Research Article

Photocatalytic Degradation of Aniline Using TiO₂ Nanoparticles in a Vertical Circulating Photocatalytic Reactor

F. Shahrezaei,¹ Y. Mansouri,^{2,3} A. A. L. Zinatizadeh,⁴ and A. Akhbari⁴

¹Academic Center for Education, Culture, and Research (ACECR), Kermanshah 67145-1317, Iran

²Environmental Epidemiological Research Center, Kermanshah University of Medical Science, Kermanshah 67146-73159, Iran

³Department of Analytical Chemistry, Faculty of Chemistry, Razi University, Kermanshah 67149-67346, Iran

⁴Water and Wastewater Research Center (WWRC), Department of Applied Chemistry, Faculty of Chemistry, Razi University, Kermanshah 67149-67346, Iran

Correspondence should be addressed to Y. Mansouri, yadollamansouri@yahoo.com
and A. A. L. Zinatizadeh, aliazinatiz@yahoo.com

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Photocatalytic degradation of aniline in the presence of titanium dioxide (TiO₂) and ultraviolet (UV) illumination was performed in a vertical circulating photocatalytic reactor. The effects of catalyst concentration (0–80 mg/L), initial pH (2–12), temperature (293–323 K), and irradiation time (0–120 min) on aniline photodegradation were investigated in order to obtain the optimum operational conditions. The results reveal that the aniline degradation efficiency can be effectively improved by increasing pH from 2 to 12 and temperature from 313 to 323 K. Besides, the effect of temperature on aniline photo degradation was found to be unremarkable in the range of 293–313 K. The optimum catalyst concentration was about 60 mg/L. The Langmuir Hinshelwood kinetic model could successfully elucidate the effects of the catalyst concentration, pH, and temperature on the rate of heterogeneous photooxidation of aniline. The data obtained by applying the Langmuir Hinshelwood treatment are consistent with the available kinetic parameters. The activated energy for the photocatalytic degradation of aniline is 20.337 kJ/mol. The possibility of the reactor use in the treatment of a real petroleum refinery wastewater was also investigated. The results of the experiments indicated that it can therefore be potentially applied for the treatment of wastewater contaminated by different organic pollutants.

1. Introduction

Aniline is one of the most toxic pollutants; it is released into the environment after its use in the manufacturing of dyes, rubber, polymers, herbicides, pesticides, fungicides, and pharmaceuticals [1]. Aniline is also found in the effluents of petroleum refinery plants. Because of its toxic and recalcitrant nature and the wide application of aniline containing chemicals, aniline is considered to be an increasing threat to both the environment and human health. Therefore, aniline has aroused great attention and is classified as a persistent organic pollutant by the European Economic Community and US Environmental Protection Agency [2]. So there is an urgent need to develop efficient and economical methods to remove this pollutant from wastewater.

Several solutions are proposed in this regard, including adsorption [3], chemical oxidation [4, 5], biological [6], and

catalytic wet air oxidation (CWAO) [7]. Unfortunately, the main drawback of these techniques relates to the disposal of the spent contaminated activated sludges, the control of the appropriate reaction conditions, low efficiencies and reaction rates, and operation only within a narrow pH range [8, 9].

During the past decade, great interest has been focused on a promising technology based on the oxidation of the hazardous and refractory organic compounds, by the use of advanced oxidation processes (AOPs) [10]. Various combinations of hydrogen peroxide, ozone, and ultraviolet light are used to generate hydroxyl radicals (HO[•]) in the AOPs. Hydroxyl radicals are the principal agents responsible for the oxidation of numerous aqueous organic contaminants and are quite energy intensive. One emerging technology, however, utilizes illuminated semiconductors and is commonly referred to as the heterogeneous photocatalysis.

FIGURE 1: Experimental setup of photoreactor.

The heterogeneous photocatalysis oxidation (HPO) process employing TiO₂ and UV light has emerged as a promising new route for the degradation of persistent organic pollutants, and produces more biologically degradable and less toxic substances [11, 12]. This process is highly dependent on the insitu generation of hydroxyl radicals under ambient conditions which are capable of converting a wide spectrum of toxic organic compounds including the nonbiodegradable ones into relatively innocuous end products such as CO₂ and H₂O.

