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Short communication

Thermodynamic parameters of activation for photodegradation of phenolics

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ABSTRACT

The photocatalytic degradation of three phenolics namely phenol, 4-chlorophenol and 4-nitrophenol were carried out in aerated aqueous suspension of TiO_2 irradiated by ultraviolet light. The influence of temperature at optimized pH and TiO_2 concentration was studied. The degradation kinetics were somewhat accelerated by increase in temperature in the range 25–45 °C and apparent activation energy was calculated to be 9.68–21.44 kJ mol^{-1}. Thermodynamic parameters of activation were also assessed for the degradation process. Formation of acidic species results in decrease in pH of solution. The appearance and the evolution of main intermediate species like hydroquinone, benzoquinone and catechol during the degradation process were computed by UV–vis spectral analysis.

1. Introduction

The presence of contaminants in wastewater has caused severe environmental problems since couple of decades. A typical group of contaminants is the phenols and its derivatives such as 4-chlorophenol and 4-nitrophenol (hereafter called phenolics) that are invariably present in the wastewater. Phenolics may occur in the environment due to its widespread use in agricultural, petrochemical, textile, paint, plastic and pesticidal industries. Phenolics are considered as EPA's priority pollutants [1]. Due to their bioaccumulation, toxic and carcinogenic properties, phenolics pose a risk to mammalian and aquatic life [2]. These compounds have significant water solubility, and have to be eliminated to preserve the environmental quality.

One of the most effective methods is the use of advanced oxidation processes (AOPs). AOPs can quickly and non-selectively oxidize organic pollutants, by the production of highly oxidative species like hydroxyl radical ($^{\bullet}OH$) [3] under ultraviolet (UV) light-catalyzed reactions [4–6]. Titanium dioxide (TiO_2) has been widely studied due to its application in heterogeneous catalysis. TiO_2 induced by UV light of wavelength shorter than 387 nm promotes electrons from valence band to conduction band to give electron–hole pairs. Electrons are accepted by oxygen molecules forming superoxide ions $O_2^{\bullet -}$, whereas holes are consumed by the hydroxyl ions on the TiO_2 surface producing $^{\bullet}OH$. These resultant ions are potential oxidants capable of oxidizing most organic pollutants [7].

An enormous literature is documented regarding photocatalytic degradation of organic pollutants using TiO_2 [7–10]. Very few studies have been published which consider the thermodynamic aspect of photodegradation. However, the quantitative data on thermodynamic parameters relating the degradation process is inadequate. To the best of our knowledge, there is lack of kinetic data, which relates thermodynamic parameters of activation with photodegradation of phenolics. Moreover, photocatalytic degradation of organic pollutants may take place through formation of intermediates that are more toxic than the parent compounds. Therefore, information on the quantification of the intermediates is also necessary in wastewater treatment.

In earlier reports, we have investigated the photodegradation of phenol under the influence of TiO_2 [11] and iron-doped TiO_2 nanoparticles [12]. This on-going study portrays the photodegradation of phenolics on UV-irradiated TiO_2 Degussa P25. UV–vis spectroscopy was employed to rationalize the result of photocatalytic degradation. The kinetic studies permit us to determine the effect of temperature. Thus the objectives were to study the thermodynamic parameters of activation and measurement of main intermediates during the photodegradation process.

2. Experimental

2.1. Materials

TiO_2 (Degussa P25, ca. 80% anatase, 20% rutile; average particle size, ca. 21 nm; BET area, ca. 50 ± 15 m^2 g^{-1}) was used as the photocatalyst directly without pretreatment. Analytical reagent grade phenol, sodium hydroxide and hydrochloric acid were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 4-

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Table 1
Operating conditions for the photocatalytic degradation of phenolics.

Phenolics	Concentration (M)	Optimized TiO_2 (mg/L)	Irradiation time (min)
Phenol	3.56×10^{-4}	400	360
4-CP	3.56×10^{-4}	300	360
4-NP	4.9×10^{-5}	200	300

Chlorophenol (4-CP) and 4-nitrophenol (4-NP) were purchased from Aladdin Chemical Reagent Co., China. Purified water was obtained from a Milli-Q apparatus (Millipore Co.).

