

Solar Induced Photo Degradation of Phenol Using Titanium Dioxide as Catalyst

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The present study investigates the photo degradation of phenol using titanium dioxide as catalyst. The key focus is on the utilization of solar radiation in treating phenolic waste for degradation after discounting for evaporation due to solar heat. Titanium dioxide was observed to be good catalyst in solar radiation induced degradation of phenol. The optimum time for initial adsorption by TiO₂ was observed to be 30 minutes. The optimum contact time and dosage were found to be 8h and 3 g/L for initial concentrations of 25ppm and 100 ppm with a removal efficiency of 98 % and 70%. The study reveals that the thermal degradation of phenol does not take place under the conditions of experiment and maximum degradation of phenol is due to the photocatalytic process only.

Key words: *Evaporation, photocatalysis, solar radiation, phenol, titanium dioxide*

Introduction

The phenomenal growth in population and subsequent increase in the necessities led to industrial revolution. The wide variety of industries generate toxic waste products (Paradesi and Patil, 2008; Shanmuga Priya *et al.*, 2008; Sarvanan *et al.*, 2009). The effluents of these industries often contain aromatic compounds which are resistant to natural degradation and often an integral part of these effluents persist in the environment (Dorian *et al.*, 2009; Paradesi and Patil, 2008). Phenol is one of the major organic pollutants found in industrial wastewaters (Paradesi and Patil, 2008; Shanmuga Priya *et al.*, 2008; Sarvanan *et al.*, 2009; Dorian *et al.*, 2009; Movahedian *et al.*, 2009). The effective concentration of phenol in the wastewater is found to range from 10–20000 ppm, production and processing industries are recycling or extracting the phenol and related compounds while coke processing unit effluents release phenol concentration of 100–500 ppm (Polat *et al.*, 2006; Shanmuga Priya *et al.*, 2008; Movahedian *et al.*, 2009).

The existence of these tainted macrobiotic compounds in wastewater bilge water is a major barrier

(Mahmoodi *et al.* 2007). Due to their stability and bioaccumulation, they remain in the environment for longer period (Wang *et al.*, 1999). High toxicity and carcinogenic character of substrate causes lot of stress on the eco-system (Gracia and Coca 1989).

As per Hazardous Wastes (Management and Handling) Amendment Rules, 2000, phenol and phenolic compounds are classified under category of Class B (B-19) of Schedule-II in the hazardous waste list. The discharge limit in inland water as per IS: 2490–1974 is 1 mg/L and in public sewers as per IS: 3306–1974 is 5.0mg/L. Photocatalysis is one the advanced oxidation processes (AOPs) for treating phenolic wastewaters. Oxidizing hydroxyl radicals generated during the photocatalytic process degrade the pollutant in wastewater. Semiconductor assisted photo degradation is widely applied in the present scenario. Titanium dioxide (TiO₂) is having a wide band gap i.e., 3.2eV proving it to be a successful semiconductor photocatalyst treating organic pollutants¹⁻⁵. Utilization of solar energy for the production of hydroxyl radicals is one of the best photo catalysis methods. In this process the near UV light induced excites titanium dioxide catalyst to produce the oxidizing radicals in

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the presence of atmospheric oxygen. These radicals react with the substrate developing heterogeneous photocatalytic reactions leading to degradation of the substrate (Sayed Javid Royae and Morteza Sohrabi, 2010, W. Liu *et al.*, 2009, M. Muruganandham *et al.*, 2006, D. Vione *et al.*, 2005, E. Forgacs *et al.*, 2004, O. Carp *et al.*, 2004, Hadaj *et al.*, 2004, Chen, L. Lei and P.L. Yue, 1999, Mills, A and S. Le Hunte, 1997).

