of Classification and Labeling of Chemicals) hazard statements, Phenol is toxic if swallowed and when contact with skin. Causes severe skin burns and eye damage. Suspected of causing genetic defects. May cause damage to organs through prolonged

or repeated exposure. As it is an important factor that there should not be any secondary treatment for the removal of pollutants on waste water. Many works are being conducted in this point of view. Advanced oxidation process is one of the methods for the removal of pollutants without generating secondary pollutants. In AOP pollutant finally degrades into carbon dioxide and water. Advanced oxidation processes (AOP) are used to oxidize complex organic compounds found in waste water that are difficult to degrade biologically into simpler end products.^{2,3} When chemical oxidation is used, it may be necessary to oxidize completely the given compound. In many cases partial oxidation is sufficient to render specific compounds more amenable to subsequent biological treatment to reduce their toxicity. The main objectives of the present work were to study the extent of removal of phenol using a combination of two catalysts TiO₂ and ZnO. Batch study was done for finding certain parameters. Main parameters needed were optimum initial adsorption time, optimum time, optimum dosage required for degradation of phenol. Optimum time was done for varying time. Optimum dosage was done for varying catalyst dosage to get the amount of catalyst needed for maximum removal efficiency of phenol and to find out the kinetics of reaction taking place in the reactor. Along with these parameters removal efficiency was found with varying initial concentration of phenol.

II. MATERIALS AND METHOD

A. Preparation Of Phenol Solution For Experimental Study

Phenol of 1000 mg/L of initial concentration was prepared by mixing one gram of phenol in 1L of deionized water. From that required concentration of phenol was prepared. Synthetic phenol solution was prepared. From that phenol of required concentration was prepared. This phenol solution was taken into the reactor. Catalyst was added to it. An aerator with bubbler was immersed into the solution. UV lamp was immersed into the reactor. The final concentration of phenol was estimated by 4-amino antipyrine colorimetric method and analyzed using UV-Vis spectrometer.

B. Initial adsorption time for adsorption of phenol on the surface of catalyst

Phenol of 10 mg/L was taken into the reactor. One gram of catalyst was added to it and it was kept for aeration. Samples were collected for every 5 min. Samples were centrifuged at 5000 r.p.m. for 30min for the settlement of catalyst. Samples were analyzed for finding the concentration of phenol in it.

C. Optimum time for the degradation of phenol

10 mg/L of phenol and 1g of catalyst were taken into the reactor. Aeration was done up to initial adsorption time. After that UV lamp was switched on. Aeration was done continuously for the supply of oxygen. After that samples were collected for different time intervals. Samples were centrifuged and analyzed for finding concentration of phenol.

D. Optimum catalytic dosage needed for degradation of phenol

10 mg/L of phenol was taken into the reactor. Different catalyst loadings of 0.75, 1, 1.5,2 g/L were taken. Experiment was run for each time with each catalytic loading for optimum time. After reaching optimum time samples were taken and analyzed for final concentration of phenol.

E. Efficiency of removal for varying initial concentration

Phenol of different concentrations 5, 10, 15, 20 mg/L were taken into the reactor. Optimum catalyst dosage was added. For each concentration of phenol experiment was conducted till optimum time. Samples were collected and centrifuged at 5000 r.p.m. for 30 min. centrifuged samples were analyzed for getting final concentrations of phenol.

F. ESTIMATION OF PHENOL

For estimation of phenol 4-amino antipyrine method was used. to the sample ammonium hydroxide was added and pH was adjusted with phosphate buffer to 7.9. 4-amino antipyrine and potassium

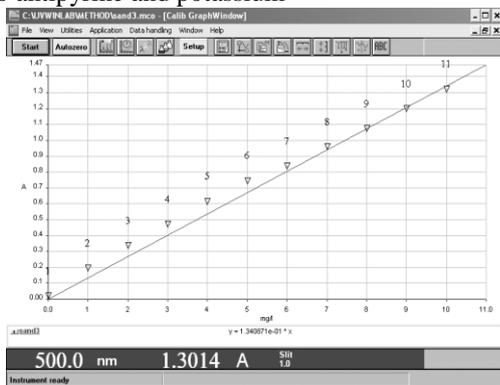


Fig 1 Standard graph for the estimation of given phenol

Ferro cyanide were added to the pH adjusted solution. In the presence of potassium ferrocyanide 4- amino antipyrine reacts with phenol and forms colored antipyrine dye. After addition of each compound mixing was done. After addition of all these, sample was kept in dark to avoid reaction of light. The concentration of

sample was measured by UV-VIS spectrometer. Before finding the concentration using spectrometer come preliminary work was done. 0,1,2,3,4,5,6,7,8,9 and 10 ppm concentrations of phenol standards were prepared. For each ppm of phenol all the above process was done for colour development. A standard graph was obtained for concentration and absorbance (Figure 1).

