

Performance Study on Photocatalysis of Phenol Solution in a UV Irradiated Reactor

Rajarshi Kar, Oindrila Gupta, Kunal Mandol, and Sangita Bhattacharjee*

Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India

Abstract

Photocatalysis is a “green” technology with potential applications in various disciplines, such as chemical synthesis and environmental technologies. In this work, heterogeneous photocatalytic degradation of phenol in aqueous solution was studied using TiO_2 photocatalyst in a UV irradiated new type of annular reactor. Degradation of phenol has been investigated against irradiation time for three different flow rates. The kinetic and equilibrium study showed that the mineralization of aqueous phenol could be modeled using Langmuir–Hinshelwood model and the rate constant has been reported.

Keywords: Photocatalysis; Annular reactor; Phenol; TiO_2 ; Langmuir-Hinshelwood model

Introduction

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In recent years, interest has been focused on the use of TiO_2 as a photocatalyst for the destruction of polluting materials. Heterogeneous photocatalysis offers an efficient technique for wastewater treatment particularly when treated for low concentration and high volume fluids. Activation of semiconductor catalyst TiO_2 is achieved through the absorption of photon of ultraviolet band gap energy resulting in the formation of electron donor (reducing) and electron acceptor (oxidising) sites. The photocatalytic activity of TiO_2 depends on the relative rates of generation and recombination of electron-hole pairs as well as the levels of adsorbed radical-forming species on TiO_2 surfaces. Hydroxyl radicals ($\text{HO}^\bullet$) and superoxide ion are the principal agents responsible for the oxidation of aqueous organic contaminants [1]. The carbon containing pollutants are oxidized to carbon dioxide and water, while the other elements bonded to the organic compounds are converted to anions such as nitrate, sulfate or chloride.

The purification of wastewater by heterogeneous photocatalysis is one of the most rapidly growing areas of interest to both research workers and water purification plants [2]. It is useful for cleaning biologically toxic or non-bio degradable materials such as aromatics, pesticides, petroleum constituents, dyes and volatile organic compounds in waste water [3]. Commercial application of the process is called advanced oxidation process (A.O.P). In recent years, interest has focused on the use of TiO_2 as a photocatalyst for the destruction of polluting materials due to its efficiency, non toxicity, high activity, photochemical inertness and low cost [4]. In another work [5] phenol degradation had been examined with combined photocatalysts TiO_2 and ZnO under illumination of a 500W super high pressure mercury lamp mounted axially. The results revealed that, both TiO_2 and ZnO were effective though the latter was much superior in activity.

Though photocatalysis has been proven to be a promising technology, new reactor design ideas are necessary for implementation of important parameters like light distribution inside the reactor, maintenance of the photocatalyst in suspension so as to ensure better mass transfer and subsequent conversion of the solute. This work examined the mineralisation of aqueous phenol solution in an indigenously designed and fabricated new type of annular photo reactor using TiO_2 as catalyst. Chemical, pharmaceutical industries, petrochemical industries as well as petroleum refinery use phenols to a great extent. Due to toxicity of

phenols and their derivatives, their disposal in receiving water bodies causes severe problem. Presence of such compounds strongly reduces biodegradation of other components. Conventional process such as adsorption onto activated carbon is effective in treatment of phenolic water but they only transfer the contaminants from one medium to another.

This investigation was aimed to study the variation of phenol concentration in aqueous solution with reactor operating time and thus to determine the conversion in this reactor. The effects of flow rate of phenol solution on degradation of phenol were investigated and reported. The model proposed by Langmuir-Hinshelwood was employed to describe the kinetics of the photodecomposition reaction of phenol and the rate constant was evaluated under specified operating condition.

Theory

The heterogeneous photocatalysis permits total degradation (mineralization) of the most toxic organic molecules in aqueous solution in the presence of a catalyst. The hydroxyl radicals generated in this process are powerful oxidant due to high reactivity. This species is unstable and must be continuously produced in situ by means of chemical or photochemical reactions.

