Wastewater Treatment using Photo-Impinging Streams Cyclone Reactor

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Tratamiento de aguas residuales utilizando un reactor ciclónico con flujos fotoincidentes (Photo-Impinging streams cyclone reactor)

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RESUMEN
Se ha utilizado un reactor ciclónico con flujos fotoincidentes (Photo-Impinging streams cyclone reactor) como un nuevo sistema para la degradación fotocatalítica de compuestos orgánicos usando nanopartículas de dióxido de titanio en aguas residuales. Los parámetros de funcionamiento, incluyendo la cantidad de catalizador, el pH, la concentración inicial de fenol y la intensidad de luz se han optimizado para aumentar la eficiencia del proceso de degradación fotocatalítica en este fotorreactor. Los resultados han demostrado una mayor eficacia y una mayor capacidad de rendimiento de este reactor en comparación con procesos convencionales. Finalmente, se presenta un modelo cinético modificado para este proceso.

Palabras clave: fenol, fotoincidencia, ciclón, reactor, degradación, TiO₂

SUMMARY
A photo impinging streams cyclone reactor has been used as a novel apparatus in photocatalytic degradation of organic compounds using titanium dioxide nanoparticles in wastewater. The operating parameters including catalyst loading, pH, initial phenol concentration and light intensity have been optimized to increase the efficiency of the photocatalytic degradation process within this photoreactor. The results have demonstrated a higher efficiency and an increased performance capability of the present reactor in comparison with the conventional processes. Finally, a modified kinetic model was presented for this process.

Keywords: Phenol, Photo, Impinging Cyclone Reactor, Degradation, TiO₂

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INTRODUCTION

Effective removal of water pollution is an essential issue in the water treatment process. The pollution removal mechanisms can be classified as chemical oxidation technique, biochemical treatment, activated carbon adsorption and Advanced Oxidation Processes (AOPs). Photo catalytic technique is classified under AOPs. Such a process has attracted considerable attention within the last few years due to its ability to decompose a wide range of organic and inorganic pollutants at ambient temperature and pressure. [1-2]. In photocatalytic degradation processes, suspension catalyst method has more efficiency in degradation (grams of contaminant degraded by number of photons entered) than immobilized or supported catalyst technique [3]. Other thing is the consideration of the easy way to remove the catalyst from the aqueous solution by using supported method than catalyst in slurry.

In case of heterogeneous photocatalysis processes, the organic compounds present in liquid phase are first degraded to their respective intermediates and if the irradiation time is further extended some of these maybe finally mineralized to carbon dioxide and water.

The overall photocatalysis reaction can be divided into five independent steps [4, 5], according these steps, there are two essential issues in the case of liquid phase reactions: photon transfer limitations and mass transfer limitations. An ideally intensified reactor, however, should be able to integrate both maximized light efficiency and mass transfer process within a single piece of equipment.

By application of impinging streams cyclone reactors both limitations may be overcome simultaneously due to the following reasons [6]:

(a) Increase in relative velocities between the phases.
(b) Increase in the residence time of particles due to oscillatory motion within the impingement zone.
(c) Enhancement of the effective area for mass and heat transfer which could be nearly identical to the total surface of the particles in the flow.
(d) Potential for excellent mixing within the impingement region which in turn enhances the overall mass and heat transfer rates.

Considering these advantages, an impinging streams cyclone reactor has been utilized as a novel apparatus in photocatalytic degradation of phenol as representative organic compounds.

Phenol and phenolic substances are used as raw materials in many petrochemical, chemical, and pharmaceutical industries. Wastewater containing phenol has received increased attention because of its toxicity and prevalence in industrial processes. In addition, phenol is considered to be an intermediate product in the oxidation of higher-molecular weight aromatic hydrocarbons. Thus, it is usually taken as a model compound for advanced wastewater treatment studies [7].

EXPERIMENTAL

Materials

Nanoparticle titanium dioxide (P25) was supplied by Degussa, Germany; nanoparticle zinc oxide with an average particle size of 25 nm and a BET surface area of 51 m² g⁻¹ was provided by Nano Amor, USA. Phenol with above 99.5% purity, Phenol test kit, Fe²⁺ test kit and COD vials were all obtained from Merck Co. Potassium trioxalatoferrate (III) trihydrate was provided by Alfa Aeser Company.

