

Photochemical Oxidation of Phenol and Chlorophenol by UV/H₂O₂/TiO₂ Process : A Kinetic Study

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Abstract—In the present work, the photochemical oxidation of phenol and chlorophenol aqueous solutions in a batch recycle photochemical reactor using ultraviolet irradiation, hydrogen peroxide and TiO₂ (as photocatalyst) was studied. The study showed that the combined treatment process was the most effective process under acidic conditions and showed a higher rate of degradation of phenol and chlorophenol at a very short radiation time. The reaction was found to follow the first order kinetics and was influenced by the pH, the input concentration of H₂O₂ and the dosing amount of the TiO₂ photocatalyst. The results indicate maximum 74.6% and 79.8% degradation of phenol and chlorophenol respectively within 90 minutes of radiation time. The experimental results showed that the optimum conditions were obtained at a pH value of 4, with H₂O₂ concentration ranging from 200-550 ml/L, and TiO₂ dosing ranging from 1-2 g/L for UV/H₂O₂/TiO₂ combined system. Finally a rough comparison of energy consumption shows that UV/H₂O₂/TiO₂ process reduced the energy consumption by 40-50% compared with the UV/H₂O₂ and UV/TiO₂ processes.

Index Terms—Photochemical oxidation; Degradation of Phenol and Chlorophenol; UV/H₂O₂/ TiO₂ system; Pseudo-first-order kinetics.

I. INTRODUCTION

Environmental regulatory requirements have become more stringent because of increased awareness of the human health and ecological risks associated with environmental contaminants. Ever increase in living standards led to setting up of various processing plants which contributes remarkably to the wastewater volumes. The focus on waste minimization and water conservation in the recent years resulted in the discovery of various treatment processes, one of them being Advanced Oxidation Processes. These refer to the chemical treatment processes which follow oxidation route and are particularly employed to degrade biologically toxic and non degradable chemicals [1]. Photocatalytic degradation oxidizes harmful environment pollutants and converts it into harmless innocuous substances.

Many processes such as chemical oxidation, Fenton and photo-Fenton processes, ultraviolet (UV)-based processes, photocatalytic redox processes, supercritical water oxidation, sonolysis, and electron beams and γ -ray irradiation come

under advanced oxidation techniques [1]. High energy requirement of photo oxidation with ozone and hydrogen peroxide is a major disadvantage when the organic or inorganic pollutants of wastewater strongly absorb UV-radiation. Waste disposal is a major issue in photo fenton process due to the production of inorganic sludge [2].

Phenol and Chlorophenol are put up under priority pollutants by U.S.EPA due to their high toxicity, carcinogenicity, and persistence [3,4] and hence required to be degraded. There are number of articles available on the oxidation of phenol and chlorophenol using UV/ H₂O₂, photo-Fenton process or photocatalysis [5-10] but very few have been studied on the oxidation of phenol and chlorophenol using UV/H₂O₂/TiO₂ combined system. In recent years the combination of solar irradiation and Fenton reagent have been used to enhance the biodegradability of chlorophenol wastewater [11]. Advanced photochemical oxidation technologies were investigated for degradation of phenol in olefin plant effluent. The study shows that the Photo-Fenton process, (a mixture of hydrogen peroxide and ferrous or ferric ion), was the most effective treatment process under acidic conditions and produced a higher rate of degradation of phenol at a very short radiation time [12]. In this study, Photocatalytic degradation rates of phenol and p-chlorophenol have been examined in the presence of TiO₂ and/or H₂O₂ under UV illumination. Effects of the pH, concentration of H₂O₂ and the dosing amount of the TiO₂ photocatalyst on degradation rate were also evaluated.

II. EXPERIMENTAL

A. Reagent

Phenol and p-Chlorophenol (CP) were purchased from Merck, India. Hydrogen peroxide solution (30% w/v) in stable form was purchased from Finar Reagents. Photocatalyst (TiO₂) and all other chemicals obtained were of reagent grade quality and were used as received. Solutions were prepared using doubly distilled, deionized water.

B. Experimental Setup

All experiments were performed in a batch reactor. The schematic diagram of the experimental set-up used in the study is shown in Fig. 1.