The heterogeneous photocatalysis is based on a semiconductor catalyst which is activated by UV light. The anatase form of Titanium dioxide is mainly used as catalyst which is activated by UV light. In this process, excitation of the of TiO_2 by a UV light wavelength of $\lambda \leq 400$ nm generates electron-hole pair (e^-_{cb}, h^+_{vb}), the hydroxyl radicals are generated by the holes which can degrade organic pollutants present in wastewater. Dissolved oxygen of the solution scavenges the electron generated, preventing the recombination of electrons and

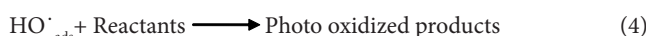
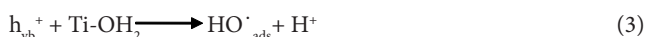
***Corresponding author:** Sangita Bhattacharjee, Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India, E-mail: sangita.bhattacharjee@yahoo.co.in

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holes. Conduction band electrons and valence band holes (Equation 1) generated from UV irradiated TiO_2 interact with surface adsorbed molecular oxygen to generate superoxide radical anions, $\text{O}_2^{\cdot-}$ (Equation 2) and with water to produce the highly reactive $\text{HO}^{\cdot}$ (3) [1].



The photodegradation efficiency or conversion was calculated by the following relation

$$X (\%) = 100 \times (C_0 - C) / C_0 \quad (5)$$

Where X is the photodegradation efficiency or conversion.

Materials and Methods

Reagents

The catalyst TiO_2 (more than 99.9% purity) was procured from Sigma, Aldrich and was used without any pre-treatment. From XRD analysis (Figure 1), it was found that, this TiO_2 contained only anatase form. Phenol with a purity >99.9 % was obtained from Merck, India. The aqueous solutions were prepared with deionised water.

Calibration curve

Six numbers of dilute solutions of phenol were prepared for construction of standard curve. Aqueous phenol solution was scanned for maximum absorbance and was found to give peak absorbance at

(λ_{max}) 270nm wavelength in a UV-visible Shimadzu spectrophotometer. The absorbance vs. concentration data was plotted. This standard curve was used extensively to determine phenol concentration during experimental runs.

Photoreactor

The photoreactor of capacity 1720 ml contained 305 mm long, four no. UV lamps each with flux 13.5 W/m^2 . The sources of irradiation were placed uniformly inside the reactor to assure the maximum energy exchange between the source of irradiation and reaction mixture that would flow out continuously. A pump was used to circulate the mixture between the reactor and the reservoir. The schematic diagram of the experimental setup is furnished in figure 2.

Experimental procedure

5 litres phenol solution (50 mg/L) was prepared using deionised water and placed in the tank of the reactor. 2 gm of TiO_2 was accurately weighed in an electronic weighing balance (Sartorius) and was mixed thoroughly with the phenol solution in the tank. The suspension was kept in circulation for 1 hour in the absence of UV light in order to reach adsorption equilibrium. Photocatalysis reaction was carried out for a period of 3 hrs. The same procedure was followed in each of three flow rate of 5, 10 and 15 Litre per hour (LPH) respectively (Figure 4). The liquid coming out of the reactor was directed to the tank and allowed to mix thoroughly with the solution in the tank. A sample of 20 ml was collected from the tank at regular interval of 30 minutes. Each sample collected was centrifuged in a Research Centrifuge, Remi (R-24) at 12,000 rpm for a period of 15 minutes to remove TiO_2 particles. The clear supernatant solution was then collected and analysed in the