In spite of the considerable success of TiO₂/UV for the treatment of various types of wastewater, its application as a possible technique for the degradation of aniline is rather scarce in the literature. The main objective of the present study, therefore, is to evaluate the reduction of aniline in aqueous solutions using UV/TiO₂ at different operating conditions.

Furthermore, most of the studies on aniline decomposition by AOPs up to date have not provided in depth on the degradation kinetics which are also important scientific information; hence, this study also investigated into more details on kinetics of aniline degradation by UV/TiO₂ in order to develop the rate equations which can provide fundamental knowledge for future use. Also, the removal efficiency was studied using real petroleum refinery wastewater to explore the applicability of the technique in industry.

2. Experimental

2.1. Chemicals. The chosen catalyst of titanium dioxide was mainly anatase (80% anatase and 20% rutile, Degussa P 25) with a particle size of 30 nm and a surface area of 50 m²/g (purchased from Plasmachem Co.). This catalyst is the best one which gives an optimal efficiency of catalysis, furthermore, good interparticle contacts are formed between

anatase and rutile particles in water [13]. Sulfuric acid and sodium hydroxide solutions were used to adjust the pH of samples [14].

2.2. Analytical Methods. The aniline concentrations in feed and permeate solutions were determined spectrophotometrically at 280 nm, after dilution with 1 M NaOH, using a UV spectrophotometer (DR 5000, Hach, Jenway, USA). TOC was determined with a Shimadzu TOC-5000 total organic carbon analyzer. The identification of the compounds in the real wastewater before and after the degradation was performed by means of the GC/MS system.

GC/MS analysis of the organic compounds was performed using an HP-6890 GC system coupled with a 5973 network mass selective detector and equipped with an HP5-MS capillary fused silica column (60 m, 0.25 mm I.D.; 0.25 mL film thickness). Real wastewater (1 µL) in hexane (HPLC grade) was injected and analyzed with the column held initially at 40°C for 1 min and then increased to 250°C with a 3°C/min heating ramp and subsequently kept at 250°C for 20 min. Other operating conditions were as follows: carrier gas, He (99.999%); with a flow rate of 1 mL/min; injector temperature, 250°C; split ratio, 1:50. Mass spectra were taken at 70 eV. The pH meter model HANNA-pH 211 was used to measure the pH. Turbidity was measured by a turbidimeter model 2100 P (Hach Co.).

2.3. Photoreactor Configuration. Figure 1 shows the experimental setup of the photoreactor used for the degradation of aniline. Experiments were carried out in a vertical reactor with the capacity of about 1200 mL and a conic shape in the lower part of its body. The UV lamp 22 cm body length and 16 cm arc length) was a mercury 400 W (200–550 nm) lamp. The UV lamp was positioned inside a quartz tube and totally immersed in the reactor. Therefore, the maximum

TABLE 1: Experimental design for photocatalytic degradation of aniline.

Factors	Values	Other conditions
Initial pH	2	—
	4	Initial concentration of aniline: 50 mg/L TiO ₂ concentration: 60 mg/L Temperature: 293 K
	6	
	8	
	10	
	12	—
TiO ₂ concentration (mg/L)	20	Initial concentration of aniline: 50 mg/L
	40	Initial pH: 6
	60	Temperature: 293 K
	80	—
Temperature (K)	293	—
	303	Initial concentration of aniline: 50 mg/L
	313	Initial pH: 6
	323	TiO ₂ concentration: 60 mg/L

light utilization was achieved. A pump was located below the reactor and provided an adjustable circulating stream, feeding from top of the reactor and discharging from the bottom just below the lamp for the well mixing and fluidizing of nanoparticles of catalyst along the quartz tube. It was not expected that a single pass of polluted water through a short reactor would give adequate degradation. If particles in the water surrounding a lamp are well mixed then each particle on average achieves equal exposure for regulating the temperature; the reactor vessel was equipped with a water-flow jacket, using an external circulating flow of a water bath. Air flow was supplied to the reactor at a constant flow rate (3 L/min) using a lab scale air compressor.