2.2. Photocatalytic measurement

Photocatalytic degradation experiments were carried out in an open Pyrex glass cell with 500 mL capacity. An aqueous suspension (200 mL) was prepared by appropriate amount of TiO_2 containing the phenolics at certain concentration. Air was bubbled in the solution to keep all the TiO_2 in the suspension. Prior to irradiation, the suspension was magnetically stirred for 15 min in the dark to ensure adsorption equilibrium, followed by irradiation with 125 W high pressure UVA bulb with the strong emission at 365 nm. The pH of the suspensions was adjusted by addition of dilute aqueous solution of HCl or NaOH. Table 1 summarizes the operating conditions used for photocatalytic degradation experiments. At certain irradiation time interval, 7 mL of the sample was collected. The samples were centrifuged at 3000 rpm for 10 min and subsequently filtered to separate TiO_2 particles. The filtered samples were stored at 4 °C prior to analysis. The degradation of phenol, 4-CP and 4-NP was followed by measuring the change in absorption intensity using Helios Gamma UV–vis spectrophotometer. The UV–vis spectrophotometer was set at a wavelength of 270, 278 and 315 nm for analysis of phenol, 4-CP and 4-NP, respectively. The main intermediate products of degradation of phenolics were also determined by UV–vis spectroscopy at their corresponding wavelength.

Ion chromatography (IC) was used to determine the chloride and nitrate generated from phenolic degradation. The IC system was a Dionex ICS-3000 equipped with a conductivity detector and a Dionex IonPac CS12A column (2 mm × 250 mm) connected with a guard column (2 mm × 50 mm). A solution containing 100 mM NaOH at a flow rate of 0.25 mL min^{-1} served as the eluent.

3. Results and discussion

3.1. Kinetics of photodegradation of phenolics

Fig. 1 describes the relative decrease in absorption intensity of phenolics as a function of irradiation time in the presence or absence of TiO_2. It can be inferred that there is no appreciable degradation when the aqueous solution was irradiated in the absence of TiO_2. It can be neglected with less than 7% degradation of any phenolic, ca. after 6 h of irradiation. The enhanced degradation by UV/TiO_2 process suggests that both UV light and TiO_2 were required for efficient degradation of phenolics. From engineering point of view, it is useful to find out a simple user-friendly rate equation that fits the experimental rate data. According to many researchers the photocatalytic degradation of organic pollutants is described by pseudo-first order kinetics [13–15].

$$-\frac{dC}{dt} = k_{app}C \qquad (1)$$

Integration of Eq. (1) with the boundary condition that at the start of irradiation ($t = 0$), the concentration is the initial one, $C_t = C_o$, yields Eq. (2):

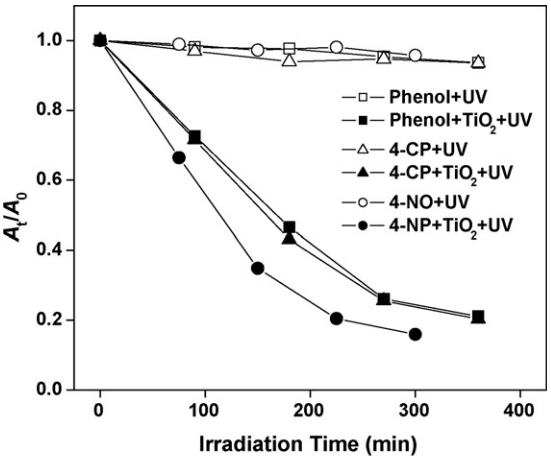

Fig. 1. Change in absorption intensity of phenolics as a function of irradiation time.

$$-\ln\left(\frac{C_t}{C_o}\right) = k_{app}t \qquad (2)$$

where k_{app} is the apparent first order rate constant (min^{-1}) and C_o and C_t is the concentration of phenolics at a given irradiation time, t (min), respectively. Kinetic studies were assessed by monitoring the change in phenolics' concentration at certain interval of time (C_t). Apparent first order rate constants (k_{app}) were determined employing Eq. (2) from plot of $-\ln[C_t/C_o]$ versus irradiation time, t. The k_{app} was determined by calculating the slope of the line obtained. The resulting first order rate constants have been used to calculate degradation rate for phenolics and thermodynamic parameters of activation.