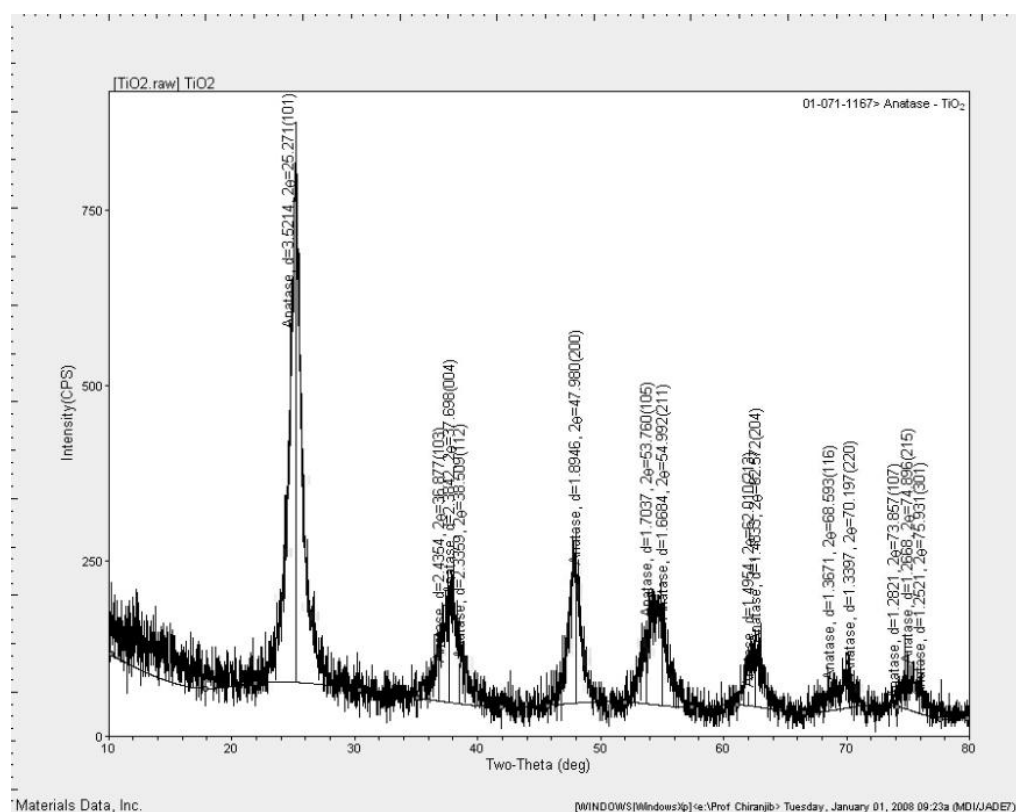
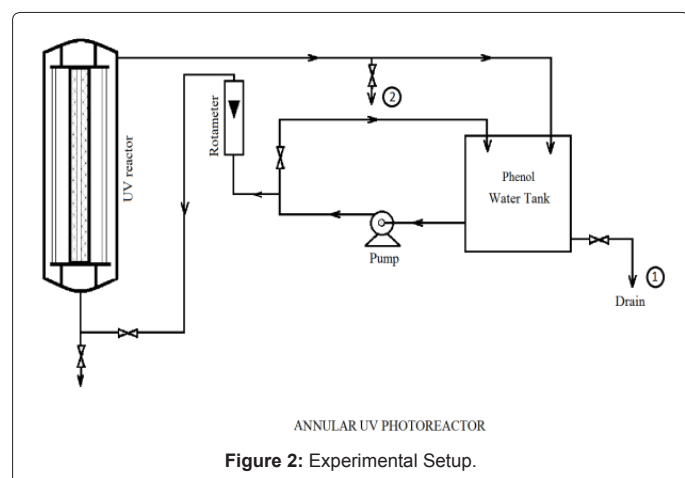


Figure 1: XRD Analysis.



Shimadzu UV spectrophotometer by measuring the absorbance at 270 nm. Using the calibration curve, the remaining phenol concentration of the samples was determined. During the reaction, the reaction temperature was maintained at 32°C using a cooling system placed between the light source and the reactor (not shown in figure 2).

Kinetic studies

The Langmuir-Hinshelwood kinetic model was used to describe the mineralization process kinetics and to assume automatically that reactions took place at the surface of the catalyst particle, without any corroborating independent evidence to support this.

The Langmuir-Hinshelwood (L-H) model was initially developed to quantitatively describe gaseous-solid reactions [4]. This model was recently employed to describe solid-liquid reactions. In this model, the rate of reaction (r) is proportional to the fraction of surface covered by the substrate (θ)

$$-r = -dC/dt = k_r \theta$$

Considering Langmuir's equation,

$$\theta = KC/(1 + KC) \quad (6)$$

[θ =fractional coverage, K =equilibrium const.]

or, $-r = -dC/dt$

$$=k_r \theta$$

$$=k_r KC/(1+KC) \quad (7)$$

Since k_r is the true rate constant, which takes into account several parameters [5] such as the catalyst's mass, efficient photon flow, O_2 layer, etc., K is the constant of adsorption equilibrium of L-H or the Langmuir constant. C is the concentration of the organic substrate at any time t . This equation can be integrated,

Since in this case, the solution is highly diluted, C (mol/l) $< 10^{-3}$ [6] the term KC becomes < 1 , when the denominator of (7) is neglected and the reaction is essentially an apparent first order reaction:

$$r = -dC/dt = k_r KC = k_{app} C$$

Where k_{app} is the apparent rate constant of a pseudo first order reaction. Integrating and using boundary condition $C=C_0$ at $t=0$ we get,