2.4. Experimental Design. Based on the literature, four operational and process factors, namely, pH (2–12), catalyst concentration (0–80 mg/L), temperature (293–323 K), and reaction time (30–120 min) were introduced with the most significant impact on the photocatalytic degradation of pollutants using TiO₂ nanoparticles and UV illumination which were considered as the system variables, and aniline removal efficiency was calculated as the process response [15]. The experimental design is listed in Table 1.

2.5. Photoreactor Operation. In the first stage, to run the experiments, 1200 mL of a sample, containing a known level of aniline (50 mg/L) and with the appropriate amount of added catalyst, was transferred to the reactor. The solution was then exposed to continuous aerating and circulating. After adjustment of temperature and pH, the UV irradiation was begun. In the second stage, the photoreactor was operated under the experiments' conditions (Table 1) to compare the effects of various factors on aniline photodegradation efficiency.

2.6. Photodegradation Kinetic Parameters. The mechanism of aniline degradation catalyzed by TiO₂ is proposed to consist of the following three steps: (1) adsorption of organic

pollutant on the surface of TiO₂ (2) surface photodegradation of organic pollutant, and (3) desorption of final products from the surface of TiO₂. The photodegradation of organic pollutants is the rate-predominant step which involves the excitation of the titanium dioxide by a UV light wavelength of $\lambda \leq 400$ nm, electron-hole pairs (e_{cb}^- , h_{vb}^+) are generated, and the hydroxyl radicals are generated by the hole which can degrade organic pollutants present in the wastewater. Oxygen, provided from the air (when the system is stirred and aerated), dissolved in the solution scavenges the electron generated, preventing the recombination of electrons and holes. UV illumination of TiO₂ yields conduction band electrons and valence band holes, which interact with surface adsorbed molecular oxygen to yield superoxide radical anions, O₂^{•−}, and with water and hydroxyl to produce the highly reactive HO[•] radicals, respectively. The latter radical species are well known to oxidize a large number of organic substrates [16–18]. Acknowledging the above-mentioned reaction steps for photocatalysis, the elementary reaction equations are expressed as the following equations:

In general, the kinetics of photocatalytic reactions of organic water impurities, including aniline, phenol and its derivatives, follows the Langmuir-Hinshelwood (L-H) which is considered to follow pseudo first- order decay kinetics [19];

$$r = -\frac{dC}{dt} = \frac{kK_{ad}C}{1 + K_{ad}C}, \quad (6)$$

where r is the reaction rate, k is the aniline degradation rate constant, K_{ad} is the adsorption equilibrium constant, and C is the concentration of substrate remaining in the solution at time (t). In this study, aniline concentration C was less than 1×10^{-3} mol/L, which made $KC \ll 1$; hence, (6) can be transformed to (7) as follows [20]:

$$r = -\frac{dC}{dt} = kK_{ad} C. \quad (7)$$

A linear form of (7) is

$$\ln \left(\frac{C_0}{C} \right) = kK_{ad} C = K_{ap} t, \quad (8)$$

where K_{ap} is the apparent reaction rate constant, which can be calculated from the slope of the $\ln \left(\frac{C_0}{C} \right)$ plot, and C_0 is the initial substrate concentration. The effects of various reaction parameters on the photocatalytic performance of TiO_2 were expressed in terms of K_{ap} .

3. Results and Discussion

3.1. Influence of Catalyst Concentration. The effect of photocatalyst (TiO_2) concentration on the degradation of aniline in the photoreactor was investigated. The experiments were conducted at various amounts of TiO_2 concentration of 0 (only UV), 20, 40, 60, and 80 mg/L while initial aniline concentration, pH, and temperature of bulk liquid used were 50 mg/L, 6, and 293 K, respectively. The effect of the amount of TiO_2 on the removal of aniline was significant as shown in Figure 2, confirming the positive influence of the increased number of TiO_2 active sites on the process kinetics. It could be seen from Figure 2 that photocatalytic degradation efficiency has increased up to 60 mg/L and then declined with increasing catalyst loading. The changes of K_{ap} versus catalyst concentration are illustrated in Figure 3 and Table 2. The values of K_{ap} increased with increasing catalyst concentration up to 60 mg/L. Then, the apparent degradation rate constant K_{ap} decreased slightly, when catalyst concentration was higher than 60 mg/L.