3.2. Effect of pH and catalyst loading

Solution pH plays an important role in the photocatalytic degradation of organic compounds on TiO_2. Fig. 2 demonstrates the effect of pH on absorption intensity of phenolics. Mild acidic pH value (ca. 5) has been found to be favorable for the photocatalytic degradation of phenolics as observed in the literature [11,12,16–18]. The reason is that point of zero charge (pH_{pzc}) of TiO_2 is pH ~6.8, its surface is positively charged in acidic medium and the phenolate ion is negatively charged so an electrostatic attraction is developed. This favors the adsorption of phenolic onto the TiO_2 surface and facilitates the degradation. Moreover, it is apparent from Fig. 2, that at the start of photocatalytic degradation, C_t is higher than C_o for phenol and 4-CP at pH 9. This may arise from desorption of phenolics stimulated by irradiation [12,19].

The effects of TiO_2 concentration from 50 to 1000 mg/L on the photocatalytic degradation kinetics of phenolics have been investigated. Fig. 3 shows the apparent rate constant as a function of TiO_2 loading at pH 5. It is obvious that k_{app} increased with an increase in concentration of TiO_2 up to a certain limit after which decrease in k_{app} was observed. This is characteristics for heterogeneous photocatalyst and is in agreement with earlier reports [10–12]. This can be attributed to the fact that increased number of TiO_2 particles will increase the availability of active sites of TiO_2 surface and number of photons absorbed. Beyond optimal TiO_2 concentration, decrease in the photodegradation may be due to the turbidity and possible aggregation of free TiO_2 particles, which results in decrease in the number of surface active sites [10,20].

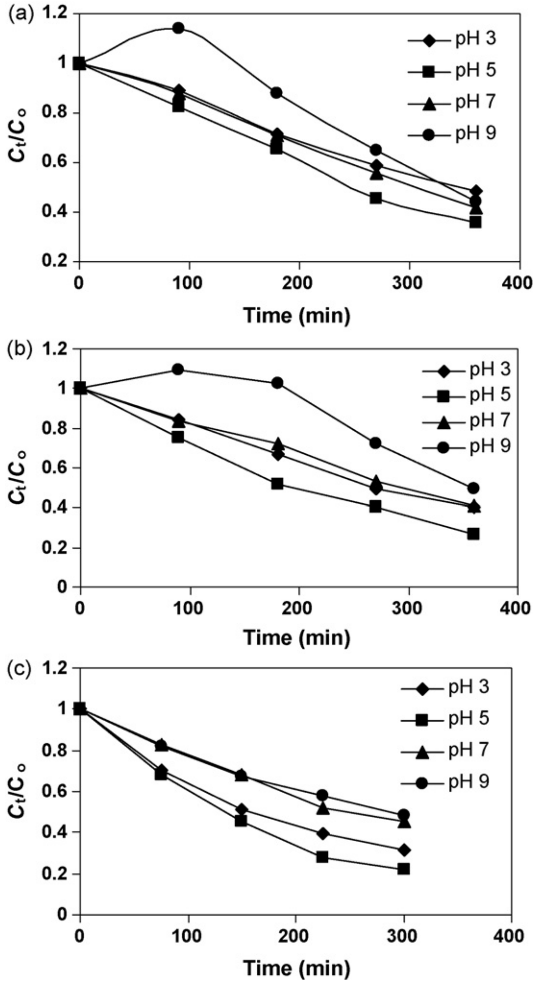

Fig. 2. Effect of pH on the aqueous solution of (a) phenol, (b) 4-CP, and (c) 4-NP at TiO_2 loading = 100 mg/L.

3.3. *Effect of temperature*

Since the reaction temperature could affect the degradation rate. Thus the effect of temperature on photodegradation process was studied at various temperatures in the range from 25 to 45 °C.