In the past few years, a number of studies and reviews were carried on photocatalytic process using various types of catalysts, semiconductors and reactors (Bahnmann, 2004; Amat *et al.*, 2005; Parida and Parija, 2006; Sarvanan *et al.*, 2009; Royee and Sohrabi, 2010; Shamaila *et al.*, 2010; Devipriya and Suguna 2010). Titanium dioxide is being used as a photocatalyst in the present study as it is economical, durable, hydrophilic and its ability to degrade a wide range of organic compounds (Lianfeng Zhang *et al.*, 2003; Rahmani *et al.*, 2008; Shamaila *et al.*, 2010). The studies focus on to investigate the efficiency of solar induced photocatalytic degradation by varying the pH, exposure time, catalytic dosage, substrate concentration mainly focusing on the operating conditions for the photocatalytic reactor.

Study area

The area of study, Tiruchirapalli (10°49'N 78°41'E/ 10.81, 78.69), is an industrial, commercial and educational hub of Tamil Nadu, India located in the central part of State situated on the banks of River Cauvery with historic monuments like Rockfort, Ranganadha Temple. With a flat topography and humid climatic conditions the mean average temperature varies from 40°C in summer to 18°C in winter. The predominant wind direction is SW and NE with a mean annual rainfall of 650mm maximum, from August to October. It is a densely populated area with a 145 sq. km cover and 8.5 lakh of population.

Materials and methods

For the batch studies the catalyst titanium dioxide (assay 99%) and the phenol (assay 99.5) of Ranbaxy Chemicals, 4-amino antipyrine and other chemicals of laboratory grade with high purity were used. The distilled water for the experiments was prepared using the ion exchange unit.

The evaporation test was conducted in a pan having dimensions (60 x 40 x 5 cm). The test was performed based on IS: 5973-1998 (reaffirmed 2003) Codal provisions. The depth of the water level was

maintained at 4.5cm and the temperature of water and atmosphere were noted using thermometers. The water level and temperature readings were noted at every hour interval from morning 7:00 A.M. to evening 5:00 P.M. The test was conducted for a period of 100 days from 20th February to 31st May, 2011. The maximum temperature recorded was 36°C and minimum temperature was 23°C, total numbers of sunny days were 48, partly cloudy days were 26, cloudy days were 20 and 6 days were excluded due to rain and average humidity was found to be 60%.

The degradation studies were conducted in a batch reactor with a capacity of 1000mL in which the phenol solution was stirred with a magnetic stirrer at 120 RPM. The reactor was placed in sunlight for UV in the months of February to May between 7.30 A.M to 5.30 P.M. The optimum TiO₂ dose was added to the system which was stirred for 25 minutes in a closed chamber for effective mixing of the catalyst in the solution. The photo degradation experiments were carried out in an ambient temperature (24°C-39°C). The pH of solution was adjusted to desired pH (6.9±0.1) by adding H₂SO₄ (0.01N) and NaOH (0.01N). The samples were collected at regular intervals of one hour for analysis. Phenol concentration was analyzed spectrophotometrically in UV-Spectrophotometer of PerkinElmer Lambda 25 series using 4-amino antipyrine method (APHA, 1971). The X-ray diffraction (XRD) analysis was performed in the instrument of Seifert Model No. 3003TT. Crystalline size was assessed based on XRD data duly utilizing Scherrer's formula. (Sarvanan *et al.*, 2009).

Results

Effect of evaporation

In solar treatment of waste water there are many mechanisms like thermal degradation, photocatalysis and adsorption out of which photocatalysis is the foremost mechanism under which the maximum removal efficiency had been reported. However, these three mechanisms were also studied so as to assess to what extent they contribute to the degradation of toxic waste water treatment.

To study the thermal degradation mechanism, 10 mg/L initial concentration of synthetic phenol solution was prepared and filled in the pan, placed under the sun for a whole day and a sample of 10 mL was collected at regular intervals of one hour, to estimate the concentration of the phenol. Error correction in the volume of the sample that was

extracted was done and the concentrations were determined. The average concentration of phenol was found to increase with the evaporation of water and hence the authors conclude that there is no degradation of phenol by thermal process.