The maximum values of the aniline removal efficiency and K_{ap} were obtained to be 62% and 0.265 h^{-1} at irradiation time and catalyst concentration, respectively, 2 h and 60 mg/L, whereas the minimum values of the responses were obtained under UV light power at 400 W without the use of TiO_2 nanoparticles. The removal efficiency and K_{ap} of the photodegradation of aniline under UV light were only 19% and 0.061 h^{-1} , respectively. Thus, it is necessary to apply the photocatalyst into the system to enhance the rate of reaction.

The increase of aniline removal efficiency and K_{ap} with increasing in catalyst concentration seems to be the results of an increase in the total surface area of TiO_2 , namely, an increase of the active sites and an increase in the hydroxyl radicals generation. However, when enough TiO_2 is present in the reactor for adsorbing aniline molecules, the extra higher quantities of TiO_2 nanoparticles would not have more positive effect on the aniline degradation efficiency. On the contrary, when TiO_2 was overdosed, the number of active sites on the TiO_2 particle surface, which was available for

FIGURE 2: Effect of catalyst concentration on aniline removal (initial pH: 6, temperature (T): 293 K).

FIGURE 3: Changes of the apparent aniline photocatalytic reaction constant K_{ap} at different catalyst concentration (initial pH: 6, temperature (T): 293 K, and irradiation time: 2h).

TABLE 2: Effect of catalyst concentration on photocatalytic degradation of aniline under UV illumination in HCBR (experimental conditions: initial aniline: 50 mg/L; initial pH: 6, temperature: 293 K).

Catalyst concentration (mg/L)	Equation	K_{ap}	R^2
0 (only UV)	$0.061x + 0.178$	0.061	0.97
20	$0.066x + 0.178$	0.066	0.897
40	$0.132x + 0.311$	0.132	0.988
60	$0.265x + 0.397$	0.265	0.939
80	$0.210x + 0.330$	0.21	0.957

the photocatalytic reaction, might approach constant or even decrease slightly because of the decrease of light penetration and the increase of UV light scattering. Therefore, there is an optimum TiO_2 dosage for aniline removal, in this case, the optimal TiO_2 dosage for aniline photodegradation was about 60 mg/L. Similar phenomena have already been reported in other TiO_2 suspension photocatalytic systems. For example, the optimum TiO_2 dosage for the photocatalytic degradation

FIGURE 4: Effect of pH on aniline removal at two typical irradiation times (1 h and 2 h); (catalyst concentration: 60 mg/L and $T = 293$ K.)

FIGURE 5: Changes of the apparent aniline photocatalytic reaction constant K_{ap} at different pH (catalyst concentration: 60 mg/L, temperature (T): 293 K, and irradiation time: 2h).

of fungicide carbendazim is about 70 mg/L [21]. This is due to the increase of internal mass transfer resistance and light shielding effect, which can further result in the decrease of overall reaction rate at very high TiO_2 dosage [22].

3.2. Effect of pH. Changing electrolyte pH can vary the surface charge at the TiO_2 surface and also shifts the potential of some redox reaction, thus, it affects the adsorption of organic solutes, consequently, its reactivity and some reaction rate. The effect of pH on aniline degradation rate was investigated in the range of 2–12 at aniline concentration 50 mg/L and TiO_2 concentration of 60 mg/L. The comparison of aniline removal rate at different pH values at two different times of 60 and 120 min is shown in Figure 4. The changes of K_{ap} versus pH were illustrated in Figure 5.

From Figure 4, it is observed that as the pH increases from acidic to alkaline the rate of aniline removal efficiency increases and is maximum at pH 12. In case of initial pH values 2, 4, 6, 8, 10, and 12.0, the percentage removal of aniline, was 27, 56, 62, 60, 66, and 76, and K_{ap} was 0.128, 0.189, 0.265, 0.266, 0.304, and 0.45, respectively, as shown in Figures 4 and 5 and Table 3. The increasing aniline removal

TABLE 3: Effect of pH on photocatalytic degradation of aniline under UV illumination in HCBR (experimental conditions: initial aniline: 50 mg/L; catalyst concentration: 60 mg/L; temperature: 293 K).