Table 2
Effect of temperature on the degradation rate constant of phenolics.

Temperature (°C)	k_{app} (10^{-2} min^{-1})		
	Phenol	4-CP	4-NP
25	0.46	0.47	0.65
30	0.51	0.52	0.79
35	0.59	0.55	0.87
40	0.71	0.57	0.98
45	0.77	0.61	1.06

Table 2 lists the apparent rate constant (k_{app}) of phenolics with increasing temperature. An increase of degradation was observed with increasing temperature. The apparent rate constant and temperature can be expressed by Arrhenius relation as follows:

$$k_{app} = Ae^{-E_a/RT} \tag{3}$$

where k_{app} is the apparent rate constant, A is the frequency factor or pre-exponential factor, E_a is the activation energy of the reaction, R is general gas constant and T is the absolute temperature.

Translation of Eq. (3) resulted in Eq. (4)

$$\ln k_{app} = \ln A - \frac{E_a}{RT} \tag{4}$$

A linear plot of $\ln k_{app}$ versus $1/T$ yielded a straight line (Fig. 4) from which the activation energy can be obtained and are given in Table 3. The augmentation of the photocatalytic degradation activity is probably due to the increasing collision frequency of molecules in the solution. For TiO_2 photocatalytic degradation, irradiation is the primary source of electron–hole pair generation at ambient temperature as the band gap is too high to be overcome by thermal activation [21]. The other thermodynamic parameters for instance free energy of activation ($\Delta G^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) were calculated (Table 3) using activation energy and apparent rate constant as follows [22]:

$$\Delta G^{\neq} = RT \times (23.76 + \ln T - \ln k_{app}) \tag{5}$$

$$\Delta H^{\neq} = E_a - RT \tag{6}$$

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} \tag{7}$$

From Table 3, it can be accomplished that semiconductor mediated photocatalytic degradation is usually not very temperature dependent. Nevertheless, an increase in temperature facilitates

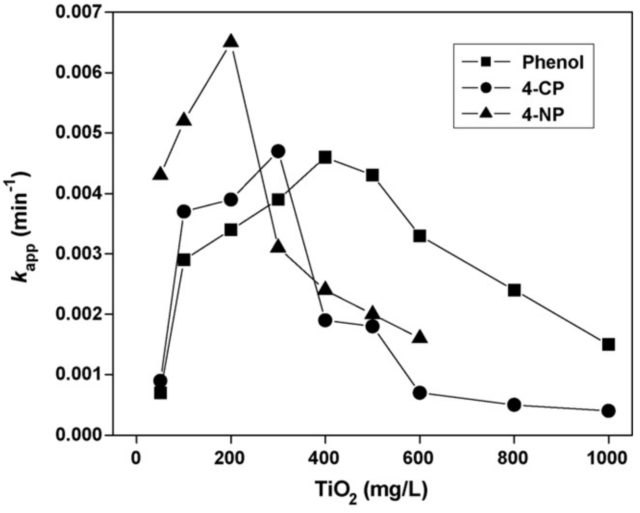

Fig. 3. Effect of TiO_2 loading on the degradation of phenolics at pH 5.0.

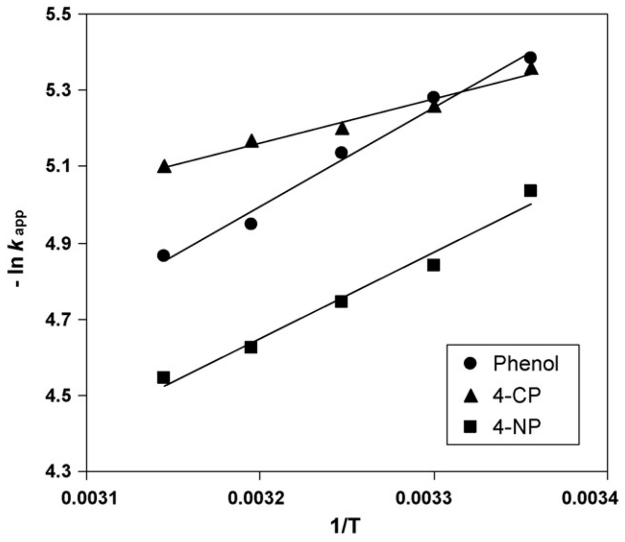

Fig. 4. Effect of temperature on the apparent rate constant of phenolics at pH 5.0.

