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# Affecting Parameters on Photocatalytic Degradation of Organic Contaminants in a Synthesized Wastewater Utilizing Concentrated Solar UV

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### ABSTRACT

In the present research, the removal of phenol from synthesized wastewater by  $TiO_2/UV$  has been investigated. An originality of this study is its use of UV solar in Mahshar, an area in the south of Iran, and obtaining experimental data. The effect of parameters is included phenol initial concentration (50, 100, 150, and 200 mg/L), pH of solution (5, 7, and 9), photocatalyst dosage (1-4 g/L), and pH 5, 7, and 9 were investigated. It is repeated three times for every single part of the experiment. The results show that the maximum degradation of 71.9% was achieved in acidic pH 5, and the optimum concentration of phenol equal to 50 mg/L. Investigation of results in terms of thermodynamic aspects revealed phenol concentration100 mg/L, pH =5, and photocatalyst dose 2 g/L were the first-order kinetic constant was achieved 0.005 min-1 with R2=0.9427. In conclusion, using photocatalyst wastewater treatment is beneficial for organic pollution.

#### GRAPHICAL ABSTRACT



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#### **1. Introduction**

Environmental pollution has become one of the most challenging issues for the whole world today. Among these, the problem of water and wastewater treatment needs to be addressed seriously [1]. The availability of clean water sources is being threatened by the rapid development of industrialization, population growth, and long-term droughts owing to the development of rapid industrialization, population growth, and long-term droughts nowadays [2]. As a result of the rapid industrialization, a lot of noxious pollutants are entering the water. Among these, phenolic compounds such as nitrophenols, chlorophenols, bisphenols, etc. play a crucial role in the environmental threats [3]. Phenolic compounds are usually found in wastewater discharged from different industries, such as petroleum refineries, chemical synthesis, plastics, coke plants, dyes, and paper, textiles, detergents, pulp pharmaceutics, pesticides, and herbicides synthesis plants [4]. These compounds cause many diseases for humans, they have also an adverse effect on the environment and animals [5]. The World Health Organization (WHO) sets 0.001 mg/L as the limit of phenol concentration in potable water, while phenol contents in the phenolic wastewater after refinement should not exceed 0.05 ppm as per USEPA standard [6,7]. Various physical and chemical methods for the treatment of phenolic wastewater are suggested. Based on wastewater properties like phenol concentration, pH solution, temperature, and flow rate.

Advanced chemical oxidation  $(Fe^{2+}/H_2O_2, H_2O_2/UV)$ , and UV/O3) is one of the common methods of phenol removal from waste effluent. The advanced oxidation processes (AOPs), which are characterized by the generation of a hydroxyl radical (OH•), can potentially destroy a wide range of organic molecules. The OH• has a high oxidation potential (estimated to be +2.8 V) more

than other oxidants, Like ozone,  $H_2O_2$ , HOCl, and chlorine. The aim of the selection of this technique was its great potential for the complete mineralization of organic effluents, non-toxicity, cost-effectiveness, and availabilities of nano photo TiO<sub>2</sub> catalyst [8].

Previous studies reveal that photocatalysts could be a good choice for organic pollution such a phenol. Faghihi et al. studied the simultaneous removal of phenol from an aqueous solution in a closed system by using titanium dioxide photocatalyst at different concentrations (50, 100, 200, 500, and 1000 mg/l). The highest rate of phenol removal was observed at a concentration of 100 mg/mL which was equal to 72.3% [16]. By using TiO<sub>2</sub> photocatalyst under solar radiation, De Lima et al. treated acidic wastewater. The results showed that the minimum removal efficiency was 60% for organic pollutants [17]. Venkatesan investigated phenol removal by photocatalyst. The results illustrated Co-C codoped TiO<sub>2</sub> nanoparticles exhibited a higher visible-light photocatalytic activity compared with Co-TiO<sub>2</sub> and bare TiO<sub>2</sub> with the maximum degradation efficiency of 98, 75, and 15%, respectively [18].