$$\ln(C_0/C) = k_{app} \times t \quad (8)$$

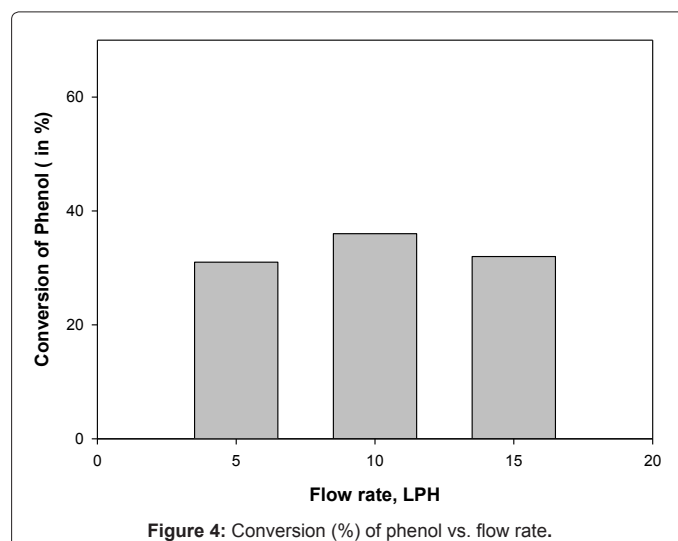
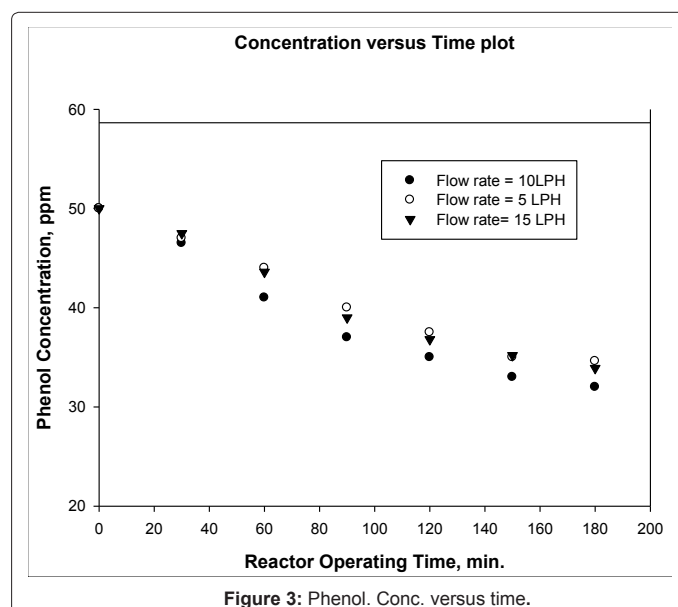
Where C is phenol concentration at time t . Hence, by plotting $\ln$

(C_0/C) against time, the apparent rate constant can be found out from the slope of the line.

Results & Discussion

Effect of flowrate

Adsorption and photodegradation of phenol was carried out with varying flow rates 5, 10 and 15 LPH. The concentration of phenol was plotted against time by measuring the residual phenol concentration in solution. The conversion of phenol into carbon dioxide and water was calculated using (5). Figure 3 depicts the change in concentration of phenol against time for a reactor operating time up to 180 phenol after 3 hours UV irradiation. It was observed that highest conversion (36%) had been achieved at a flowrate of 10 LPH and lowest was 32% at 5 LPH. These results can be explained based on the fact that at lowermost flow rate (5LPH), the residence time (per pass) in the reactor was highest, but exposure time of the entire volume of phenol solution to UV irradiation was the least hence conversion was the lowest. However at highest flowrate (15 LPH), the residence time inside the UV reactor



is least but the overall exposure of phenol solution to UV irradiation is more. At a flowrate of 10 LPH, both the residence time (per pass) within the UV reactor and overall exposure were moderate- hence, highest efficiency of degradation or conversion of phenol was achieved at this flowrate.

Kinetic study

The kinetics of the reaction was also studied using Langmuir-Hinshelwood model. Since here the phenol concentration is very dilute, much less than 5×10^{-3} mol/l [7], the reaction rate could be approximated as a pseudo-first order type (8). From the slope of $\ln(C_0/C)$ against time, the apparent rate constant was evaluated. The value of the rate constant for phenol degradation corresponding to the flowrate of 10 LPH and 0.4 g/L TiO_2 dosage was evaluated to be 0.00288 min^{-1} .

Conclusion

From the present work, it was found that the UV annular reactor was a promising technology to degrade phenol. The photodegradation of phenol in presence of TiO_2 suspension proved to be an efficient method for mineralization of phenol. Effect of flowrate on conversion of phenol was investigated by varying flowrate at 3 different values i.e. 5 LPH, 10 LPH and 15 LPH. Starting with an initial concentration of 50 ppm, 36% conversion of phenol was achieved after a reactor operating

time of 3 hours with a flowrate of 10 LPH. It was also observed that photocatalysis of phenol followed a pseudo first order reaction in dilute solution.

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