Analytical procedures

The concentration of phenol was measured by visible spectrophotometer (DR 2800 Hach Co.) at a wavelength of 495 nm using 4-aminoantipyrine method. Owing to presence of TiO₂ powders in the system, the samples were first filtered using a 0.22 μm syringe filter (Millipore) to remove particles. In addition, the COD of solution was measured at a wavelength of 445 nm using COD vials.

The radiation intensity within the photoreactor was determined by ferrioxalate actinometry following the method of Hatchard and Parker [8].

Photo-reactor

In the first step, a batch circulation photocatalysis experiments were performed to determine the optimum operating conditions. A schematic diagram of the photo-impinging streams reactor used in this step is shown in Fig. 1a. The apparatus consisted of a cylindrical vessel made of pyrex and equipped with eight low-pressure mercury vapour lamps, with a dominant emission line at 253.7 nm (TUV 8W from Philips Co.) as irradiation sources at centerline of vessel. Photon flux density was determined $1.5E^{-5}$ Em⁻² cm⁻² by ferrioxalate actinometry. The two streams of suspension (TiO₂ + Phenol Solution) were fed through symmetrically positioned acceleration pipes. The accelerated suspension feed streams impinged at the annular space and dropped instantly along the inner discharge tube down to the outlet port.

![Fig.1. Schema of Photo-Impinging Streams Cyclone Reactor.](image_url)

In a typical experiment, the initial phenol concentration and the amount of suspended TiO₂ were set at 100 mg l⁻¹ and 1 g l⁻¹, respectively. A stream of air with a flow rate of 2 L min⁻¹ was continuously supplied to the slurry solution. To prevent hole/electron formation, prior to turning on the illumination, the catalyst was placed in the feed reservoir at dark. The phenol solution was then added and the suspension was saturated with air and stirred by pumping the slurry in darkness for 30 min to establish the adsorption-desorption equilibrium. The lamps were then switched on and the suspension, after passing thorough the two nozzles, was irradiated with UV light and collided in the impingement zone. Samples were regularly withdrawn from the reactor and filtered to remove all the suspended solid particles prior to analysis. The pH of the solution was...
adjusted by adding 0.1 mol l⁻¹ NaOH or H₂SO₄ and monitoring with a digital pH meter. The temperature of the photo reactor was maintained at 40 ± 1 °C by a water-cooled jacket around the reactor and feed reservoir.

RESULTS AND DISCUSSION

Certain pertinent operating parameters in heterogeneous photocatalysis reactions are: type of catalyst, catalyst loading, substrate concentration, pH and light intensity [9, 10]. Streams flow rates are a crucial parameter in the design of impinging stream reactors. Investigation of the continuous treatment is essential for evaluation of the performance capability of the wastewater treatment system.

Effect of Flow rate
To study the effect of flow rate on the efficiency of the impinging streams cyclone reactor, a range of flow rates (20, 30, 40, 50, 55 l min⁻¹) were applied. Results presented in Fig. 2 may indicate that at low flow rates, the degradation of phenol did not exceed 20% after 4 hours. This may be explained by noting that at low flow rates, the intensity of collisions is reduced and as such, the irradiation absorbed by the solution is decreased. Consequently, conversion is low. While at higher flow rates the collision rate, turbulency of flow and renewal of catalyst surface are all enhanced and thus, the irradiation absorbed by the slurry within a fixed period of time is promoted. These phenomena are led to a higher degradation rate. Regarding the results obtained, the optimum flow rate of phenol solution was selected as 50 l min⁻¹.