Effect of photocatalyst dosage

Batch studies were performed for the determination of optimum dosage of catalyst to achieve maximum removal efficiency. The studies were performed by varying the dosage of TiO_2 from 25mg/100mL, 50mg/100mL to 500mg/100mL at a step interval of 50mg/100mL for a initial substrate concentration of 25ppm and 100ppm. The experiments were performed at a pH of 6.9 ± 0.1 and samples were collected at every one hour interval from 7:30 AM to 5:30PM and analyzed for phenol concentration. A graph was plotted between the removal efficiency and photocatalyst dosage in g/L (Fig 1). The removal efficiencies for 25 ppm and 100ppm initial concentrations were observed to be 98% and 70% for 300mg/100mL TiO_2 dosage. The influence of the catalyst was studied stepwise and it was observed that the initial adsorption process took place when placed in a closed chamber. The phenolate ions surrounded the catalyst, when solar light was induced, increasing the quantity of active sites facilitating photodegradation of substrate. The increase in the dosage after optimum level induced scattering effect, dispersing the light decreasing the percentage formation of hydroxyl ions in turn reducing removal efficiencies (Parida and Parija, 2006).

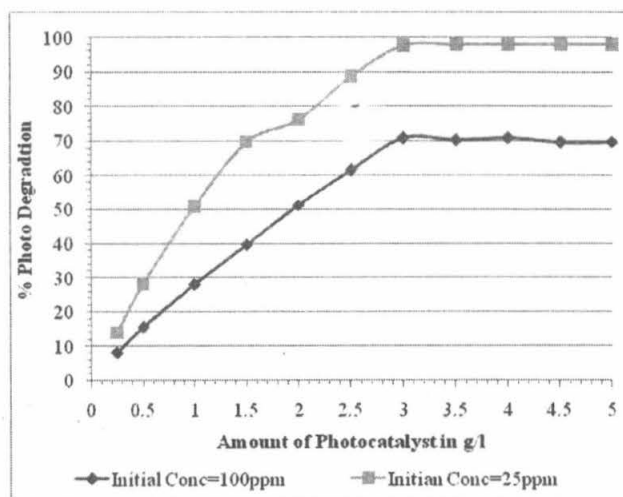


Fig 1: Effect of photo catalyst amount on degradation efficiency (exposure time = 8h, pH=6.9±0.1)

Effect of irradiation time

Batch studies were performed for the determination of optimum irradiation time to achieve maximum removal efficiency. The experiments were performed at a pH of 6.9 ± 0.1 , and catalytic dosage of 300mg/100mL for an initial substrate concentration of 25ppm and 100ppm. Samples were collected at every one hour interval from 7:30 AM to 5:30PM and analyzed for phenol concentration. A graph was plotted between the removal efficiency and exposure time in hours, presented in Fig 2. A removal efficiency of 98% for 25ppm initial substrate concentration and 70% removal efficiency for 100ppm initial substrate concentration was observed for the exposure time of 7 hours. The production of OH^- ions with the increase in the exposure time facilitated higher removal efficiencies. As the concentration increases the increase in the exposure time induced sintering effect as a result the percentage of photodegradation decreased (Parida and Parija, 2006).