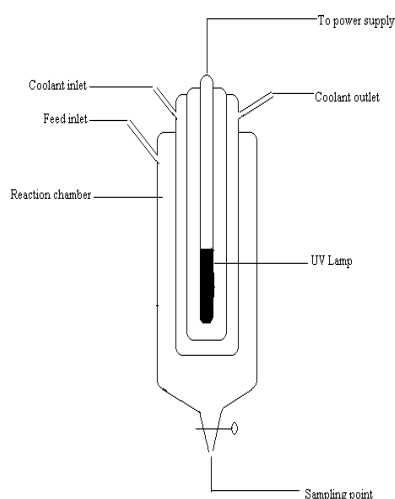


Figure 1: Experimental set up

The reactor was cylindrical with 250 ml volume and was made from quartz glass which was available for the transfer of the radiation. Irradiation was achieved by using UV lamp of 125W (medium pressure lamp) which was immersed in the glass tube. The UV lamp was equipped with a cooling water space which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system. Mixing was accomplished using air bubbler to keep the photocatalyst in suspension

C. Photodegradation Process

For each experiment, synthetic aqueous solution of 50-200 mg/l phenol and p-chlorophenol was prepared separately in ultrapure deionized water. The laboratory unit was filled with 100 ml of the solution. For runs using UV/H₂O₂ system, hydrogen peroxide at different volumes was injected in the reactor before the beginning of each run and for runs using UV/TiO₂ system, TiO₂ in different amounts were used into the solution before the beginning of each run. The pH value of the solution was adjusted by the addition of HCl and NaOH solution. The suspended TiO₂ solution was mixed very well using stirrer for 30 minutes so that adsorption equilibrium was reached. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment. Air was bubbled into the solution throughout the experiment for the continuous supply of oxygen.

D. Analytical Methods

Samples were taken at every 15 minutes time interval from the reaction vessel and pipetted into test tubes. The samples were immediately analyzed to avoid further reaction. Concentration changes of phenol and p-chlorophenol were determined by UV-vis spectrophotometer.

III. RESULTS AND DISCUSSION

The effect of pH was evaluated by taking a random amount of oxidant (H₂O₂ = 75ml/L) and photocatalyst (TiO₂ = 0.5g/L) and substrate concentration of 50 mg/L. After 90 minutes of

irradiation the samples were analyzed and the percent degradation was found to be 68.2%, 50.7% and 39.1% for phenol at pH 4, 7 and 9 respectively and 70.4%, 55.7% and 42.3% for p-chlorophenol at pH 4, 7 and 9 respectively.

The results revealed a maximum efficiency at acidic pH. This may be because of acidic pH makes the photocatalyst surface positively charged hence attracts the pollutant molecule leading to greater adsorption and hence higher degradation rate. At basic pH, the photocatalyst surface becomes negatively charged and hence low degradation rate. So keeping feed solution pH 4, the optimum amounts of oxidant and photocatalyst was calculated.

A. Effect of initial H₂O₂ concentration

Oxidant concentration greatly influences the rate of photocatalytic oxidation. To evaluate this effect, experiments were performed at different concentrations of H₂O₂ maintaining acidic feed phase (pH at 4.0) and a fixed concentration of pollutants. The H₂O₂ concentration was varied from 100-650 ml/L and the pollutant concentration from 50-200 ppm for both phenol and p-chlorophenol. Fig. 2 and Fig. 3 clearly indicate the effect of H₂O₂ concentration on degradation efficiency of UV/H₂O₂ process. For both phenol and p-chlorophenol, with the increase in H₂O₂ concentration, the percent degradation increased till optimum condition is reached (200-550 ml/L).

Further increase in H₂O₂ concentration lowered the degradation rate. This is because of the excess H₂O₂ reacts with the hydroxyl radicals earlier formed and hence acts as an inhibiting agent of degradation by consuming the hydroxyl radicals responsible for degrading the pollutant molecule [8].