Type of catalyst
A number of semiconductors have been examined and applied as photocatalysts for the degradation of organic contaminants [9, 11, 12]. Among the semiconductors employed, both TiO₂ and ZnO have demonstrated a number of advantages as photocatalysts. These compounds are inexpensive, non-toxic and highly effective [13]. Preliminary experiments were thus carried out to examine the activity of the selected catalysts for degradation of phenol. The results indicated a higher photocatalytic activity of TiO₂ compared with ZnO (Fig 3.). Hence, TiO₂ was selected as a suitable catalyst and applied in the process. Optimization of certain key parameters of the photodegradation of phenol was carried out using such a catalyst.

Effect of catalyst loading
To avoid an ineffective excess of catalyst within the system and to ensure total absorption of efficient photons, the optimum mass of catalyst has to be found [9, 14, 15]. To determine the optimal loading of photocatalyst, various amounts of P25 TiO₂ (0.5 – 2.0 g l⁻¹) were mixed with 100 mg l⁻¹ of phenol solutions. Fig. 3a shows the results at pH free. In Figure 3a it can be seen that UV irradiation in the absence of TiO₂ catalyst (i.e., direct photolysis) results in a low removal of phenol. However when TiO₂ loading was increased from 0.5 to 1 g l⁻¹, the photodegradation was enhanced from 81 to 94% after 4h. However, further increase in TiO₂ loading led to a slight decrease in phenol removal. Results from extensive studies have demonstrated that the rates of photodegradation for organic pollutants are strongly affected by the number of active sites and the photo-absorption ability of the catalyst used [15, 16]. Increased loading of the catalyst increases the generation rate of electron/hole pairs and thus, formation of *OH radicals leading to the enhancement of photodegradation. On the other hand, an excess of catalyst decreases the light penetration due to shielding by the suspended particles [14, 17] causing reduction of the rate of photodegradation. Such a rate reduction may be also attributed to a screening effect of the redundant dispersion of UV radiation as the result of substantial amount of suspended particles leading to reduction of the radiant flux. Under these conditions particles tend to agglomerate, making a significant fraction of the catalyst inaccessible to either adsorbing the molecules or adsorbing the radiation, with consequent decrease in the active sites available to the catalytic reaction. Thus a balance exists between these two opposing effects that resulted in an optimum catalyst loading of 1.0 g l⁻¹ ZnO providing the maximum efficiency.

Owing to the highly turbulent condition of slurry in this reactor, increased loading of TiO₂ leads to formation of foam within the reactor creating a pumping problem and reduces the photodegradation rate.
Effect of catalyst loading on the photo catalytic degradation of phenol, (a) TiO₂ (b) ZnO. 
[PhOH] = 100 mg l⁻¹, Temperature = 40°C, pH = Free.

Fig. 3. Effect of catalyst loading on the photocatalytic degradation of phenol.

Effect of pH
As expected, TiO₂ exhibits amphoteric behaviour in aqueous media. The point of zero charge (pzc) of TiO₂ P25, i.e., the point when the surface charge density is zero, is reported to be between 6.2 and 6.8 [14, 18, 19]. This means that the surface of the catalyst is positively charged at pH < pH_pzc (Eq 1), negatively charged at pH > pH_pzc (Eq 2), and remains neutral at pH = pH_pzc:

\[
\text{TiOH} + H^+ \rightarrow \text{TiOH}^+ \quad (2)
\]

\[
\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \quad (3)
\]

where, TiOH⁺, TiOH, and TiO⁻ are the positive, neutral, and negative surface hydroxyl groups, respectively. Such a behavior, significantly affect not only the adsorption–desorption properties of TiO₂ surface, but also the changes of the pollutant structure at various pH values. In aqueous media, phenol has a pKₐ of 9.9 (at 25°C) indicating that in solutions with pH < P_Kₐ, phenol is in the molecular form (C₆H₅OH). Whereas, at pH > P_Kₐ the phenol molecule undergoes deprotonation, becoming negatively charged (C₆H₅O⁻) [14, 15, 18]. Thus, electric charge properties of both, catalyst and substrate play an important role in adsorption process, i.e., the interaction and affinity between both TiO₂ and phenol will vary with the solution pH.