Accordingly, phenol and its derivatives are important pollutants produced in petrochemical industries. In light of the fact that a large amount of this type of wastewater is contaminated with organic pollutants, the environmental engineers have to find the most suitable method to treat the wastewater. While this study was carried out at a Petrochemical Complex in the south of Iran where the UV solar power is readily available, the use of this technology may be interesting due to its availability in the region. In addition, TiO<sub>2</sub> photocatalyst is a good choice for collecting the UV solar power because it is a low-cost, environmentally friendly catalyst. Therefore, it was possible to identify the most important factors that made this process effective. As a result, in the present study, the effects of various parameters on the phenol removal from synthesized wastewater utilizing  $TiO_2/UV$  technique were performed and reached data were compared with the other experiences.

#### 2. Experiments

The chemical materials including phenol, NaOH, and HCl, are sourced from Merck, while TiO<sub>2</sub> comes from Degussa- P25. A batch reactor with a capacity of 250 mL was used for all experiments in the laboratory of an Iranian petrochemical company in Ahvaz. The phenol solution was prepared at a concentration of 50, 100, 150, and 200 ppm and the pH value of the solution was adjusted by the addition of NaOH or HCl. After adding a photocatalyst to the solution, each sample was exposed to the UV light (sunlight) for 2 hours. A converging mirror with a diameter of 70 cm and focal length of 1 m was used to concentrate the solar UV at 12:00-2:00 p.m. at the highest UV radiation. The phenol concentration of effluent was estimated by spectrophotometry (cary50 (Varian) model). The properties of the photocatalyst used in the present study are summarized in Table 1. In the photocatalytic oxidation process, the organic pollutants are destroyed in the presence of semiconductor photocatalysts, an energetic light source, and an oxide

zing agent such as oxygen or air. The illumination of the photocatalytic surface with sufficient energy leads to the formation of a positive hole (h+) in the valence band and an electron (e-) in the conduction band (CB). The positive hole causes the pollutant directly or water to produce hydroxyl radical OH-, whereas the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst (TiO<sub>2</sub>). In this reaction, h+ and e- are powerful oxidizing and reductive agents, respectively. In degradation of the pollutants, the hydroxyl organic radical generated from the oxidation of adsorbed water where it is adsorbed as OH-, is the primary oxidant, and the oxygen presence can prevent the recombination of an electron-hole pair. The OHattacks organic compounds e.g., chlorinated aromatics, aniline, and nitrophenols which result in various reaction intermediates depending on the nature of the compounds. The resulting intermediates further react with OH-to produce final degradation products such as CO<sub>2</sub> and H<sub>2</sub>O• [9,11]. The effects of some factors like phenol concentration, acidic condition, and amount of photocatalyst on the phenol removal are very important and are considered in this study.

Table 1. Specification and characteristics of 1102 catalyst			
Characteristic	Value	Units	
Specific surface area (BET)	50±15	m²/g	
Crystal size	21	nm	
Humidity	<u>_1.5</u>	Wt.%	
рН	6.8	-	
Table 2. Operating conditions			

Table 1	. Specification	and characteristic	cs of TiO <sub>2</sub> catalyst

5, 7, and 9	
25	
50, 100, 150, and 200	
1, 2, 3, and 4	

#### 3. Results and Discussion

#### 3.1. Effects of solution pH

The influence of the solution pH has been investigated performing different experiments in the condition of  $TiO^2 = 1$  g/L, initial phenol concentration= 50 mg/L and pH range = 5,7,9. As displayed in Figure 1, at higher pH the phenol removal decreases, while under the acidic

at $pH \prec P_{zc}$  $TiO_2 + H^+ \rightarrow TiOH_2^+$ Eq. 1at $pH \succ P_{zc}$  $TiOH + OH^- \rightarrow TiO^- + H_2O$ Eq. 2

The results obtained by other research confirmed the experimental data of the present study.