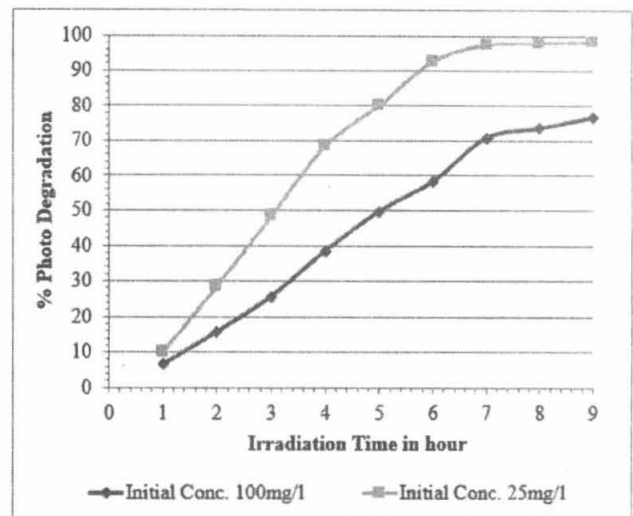


Fig 2: Effect of irradiation time on degradation efficiency (amount of photo catalyst = 300mg/100mL, pH=6.9±0.1)

Effect of initial concentration

The effect of initial substrate concentration was studied for an initial concentration varying from 25–100ppm at a step interval of 25ppm to 100ppm. It was observed the removal efficiencies decreased by 50% giving conclusion that design parameters shall have to be varied for higher concentrations or combined photocatalytic and biological degradations mechanisms are to be adopted for the removal.

In the process of photocatalysis the TiO_2 under the action of UV light is excited by donating an electron which reacts with water present in the solution to form OH^\cdot and O_2^\cdot free radicals which react with the hydroxyl group in phenol to form phenolate ion, which further degrades into simpler compounds. As the pH of the solution and catalytic dosage remain constant the effective number of sites available for substrate removal decreases, in turn decreasing the removal efficiency. As in case of 25ppm initial concentration, milk white solution was turned to chocolate brown at 4hours and restored to creamy white at the end indicating complete mineralization, while for 100ppm initial concentration the solution remained pale brown even after 8hours indicating incomplete mineralization. A graph was plotted between the initial concentration and exposure time in hours, as presented in Fig 3. During the final stages of degradation, the catalytic surface became saturated with the increase in substrate ions. As the catalytic dose is constant the number of active sites for degradation decreases resulting in decrease of overall removal efficiency as concentration increases (Parida and Parija, 2006).

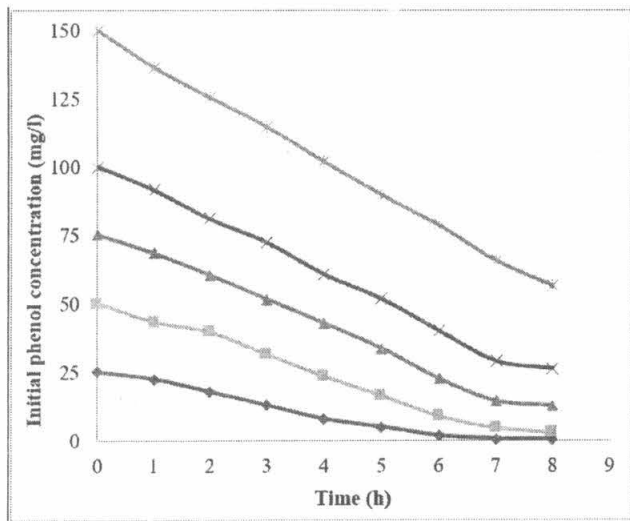


Fig 3: Effect of concentration of phenol on degradation efficiency (amount of photo catalyst = 300mg/100mL, exposure time = 8h, pH=6.9±0.1)

Effect of pH

The major parts of the studies were conducted at a pH 6.9±0.1. Further investigations were carried out to study the impact of variation of pH of solution on removal efficiencies of substrate. At present most of the industries are constructing equalization or

neutralization units to control pH and organic loading rate which play a vital role in the operation and maintenance of the succeeding units. It was observed that the removal efficiency was high in the range of pH 5.0 to 6.0 which can be controlled in the neutralization unit resulting to better disposal of the effluent and proper operation of the effluent treatment plant.