The pH of the suspensions was varied to study the effect of this parameter on the photocatalytic degradation of phenol. As it may be observed from Fig. 4, decrease in pH from pH free (about 5.8) to 3.5 has no appreciable effect on the process. However, at pH 11.5, the photocatalytic reaction rate decreases drastically, and phenol removal becomes extremely slow. Under such conditions, both catalyst and substrate are negatively charged and thus, repulsive forces are generated between the two, leading to the reduction of substrate adsorption. With either acidic or basic conditions of the starting solutions, it was observed that with continuation of the reaction, the solution pH tends to neutral value. In addition, with both acidic and neutral initial solutions the rate of degradation was almost identical. However, when the initial solution was basic, the rate of phenol removal was usually retarded. Such an observation may indicate an initial low acidic condition for effective phenol degradation.

Effect of the initial phenol concentration
It is important both from a mechanistic and an application point of view to study the dependency of the photocatalytic reaction rate on the substrate concentration. Thus, the initial phenol concentration (prior to the adsorption in dark) was varied from 20 to 100 mg l⁻¹. Results showed that beyond this range of concentrations, any increase in phenol quantity, may lead to the decrease in degradation rate (Fig. 5). By increasing the phenol concentration, higher amounts of reactant and reaction intermediates are adsorbed at the surface of the photocatalyst, and thus the generation of hydroxyl radicals is declined due to the reduction in the number of active sites available for adsorption of hydroxyl anions. On the other hand, when the phenol concentration is low, while the catalyst loading and light intensity are kept unchanged, larger numbers of active sites and hydroxyl radicals are available to intermediates. As the consequence, the total COD of solution decreases sharply (Fig. 8). In addition, during photocatalytic oxidation, the decomposition of the organic substrate is dependent upon photonic efficiency. At high-substrate concentrations, however, the photonic efficiency diminishes and the titanium dioxide surface becomes saturated with the substrate and intermediates, leading to catalyst deactivation [20].

Fig. 4. Effect of pH on the photocatalytic degradation of phenol.

[PhOH] = 100 mg l⁻¹, Catalyst loading = 1 g l⁻¹, Temperature = 40°C

Fig. 5. Effect of the initial concentration of phenol on the reaction time.
Catalyst loading = 1 g l⁻¹, Temperature = 40°C, pH = Free.
Fig. 6. Effect of the initial concentration of phenol on COD removal. Catalyst loading = 1 g l⁻¹, Temperature = 40°C, pH = Free. a) [PhOH] = 100 mg l⁻¹, b) [PhOH] = 50 mg l⁻¹, c) [PhOH] = 20 mg l⁻¹.

The rate of photocatalytic reactions depends largely on the radiation absorption of the photocatalyst. A review by Ollis et al. [21] on the effect of light intensity upon the kinetics of the photocatalysis process demonstrated that:
(i) at low light intensities (0–20 mW cm⁻²), the rate would increase linearly with increasing light intensity (first order);
(ii) at intermediate light intensities, beyond a certain value (approximately 25 mW cm⁻²), the rate would depend on the square root of the light intensity (half order), and
(iii) at high light intensities the rate would level off to become independent from the light intensity. Such an observation may be interpreted as follows: at low light intensity, reactions involving electron–hole formation predominate while the electron–hole recombination is negligible. However, as the light intensity is increased, electron–hole pair separation competes with electron – hole recombination, retarding the reaction rate.

To study the influence of different light intensity on the photocatalytic degradation of phenol, the photoreactor was equipped with eight low-pressure mercury vapor lamps. A number of experiments were carried out, applying various light intensities generated from 2, 4, 6 and 8 lamps. Radiation intensities were determined by ferrioxalate actinometry and are here presented as fractions of the initial photonic flow. Within the range of intensities studied, the pseudo-first-order kinetic constants were observed to change linearly with the photonic flow (Fig. 7), which may confirm the photo-induced nature of the catalytic process.

Fig. 7. Initial reaction rates as a function of light intensity. [PhOH] = 100 mg l⁻¹, Catalyst loading = 1 g l⁻¹, Temperature = 40°C, pH = Free.