pH	Equation	K_{ap}	R^2
2	$0.128x + 0.058$	0.128	0.991
4	$0.189x + 0.451$	0.189	0.989
6	$0.265x + 0.397$	0.265	0.94
8	$0.266x + 0.304$	0.266	0.91
10	$0.304x + 0.502$	0.304	0.951
12	$0.450x + 0.504$	0.450	0.991

efficiency and K_{ap} with increasing pH can be attributed to the increase in the number of OH^- ions at the surface of TiO_2 , since OH^- can be formed by trapping photo-produced holes. Also, the dissociation of aniline probably changes its reactivity. Similarly, the decrease at the lowest pH can be explained by the lack of OH^- ions. Richard et al. [23] found that OH^- was the sole oxidant under the condition of pH 11 and its role was larger in this case than in neutral and acid medium. So K_{ap} increases rapidly with the increasing of pH when greater than 10. In general, the results indicate that the efficiency of the process is not much affected over a wide range of pH, which is quite satisfactory in view of applications.

3.3. Effect of Temperature. In general, the activated energy of photocatalytic reaction is slightly affected by the temperature, but consecutive redox reaction may be largely influenced by temperature which affects both collision frequency of molecules and adsorption equilibria [15]. So the overall effect on the photocatalytic performance will depend on the relative importance of these phenomena. The effect of temperature on the aniline photodegradation in aqueous solution with the presence of TiO_2 and UV was investigated in the range of 293–323 K. The results are demonstrated in Figure 6. As seen in the figure, increase in temperature from 293 to 323 K has reduced the required time for the aniline removal. For the removal of around 60%, for instance, the required time has been decreased from more than 120 min to about 30 min. As noted in Figure 6, the maximum aniline removal was determined to be 82% at irradiation and temperature of 2 h and 323 K, respectively.

The reason of this observation is thought to be the fact that temperature is an important factor affecting the adsorption and photocatalysis. In the case of photocatalytic process, the photocatalytic degradation rate increases with increasing temperature. However, the results indicate that the reaction rate plays a more important role than adsorption rate in the degradation process of aniline. In other words, higher temperature provides higher TiO_2 electron transfers in valance bond to higher energy levels and hence facilitating the electron-hole production that could be utilized in initiating oxidation and reduction reactions, respectively [24]. The species photon-generated holes (h_{vb}^+), and electrons (e_{cb}^-), and hydroxyl radicals ($\text{OH}^\bullet$) can thus degrade organic pollutant to intermediates, and then the intermediates are further degraded to CO_2 and H_2O .

FIGURE 6: Effect of temperature on aniline removal (initial pH: 6, catalyst concentration: 60 mg/L).

FIGURE 7: Linear fit of reactions at different temperature (initial pH: 6, catalyst concentration: 60 mg/L).

In order to obtain activation energy (E) for photocatalytic degradation of aniline, the rate data were modeled by first-order kinetics as in the following equation:

$$\frac{dC}{dt} = -kC, \quad (9)$$

where t is reaction time, C is concentration of aniline, and k is the rate constant which has the following temperature dependency:

$$k = A \exp\left(\frac{-E}{RT}\right), \quad (10)$$

where A is the preexponential factor, E is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. Integrating (9) gives

$$\ln\left(\frac{C_0}{C}\right) = k \cdot t. \quad (11)$$

Figure 7 shows the correlation between the $\ln(C_0/C)$ and the reaction time (t) in the photoreactor drawn based on

TABLE 4: Effect of temperature on photocatalytic degradation of aniline under UV illumination in HCBR (experimental conditions: initial aniline: 50 mg/L; catalyst concentration: 60 mg/L; pH: 6).

Temperature (K)	Equation	K_{ap}	R^2
293	$0.266x + 0.397$	0.266	0.969
303	$0.286x + 0.466$	0.286	0.984
313	$0.459x + 0.397$	0.459	0.956
323	$0.539x + 0.646$	0.539	0.985

FIGURE 8: Effect of temperature on rate constants.

(11) under conditions (pH of 6, catalyst concentration of 60 mg/L) at four different temperatures (293, 303, 313, and 323).