The effect of pH on the efficiency of photo catalytic degradation of phenol was studied in the pH range of 4 – 11. It was observed that, phenol degradation was favorable at weakly acidic and neutral solutions. In weakly acidic condition, most of the phenol molecules remain undissociated, hence maximum number of phenol molecules were mineralized on the surface of catalyst, due to which maximum photo degradation was observed. In alkaline medium surface of titanium dioxide was negatively charged and phenolate ion intermediates may be repelling away from the catalyst surface resulting towards decrease in mineralization of substrate molecules on the surface of the photo catalyst. As a result, photo degradation of substrate in alkaline medium was found to be decreased. Fig 4 shows the graph plotted between photo catalytic degradation and pH (4–10). Fig 5 shows the graph plotted between photo catalytic degradation and pH in the range of 5 to 6 at a step interval of 0.2.

It was observed that complete mineralization of the substrate drastically increased between pH 5.2±0.01 to 6±0.01 with a maximum removal efficiency of 98 % at pH of 5.6±0.01 for an initial concentration of 100ppm. The formation of the free radicals was increasing in this range of pH which reacts with the hydroxyl group in the substrate enhancing the rate of reaction.

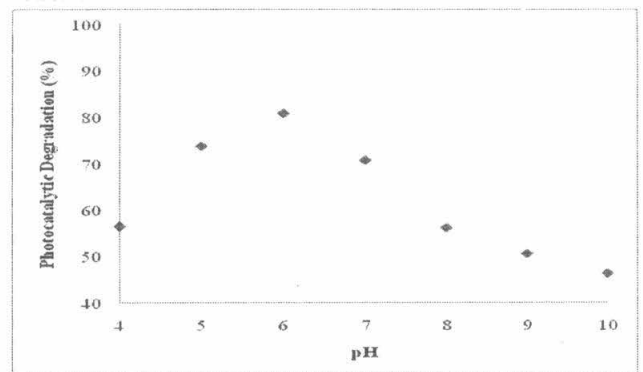


Fig 4: Effect of concentration of phenol on degradation efficiency (concentration of phenol = 100 ppm, amount of photo catalyst = 300mg/100mL, exposure time = 8h)

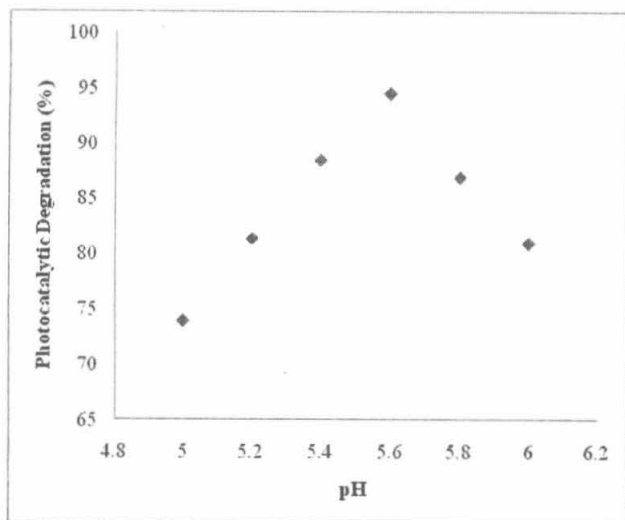


Fig 5: Effect of concentration of phenol on degradation efficiency (concentration of phenol = 100 ppm, amount of photo catalyst = 300mg/100mL, exposure time = 8h)

X-Ray diffraction analysis

The results of X-ray diffraction (XRD) analysis showed that the width of the peaks obtained was narrow. This implies that crystalline structure was present in both types of TiO_2 . The crystalline grain size of the catalysts was determined using Scherrer's formula. The crystallite size of pure TiO_2 was found in the range of 10 -25 nm. On the other hand treated TiO_2 crystalline size was also found to be in same range. As both the graphs coincide with each other it can be inferred that the conversion of catalyst structure from crystalline form to amorphous structure did not occur and hence it can be reused. Fig 6 shows the X-Ray diffraction graph.