#### 3.2. Effects of photocatalyst concentration

The influence of the photocatalyst concentration on removal of phenol has been investigated at (pH=5, phenol concentration= 50 mg/L, and TiO2 ranging= 1, 2, 3, and 4 g/L). Figure 2 illustrates that the maximum degradation rate was achieved at a photocatalyst concentration of 2 g/L. Because the generation of OH• radicals decreases when the amount of  $TiO_2$  is less than the optimum amount. This nature is due to increases and ultraviolet rays start getting scattered, hence reducing the optical path [10,11]. This lowers the rate of degradation above an optimum catalyst loading (2 g/L). In Figure 2, Goud [7] performed a similar experiment and achieved the optimal performance with 1.5 gr/l of photocatalyst and 20% pollutant removal. This dosage was higher than the other dosages of TiO<sub>2</sub>, and removal of lower points and higher points decreased. Such studies have been carried out by Ahmed [8], as demonstrated in Figure 2.

#### 3.3. Phenol initial concentration

The initial concentration of phenol plays an important role in its removal from wastewater. In this research, 4 phenol concentrations were tested under the acidic condition tested pH =5 and photocatalyst = 2 g/L. The highest removal was observed at 50 mg/L phenol initial

concentration as shown in Figure 3. This is due to the adsorption of phenol molecules. When phenol concentration phenol is high, more phenol molecules are adsorbed on the catalyst surface. With the increase in the phenol concentration, the catalyst surface active site will cover by pollutant ions and the adsorption of photons on the catalyst surface will decrease. Therefore, the generation of OH• radicals on the photocatalyst surface decreases. Hence, the available OH• radicals are inadequate for pollutant degradation at the higher concentrations. Consequently, the degradation rate of pollutants decreases as the concentration increases. Moreover, an increase in substrate concentration can lead to the intermediates generation which may adsorb on the catalyst surface. Slow diffusion of the generated intermediates from the catalyst surface can result in the deactivation of active sites of the photocatalyst, and consequently result in a reduction in the pollutants degradation rate. Therefore, when the initial concentration was almost low, the catalyst was better exposed to the light. The reaction between ultraviolet rays and electrons increased the generation of OH• radicals that which is not possible in the high concentration of pollutants [13-15]. In other studies, [7,8] illustrated in this figure, the pollutant removal rate decreases with increasing initial concentration.

conditions, the positive charge of the catalyst surface increases as the pH decreases which makes moving electrons easier and electron-hole. Therefore, at high pH, the negative charge at the catalyst surface increases with increasing pH (Equations 1 and 2) [10-12]. In Figure 1, previous studies [8,9] are shown consistent with these results.

### **Degradation Rate Kinetics**

The kinetics study of photodegradation of phenol was investigated for the  $UV/TiO_2$  systems. The loss of phenol was observed as a function of irradiation time and data were fitted to the first-order rate kinetic model, as demonstrated in

Figure 4. As a result, phenol concentrations were decreased during that period.

The results illustrated k=0.005 min -1 with R2= 0.9427. The comparison of the results of this study with others was presented in Table 3.

Table 3. Kinetic constant comparison between the present study and previous research			
K (min <sup>-1</sup> )	R <sup>2</sup>	Ref.	
0.00	0.94	Present work	
0.01	0.91	[7]	
0.58	-	[12]	



Figure 1. Influence of pH on the photocatalytic degradation of phenol pollutant



**Figure2.** Influence of TiO<sub>2</sub> loading on the photocatalytic degradation of phenol pollutant



Figure 3. Influence of initial pollutant concentration on the photocatalytic degradation at various concentrations



Figure 4. Concentration Vs time at pH =5, intial of phenol=100 ppm, and catalyst dose=2 g/L.

#### 4. Conclusion

In the present study, the suitability of phenol removal was investigated by the advanced oxidation. Different operating parameters affected photocatalytic degradation were studied. It is repeated three times for every single part of the experiment. According to the results, the maximum degradation rate of 71.9% was achieved in acidic pH equal to 5, and an optimum concentration of photocatalyst equal to 2 g/L was achieved at a phenol concentration of 50 mg/L. The results show that utilizing TiO2/UV could remove the organic pollutants from industrial wastewater with the kinetic rate of the first order. Thermodynamic analysis showed that 100 mg/L of phenol, pH = 5, and 2 g/L of photocatalyst produced the first-order kinetic constant of 0.00 min-1 with R2=0.94. In conclusion, using photocatalyst wastewater treatment is beneficial for organic pollution.

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