Table 3
Thermodynamic parameters for the photocatalytic degradation of phenolics.

T (°C)	E_a (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
Phenol				
25	21.44	86.32	18.97	−0.226
30		87.55	18.92	
35		88.66	18.88	
40		89.66	18.84	
45		90.92	18.80	
4-CP				
25	9.68	86.26	7.21	−0.265
30		87.50	7.16	
35		88.84	7.12	
40		90.23	7.08	
45		91.53	7.04	
4-NP				
25	18.86	85.46	16.38	−0.232
30		86.44	16.34	
35		87.66	16.30	
40		88.82	16.26	
45		90.07	16.21	

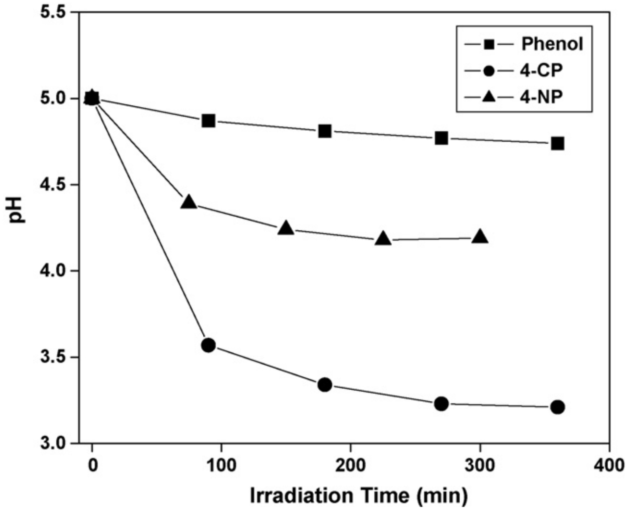

Fig. 5. Change in pH during the photocatalytic degradation of phenolics.

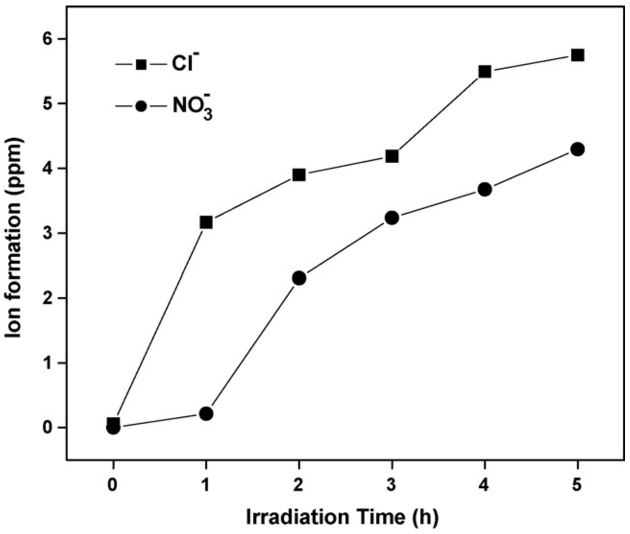

Fig. 6. Formation of Cl$^-$ and NO$_3{}^-$ during the photocatalytic degradation of 4-CP and 4-NP.

the reaction to compete more efficiently with electron–hole pair recombination.

3.4. Decrease in solution pH

The pH value of the phenolic solution versus irradiation time, varied during the photocatalytic degradation, is reported in Fig. 5.