The data fitted well with an $R^2 > 0.96$. The high values of the determination coefficients (R^2) clearly indicate that first-order kinetics can be applied with a good degree of precision. The values of kinetic constant (k) were calculated to be in the range of 0.266–0.539 (h^{-1}) (Figure 7 and Table 4). As expected, the rate constant k increases with increasing temperature, and k is very sensitive to the change of temperature. To calculate the activated energy E and constant A , (10) was transformed into a logarithmic form, which was plotted in Figure 8. From the slope and intercept of the best-fit line, the following values were found, $A = 1048.1$ and $E = 20.337$ kJ/mol.

Finally, the reaction kinetic equation of photocatalytic degradation of aniline is

$$-\frac{dC}{dt} = 1048.1 \exp\left(\frac{20327}{RT}\right) \text{COD}. \quad (12)$$

This indicates that the reaction has high activation energy.

3.4. Investigation on Mineralization of Aniline. Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a nonspecific indicator of water quality. Using this criterion, the mineralization of aniline was investigated under the process of photocatalytic degradation under optimum operating conditions. For the initial concentration of 50 mg/L of aniline and under the optimum conditions, the TOC values were

FIGURE 9: Comparison of chromatograms for degradation of aniline and other compounds in real petroleum refinery wastewater (catalyst concentration: 100 mg/L, initial PH: 7, temperature (T): 293 K, and irradiation time: 2h).

measured at different times and the appropriate conversion was calculated. Using the photocatalysis process and after 120 min, TOC decreased from 39 mg/L to about 12.4 mg/L, equivalent of about 68.2% efficiency. The results indicate an effective mineralization of aniline a short time (about 60 min).

3.5. Treatment of Petroleum Refinery Wastewater containing Aniline in the Vertical Circulating Photocatalytic Reactor.

In order to investigate the performance of this circulating photocatalytic reactor in the removal of aniline from real wastewater, a laboratory test was performed using the pretreated petroleum refinery wastewater sample (after electrochemical methods). The sample was collected from the point that the wastewater is just leaving the dissolved air flotation (DAF) and just into the biological treatment unit in the Kermanshah refinery plant. Total chemical oxygen demand (TCOD), measured at this point, was about 220 mg/L. Other specifications were, pH: 7.1, turbidity: 85 NTU, and total dissolved solids (TDS): 560 mg/L. In the line with this, the reactor was operated under conditions (pH of 7.1 (natural), catalyst concentration of 100 mg/L, and irradiation time of 120 min) at temperatures of 293 K. In order to identify the present organic compounds in the samples and to compare the efficiency of degradation for different compounds, 10 mL samples of wastewater were taken before and after the degradation. The catalyst particles were separated and analyzed by means of the GC/MS. In Figure 9, (a) and (b) present the chromatograms of the analyzing wastewater before and after the degradation under optimum conditions. The major peaks have been labeled by name according to the GC/MS identification. Comparison of two chromatograms in the figure proved that all pollutants were degraded at relatively high efficiencies. The maximum

TCOD removal efficiency was found to be more than 85%.

4. Conclusions

The influences of catalyst concentration, initial pH, temperature, and irradiation time on the degradation rate of aniline were investigated in a vertical circulating photocatalytic reactor. The variation of pH has a pronounced effect on degradation rate; alkaline condition promotes the rate considerably because of change of surface charge, whereas acidic environment casts a negative effect on degradation. Besides, the catalyst concentration also influences the degradation rate, and the rate constant reaches the peak when the TiO_2 concentration is 60 mg/L and then decreases when increasing to 80 mg/L. The temperature (in the range of 293–313 K) did not show a strong effect on the process, as only a small difference is observed in the results obtained with different temperature (293, 303, and 313 K). However, the results reveal that the aniline degradation efficiency can be effectively improved by increasing pH from 2 to 12 or increasing the temperature from 313 to 323 K. Conclusively, an optimum condition for vertical circulating photocatalytic reactor operation with initial aniline concentration of 50 mg/L was achieved as follows: initial pH at 12, catalyst concentration at 60 mg/L, and temperature at 323 K. The activation energy for the photocatalytic degradation of anilines is 20.337 kJ/mol and Langmuir Hinshelwood can be used to describe the photodegradation reaction. The possibility of vertical circulating photocatalytic reactor in the treatment of petroleum refinery wastewater was also investigated. The results of the experiments indicated that it can therefore be potentially applied for the treatment of wastewater contaminated by different organic pollutants.

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