KINETICS

Kinetics of the reaction was done for finding the order of reaction and specific reaction rate constant of the reaction. Differential method of analysis of data was done for finding order and reaction rate constant of reaction. That was explained as given below.⁴ Initially a graph was drawn between the remaining concentrations at particular time Vs time. After that a smooth curve was drawn between Conc. Vs time. It was not needed to pass through all the points. Equation for that smooth curve was found. By using that equation time was found for particular conc. Then derivative of curve was found at a particular point of time.

Rate of equation is

$$r = -\frac{dC}{dt} = kC^n \dots \dots \dots (1)$$

Taking log on both sides for the given equation

$$\ln\left(\frac{dy}{dx}\right) = \ln k + n \ln C \dots \dots \dots (2)$$

Where, r is the rate of reaction

C is the concentration

remaining at time 't'

K is the specific

reaction rate constant

n is the order of the

reaction

III. RESULTS AND DISCUSSION

A. Optimum Initial Adsorption Time

Optimum adsorption time gives the information about the time needed for the adjustment of catalyst to the given conditions.⁶ One liter of phenol of 10ppm solution was taken for finding optimum initial adsorption time

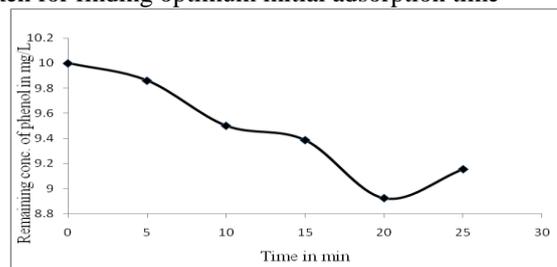


Fig 2 Adsorption of phenol with varying time for 10mg/L of phenol with 1g/L of catalyst loading

From the Figure 2, it is clear that the optimum time for adsorption was 20min. Up to 20 min remaining concentration of phenol is decreasing and later it is increasing. Increase in phenol concentration might be due to desorption of phenol on catalyst sites.

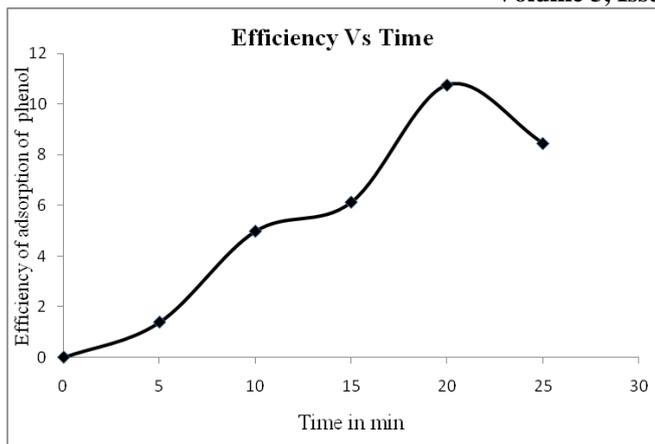


Fig 3 Efficiency of adsorption of phenol with varying time for 10mg/L of phenol with 1g/L of catalyst dosage

In Figure 3, it is shown that the efficiency of adsorption of phenol is high after 20 min of aeration.

B. Optimum Time for the Degradation of Phenol

Optimum time needed for the elimination of extra power consumption to run the experiment. It gives the minimum time needed for maximum removal efficiency of phenol of given specific concentration.

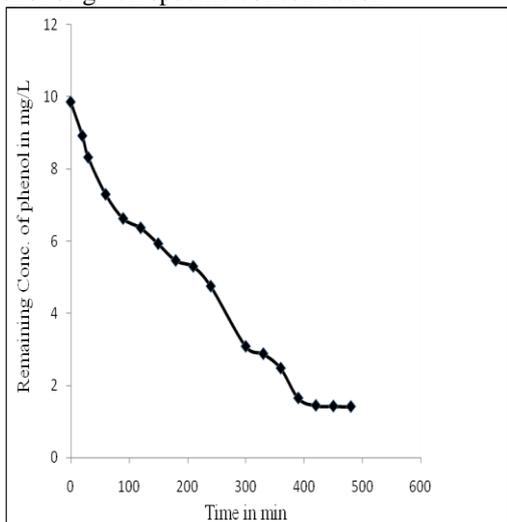


Fig 4 Removal concentration of phenol with varying time for 10mg/L of phenol with 1g/L of catalyst dosage

Figure 4 shows remaining concentration with varying time for 10 mg/L of phenol with catalyst dosage of 1g/L. From the graph it is clear that after 420 min reduction in concentration of phenol got stabilized and no appreciable increase in removal efficiency does seen.