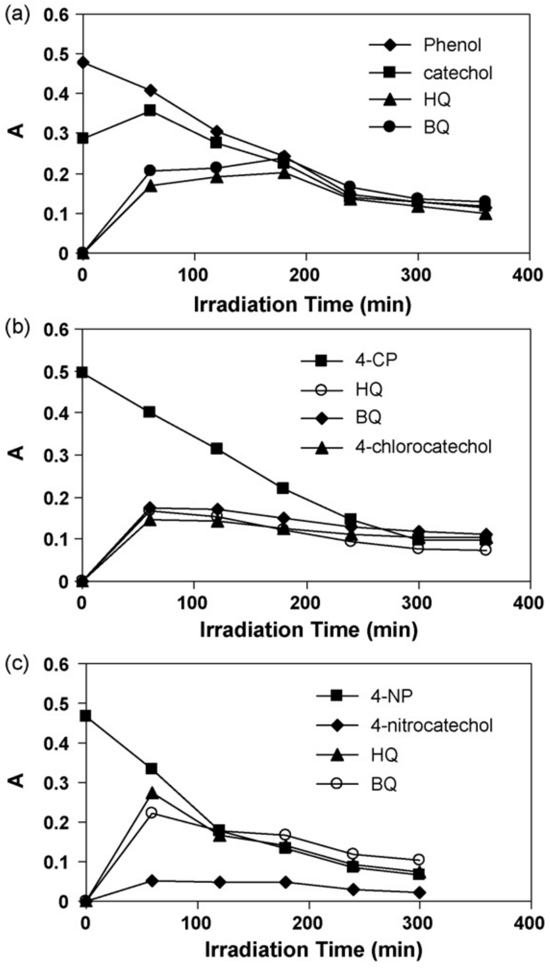

Fig. 7. Evolution of the main intermediates during the degradation of (a) phenol, (b) 4-CP, and (c) 4-NP.

The pH value of the solution changed from an initial pH 5.0 to 4.74, 4.19 and 3.21 for phenol, 4-NP and 4-CP, respectively. The pH value decreased could be due to the formation of transient acidic species such as HNO_3 and HCl. Since ions such as Cl^-, NO_3^- and H^+ were detached away from the phenolics during the photocatalytic degradation, thus pH value of solution decreased with the increase in irradiation time [23]. Fig. 6 shows the formation of Cl^- and NO_3^- during the photocatalytic degradation of phenolics and was analyzed by an ion chromatography, which resulted in pH variations.

3.5. *Evolution of intermediates*

The kinetics of phenolics and evolution of main intermediates during the photodegradation with TiO_2 were studied. The phenolics yield hydroquinone (HQ), benzoquinone (BQ) and catechol (CC) as main intermediates. The maximum absorption band of each intermediate in the UV–vis region was utilized to measure absorbance. Fig. 7 shows the evolution of the intermediates formed during the photodegradation of phenolics. As shown in Fig. 7, the intermediates reach their maximum of concentrations around 90 min. After which their concentration decreases and levels off to a certain extent. Although HQ is the principal intermediates in the aerated system. It is well know that, in an aqueous system, HQ is in equilibrium with BQ. It is obvious that hydroxyl radical ($^\bullet$OH) is reactive specie that constitutes intermediates. Direct attack of $^\bullet$OH and reaction on ortho position is responsible for the evolution of HQ and CC. It can be seen that the absorbance of all compounds does not fall to zero due to undegraded phenolics in the irradiated system. The intermediates formed during photodegradation are also reactive towards $^\bullet$OH. As a consequence, phenolics and its intermediates compete effectively for $^\bullet$OH, reducing the degradation efficiency of phenolics [24].

4. Conclusion

The present studies showed the kinetics and thermodynamics of the photocatalytic degradation of phenolics by a TiO_2 catalyst under irradiation by UV light. The degradation was examined to follow pseudo-first order kinetic. An increase of the temperature has kind effect on kinetics and facilitates the degradation process to some extent. The effect of temperature from 25 to 45 °C showed that the apparent rate constants follow the Arrhenius relation. The activation energies of the degradation of phenolics were found to be 9.68–21.44 kJ mol^{-1}. Decrease in pH of the solution was observed due to the formation of acidic species like HCl and HNO_3. Formation of Cl^- and NO_3^- was monitored by ion chromatography. The most probable intermediates cultivated during the photocatalytic degradation were found to be hydroquinone (HQ), benzoquinone (BQ) and catechol (CC).

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