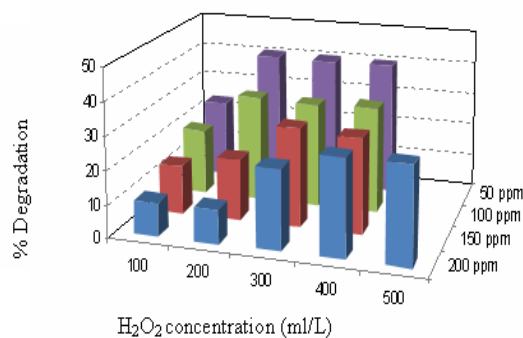


Figure 2: Effect of H₂O₂ concentration on phenol degradation

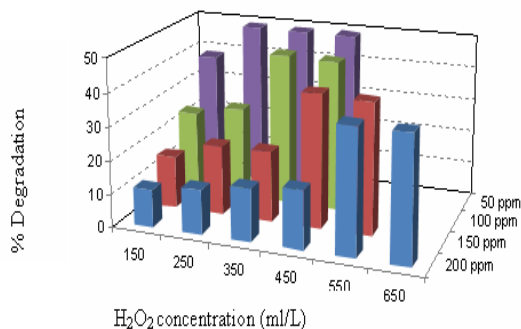


Figure 3: Effect of H₂O₂ concentration on p-chlorophenol degradation

B. Effect of dosing amount of TiO₂ photocatalyst

To determine the effect of catalyst loading on the reaction

rate, several experiments were conducted at catalyst loading from 1.0-2.5 g/L (feed phase pH at 4) and pollutant concentration from 50-200 ppm for both phenol and p-chlorophenol.

Fig. 4 and Fig. 5 clearly indicate that the increase in amount of catalyst loading increases the rate of degradation up to a certain catalyst amount. The increase in degradation rate may be explained by the fragmentation of catalyst which produces higher surface area. Thereafter with further increase in catalyst loading the degradation rate starts declining. This nature is due to the screening effect i.e., above a certain amount of catalyst loading, the turbidity of the solution increases and ultraviolet rays start getting scattered, hence reducing the optical path [13]. This lowers down the rate of degradation above an optimum catalyst loading (1-2 g/L).

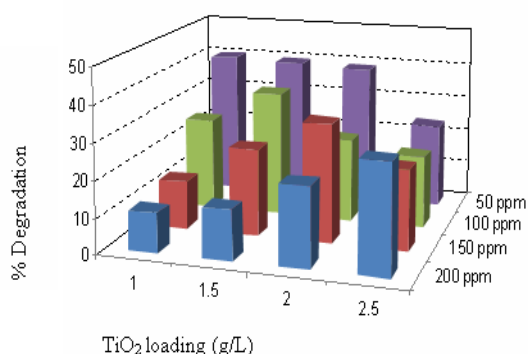


Figure 4: Effect of TiO₂ loading on phenol degradation

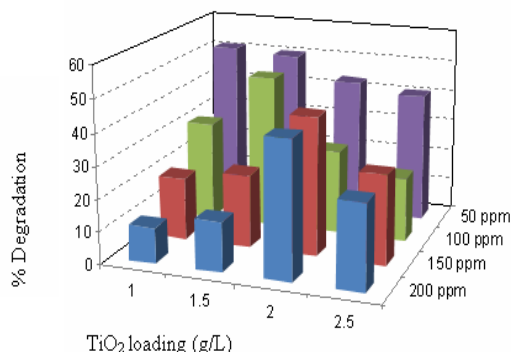


Figure 5: Effect of TiO₂ loading on p-chlorophenol degradation

C. Degradation Rate Kinetics

The kinetics study of photodegradation of phenol and p-chlorophenol was investigated for UV/H₂O₂/TiO₂ systems. The loss of phenol and p-chlorophenol was observed as a function of irradiation time and data were fitted to a first-order rate model (Fig. 6 & 7).

$$\ln(C_t/C_0) = -k t \quad (1)$$

where C_0 and C_t are the concentration of pollutant at irradiation times 0 and t , k is a first-order rate constant (min^{-1}) and t is the irradiation time (min).

For both compounds, first order reaction was found to have maximum value of R^2 as compared to the second order. Hence kinetic constant based on phenol and CP degradation by UV calculated for first order reaction. Fig. 6 and Fig. 7 give the first order plot for phenol and CP respectively.