From the Figure 5, it is clear that after 420 min (including initial adsorption time) reduction in concentration of phenol is very less. Efficiency obtained at 420 min was 85.66%. It may due to the fact that availability of less concentration of phenol. There may be a chance of overlapping of catalyst particles. There may be a chance of blockage of light to pass through the catalyst to reach the catalyst particles which were adsorbed the phenol.

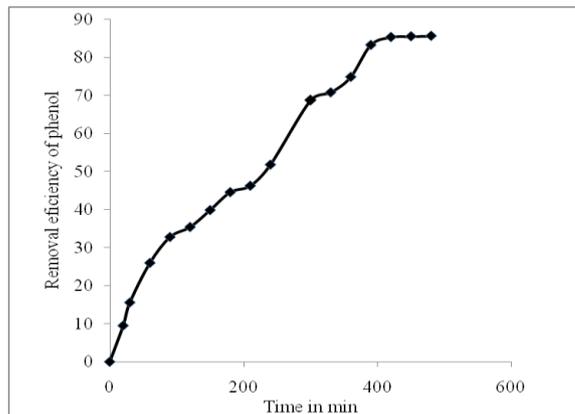


Fig 5 Variation of Removal efficiency of phenol with varying time for 10 mg/L of phenol with 1g/L of catalyst dosage

C. Optimum Catalytic Dosage

Catalyst of low concentration leads to the presence of less no. of active sites for the adsorption of phenol. Presence of more amount of catalyst blocks the passage of light.⁸ Optimum catalyst dosage needed to eliminate these problems. In Figure 6 the variation in removal efficiency with varying catalytic dosage (0.75,1,1.5,2 g/L) is shown for 10 mg/L Concentration of phenol. From the Figure 6, it is clear that for 1.5 g/L of catalyst dosage efficiency of removal of phenol was more. It may be due to the presence of optimum number of catalytic sights required for the removal of phenol.⁷

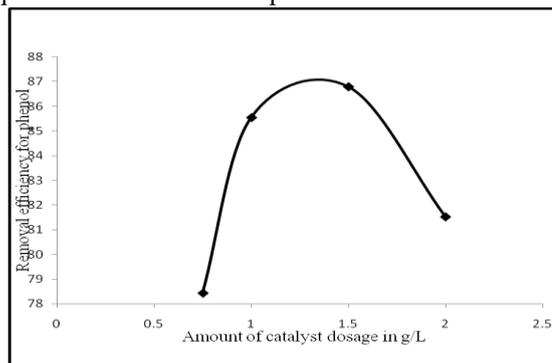


Fig 6 Variation in efficiencies for varying the amount of catalytic dosage (0.75, 1, 1.5, 2g/L) for 10mg/L of phenol.

Table.1 Gives the information about the removal efficiency of phenol with varying catalytic dosage. Removal efficiency is 86.65% with catalyst loading of 1.5g/L.

Table 1: Removal efficiency of phenol with varying catalyst dosage

Dosage of catalyst used for 10mg/L of phenol in g/L	Removal efficiency of phenol
0.75	78.44%
1	85.55%
1.5	86.65%
2	81.53%

D. Efficiency for Varying Initial Concentration Of Phenol

Efficiency for varying initial concentration of phenol was done to know the removal efficiency of phenol for particular initial concentration of phenol. Table.2 gives the efficiency of removal of phenol with different initial concentrations (5,10,15,20 mg/L) of phenol with 1.5g/L of catalyst dosage.

Table 2: Removal efficiencies for various initial concentrations of phenol

Initial concentration of phenol taken	Efficiency of removal of phenol
5	84.27
10	86.70
15	88.86
20	90.14

From Table. 2 it was clear that efficiency varies from 84.27% to 90.14% for initial concentration range of 5 to 20 mg/L. The variation of efficiencies for phenol with varying time for initial phenol concentrations of (5,10,15,20 mg/L) is given in the Figure 7. From this Figure it is clear that initial adsorbed concentration of phenol decreases for the increase in initial concentration of phenol. It may be due to the availability of less catalyst sites when concentration was more.^{5,6} From the Figure 7, it is clear that the removal efficiency of degradation of phenol increases with increase in initial concentration of phenol. It may be due to the presence of sufficient concentration of phenol after degradation was taken for certain time. So phenol was easily adsorbed by the catalyst and degradation may takes place. There were some cases where The removal efficiency of contaminant was increased with up to certain extent in increase of initial concentration. After that efficiency will decrease.^{8,9}