Kinetic study
Determination of phenol concentrations and COD values during degradation (Fig.6), may lead to the following conclusions: (i) phenol decays gradually during the experimental run and eventually drops to zero concentration; (ii) concentrations of the main reaction intermediates rise initially and attain maximum values, but then decline and disappear almost completely at the end of the reaction. According to the previous discussion, when phenol concentration is decreased, larger numbers of active sites and hydroxyl radicals become available to react with phenol and intermediates. Measurements of concentrations of intermediates and variation of COD with different initial phenol concentrations reveal that by reducing the initial phenol concentration in solution, the time needed to attain the maximum amount of reaction intermediates ($t^*$) is also decreased (Fig. 8).
The Langmuir–Hinshelwood model is usually applied to describe the kinetics of photocatalytic reactions of aquatic organics. The following mechanism, could be proposed for this process.

\[ P + S \leftrightarrow P.S \]  
\[ P.S \rightarrow I.S \]  
\[ I.S \leftrightarrow \cdots \rightarrow CO_2 + H_2O \]  
\[ I + S \leftrightarrow I.S \]

Where, \( P \) is Phenol, \( I \) is an intermediate and \( P.S \) and \( I.S \) are adsorbed phenol and intermediate on active sites, respectively. Assuming that reaction (5) is the rate controlling step, the resulting rate equation may be presented as follows:

\[-r_P = \frac{k_1 K_p C_p}{1 + K_p C_p + K_I C_I} \]  
\[ r_I = \frac{k_1 K_p C_p - k_2 K_I C_I}{1 + K_p C_p + K_I C_I} \]

Where, \( C_p \) and \( C_I \) are the concentrations of phenol and intermediate, respectively; \( K_p \) and \( K_I \) are the apparent chemisorption constants related to the competitive adsorption of phenol and intermediate onto TiO$_2$ surface, respectively; \( k_1 \) and \( k_2 \) are the kinetic coefficients of phenol and intermediate degradation, respectively. Since the latter is a function of absorbed light intensity, which in turn is proportional to the incident light intensity \( I \), it follows that \( k_2 \) is also a function of absorbed light intensity:

\[ k_1 = a I^b \]  
where, \( a \) is a proportionality constant and \( b \) is equal to 1.0 or 0.5 at low and mediocre absorbed light intensities, respectively.[21]

At \( t^* \), when \( C_I \) is dropped to a small value, Eq. (8) approaches to a pseudo-first-order kinetic equation,

\[-r_P = k_{app} C_p \]  

By integrating between \( t^* \) and \( t \), the following expression is obtained,

\[ Ln \left( \frac{C_p}{C_{p^*}} \right) = -k_{app} \left( t - t^* \right) \]  

Thus, in lower initial concentrations of phenol that \( C_I \) and \( t^* \) are small value, may be ignored \( t^* \) and estimated \( C_p^* \) by \( C_{p^*} \) and the reaction rate could be described by following expression,

\[ Ln \left( \frac{C_p}{C_{p^0}} \right) = -k_{app} t \]  

Fig.9.a. shows the plot of Eq. (12) at 20, 50, 100 mg l$^{-1}$ of initial phenol concentration. When the initial phenol concentration is 20 mg l$^{-1}$, plot of Eq. (13) has been also demonstrated in Fig. 9.b.

CONCLUSION

Regarding the present observations, it seems that by application of a Photo-Impinging Stream Cyclone Reactor (PISCR) the photon and mass transfer limitation are both eliminated leading to a higher efficiency for phenol degradation. Results showed that during 4h reaction time in presence of nano-TiO$_2$ phenol was completely decomposed. With regard to the higher concentration of phenol (3 L solution containing 100 mg L$^{-1}$ phenol) and the lower degradation time observed in the present study in com-
The photocatalytic process is influenced by several design and operating parameters including feed flow rate, catalyst loading, initial phenol concentration, pH of the medium and irradiation intensity. The maximum degradation rate of phenol was observed in case of approximately neutral solutions. Finally, a modified kinetic model was presented for this process. Obtained results show that in lower initial phenol concentrations that intermediate concentration is also low, the reaction rate could be described by a pseudo-first order kinetic model.

REFERENCES