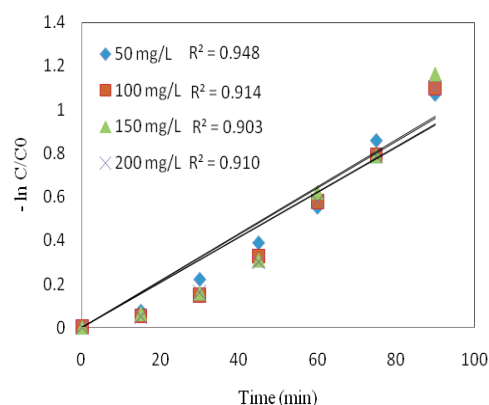


Figure 6 : Phenol degradation rate kinetics for UV/H₂O₂/TiO₂ process at concentrations 50 – 200 mg/L

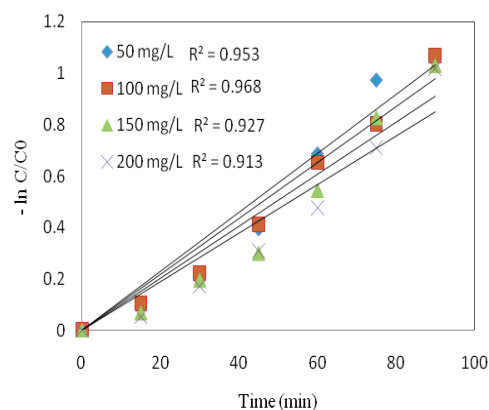


Figure 7 : CP degradation rate kinetics for UV/H₂O₂/TiO₂ process at concentrations 50 – 200 mg/L

TABLE 1: RATE CONSTANT DATA FOR UV/H₂O₂/TiO₂ PROCESS

Substrate	Concentration(mg/L)	k (min ⁻¹)
Phenol	50	0.0143
	100	0.0132
	150	0.0135
	200	0.012
p-Chloropheno	50	0.0119
	100	0.0103
	150	0.0099
	200	0.0086

D. UV/H₂O₂/TiO₂ process

Lastly using an optimum amount of H₂O₂ (oxidant) and TiO₂ (photocatalyst) phenolic wastewater (synthetic feed mixture) was irradiated under ultraviolet rays for initial pollutant concentrations varying from 50-200 ppm. The application of both oxidant and photocatalyst enhances the degradation mechanism and hence gives much higher removal. The combined process gave a maximum of 74.6% and 79.8% degradation for phenol and p-chlorophenol respectively.

E. Energy consumption

Energy consumption for different systems used was studied and compared (Fig.8). It was observed that the highest amount of energy was consumed by UV/H₂O₂ system as

compared to UV/TiO₂ and UV/H₂O₂/TiO₂ systems for same irradiation time.

$$\text{Daily consumption (KWh)} = \text{Wattage} \times \text{hours used per day} \times 1000$$

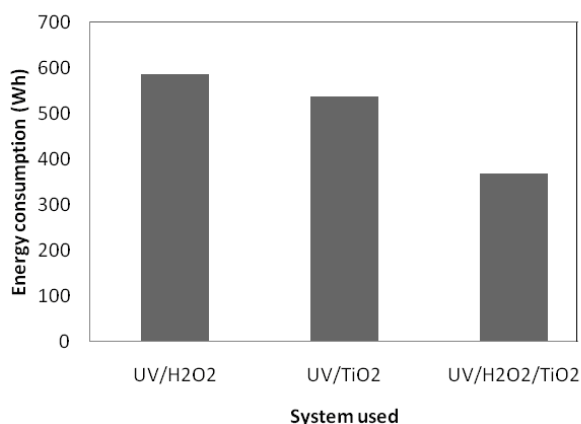


Figure 8: Energy consumption by different processes at optimum conditions

IV. CONCLUSION

This study showed the potentialities of photocatalytic degradation in water purification. Out of different processes employed, a significant enhancement of the photocatalytic activity was observed in the system using combination of oxidant and photocatalyst irradiated under UV light. Concentration of both oxidant and photocatalyst greatly influences the degradation rate. Also the process was observed to be strongly pH dependent. The degradation follows first order kinetics. Photodegradation can be a recommended approach for the treatment of phenolic wastewaters. Keeping in view all the factors, it can be easily said that the combined system is an efficient one amongst all other processes.

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