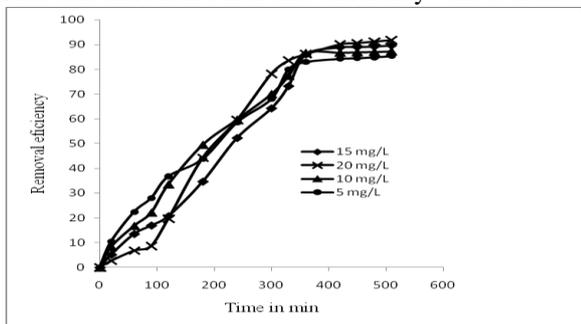


Fig 7 Removal efficiency of various initial concentrations of phenol

KINETICS

For the given reaction the relation between the rate of reaction and kinetics was given by kinetics of the reaction. In Figure 8, the trend of variation of concentration of phenol with varying time is observed. This is the smooth curve obtained from the Figure 4. From the Figure 8, time for the removal of various concentrations were found and derivative of the curve at that time values were found. $-dC/dt$ and at particular

concentration was obtained. Graph drawn between $\ln\left(-\frac{dy}{dx}\right)$ and $\ln C$.

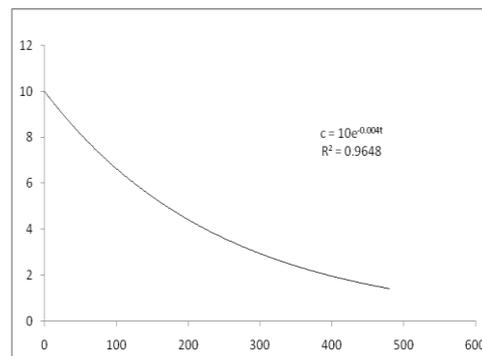


Fig 8 Smooth curve between Conc. With varying time

Figure 8, shows the graph drawn between $\ln\left(-\frac{dy}{dx}\right)$ and $\ln C$. Order of the reaction 'n' was found from the slope of the line and rate of the reaction was found from the intercept .

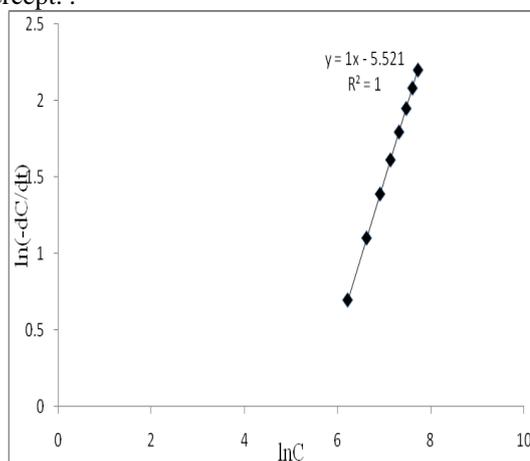


Fig 9 ln(dC/dt) Vs ln C for finding kinetic parameters

From the Figure 9, it is clear that order of the reaction $n=1$

And $\ln k = -5.5215$ $k = 3.9998 \times 10^{-3} \text{ min}^{-1}$
 $= 0.24 \text{ hr}^{-1}$

From Table.3. the order of the reaction was one and specific reaction rate was 0.24 h^{-1}

Table 3: Kinetics of the reaction taking place in the reactor

order	Specific reaction rate
1	0.24 r^{-1}

IV. CONCLUSION

Optimum initial adsorption time was found to be 20 min for 10mg/L with 1g/L if catalyst. After 20 min desorption will occur. Optimum time for removal of 10mg/L conc. phenol was found to be 420 min including initial adsorption time with catalyst loading of 1g/L. After 420 min removal is very less. Less efficiency may be due to the presence of less concentration after 420 min. Optimum dosage was found to be 1.5g/L. Efficiency of

removal of phenol was observed to be 86%. Less than 1.5g/L leads to the insufficient binding sites and greater than this leads to blockage of UV light. Increase in initial concentration increases the efficiency of removal and decreases initial adsorbed concentration of phenol. Efficiency of removal of phenol was more due to the presence of sufficient concentration after certain time. Kinetics of the reaction gave the data about order of reaction as one and specific reaction rate constant as 0.24h^{-1} .

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