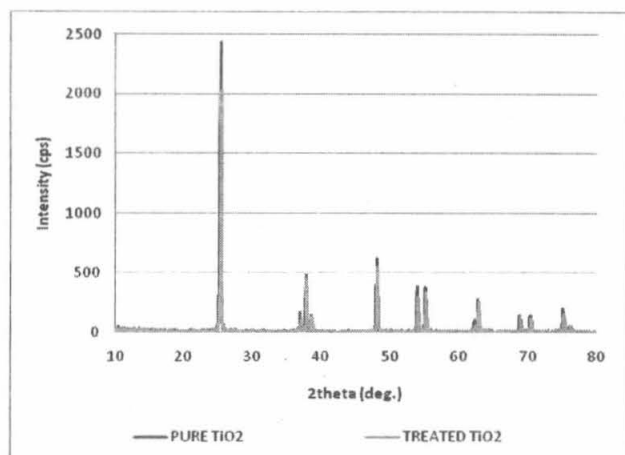


Fig 6: XRD analysis of the photocatalyst

Reusability studies

To study the reusability properties, catalyst agitated water was allowed to stand still till the catalyst settled down. The supernatant was collected and the sludge was filtered through ash less whatman filter paper No.42, washed with distilled water in water bath, filtered and dried at 120°C in a hot air oven. The residue obtained was reused for photocatalytic experiments. It was observed that the removal efficiency of substrate was 70% when pure form of catalyst was used, while it reduced to 50% when it was reused fourth time. From this study and XRD results it can be resolved that the catalyst was stable. Fig 7 shows the phenol degradation efficiency for reused photo catalyst. In the reactor design few standby units shall be provided where the catalyst shall be allowed to be sun dried and the same shall be used for the treatment of the substrate, which helps in operation and maintenance of the reactor periodically. In the Table 1, reusability of various catalysts is presented.

Table 1: Reusability of catalyst in various studies

Sr. No	Author	Catalyst	No. of times Used
1	Paradesi and Patil, 2008	ZnO	4
2	Dhanus suryman, 2008	TiO ₂	4
3	Enrico. Mendes et al., 2011	TiO ₂	5
4	Present Study	TiO ₂	4

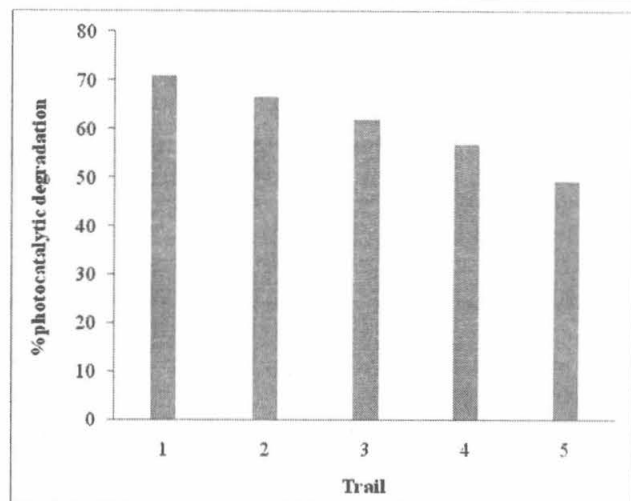


Fig 7: Reusability of the photo catalyst (concentration of phenol = 100 ppm, amount of photo catalyst = 300mg/100mL, exposure time = 8h, pH=6.9±0.1)

Conclusions

- Titanium dioxide catalyst was observed to be very good in solar radiation induced photo degradation of phenol.
- The substrate removal efficiency was as high as 98% at an initial concentration of 25 ppm and for initial concentration of 100ppm, it reduced to 70%.
- Thermal degradation of phenol does not take place and maximum degradation of phenol was due to photo catalytic process. The catalyst was a poor adsorbent.
- Reusability properties for the catalyst were high as the crystalline structure was undisturbed.
- It is easy to operate and maintain reactor units on an industrial scale.

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