ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 67–72

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

# The reactivity of phenol in irradiated aqueous suspensions of $TiO_2$. Mechanistic changes as a function of solution pH

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Received 19 January 1995; accepted 19 April 1995

## Abstract

The reactivity of phenol under oxic and anoxic conditions in irradiated (350 nm) aqueous suspensions of $TiO_2$ as a function of pH was studied. The initial rate of disappearance of phenol is significantly influenced by solution pH. The initial disappearance rates and Langmuir–Hinshelwood kinetic parameters are comparable over a range from pH 3 to 9 and at pH 13.7, while substantial changes are observed at pH 1 and 11. These differences are attributed to speciation of the reactants and changes in the surface of the $TiO_2$ as a function of solution pH. The involvement of oxide radical anion $^{\bullet}O^-$ is proposed at pH $\geqslant 12$. Under highly acidic or basic conditions, colored oligomers are formed as a result, at least in part, of direct photolysis. In the presence of $TiO_2$ the colored oligomers are readily degraded, while in the absence of $TiO_2$ the color continues to develop upon extended irradiation.

*Keywords:* Photocatalysis; Titanium dioxide ($TiO_2$); Hydroxyl radical; Oxide radical anion; Photooxidation

## 1. Introduction

The $TiO_2$-catalyzed photo-oxidation of phenols has been studied in aqueous media and complete mineralization has been successfully achieved under a variety of conditions, suggesting that this is a plausible technique to decontaminate wastewaters [1–4]. Although phenol has been extensively studied and used as a model compound to test various $TiO_2$ photocatalytic systems, careful examination of previous studies on the effects of solution pH reveals significant discrepancies. Wei and Wan reported maximum phenol removal at neutral pH [5], while others report that optimum removal occurs under acidic conditions [1a]. Increases in the degradation rates with pH have been reported and rationalized by employing arguments regarding competitive adsorption between phenol/phenoxide and hydroxide ion [4,5]. In a separate study a relative maximum was observed at pH 3 with a gradual decrease to pH 11 followed by a dramatic increase above pH 11 in the degradation of phenol [1c]. Goldstein et al. reported significant changes in $TiO_2$ photocatalysis of phenol over a relatively small pH range from pH 2.0 to 3.3 [6]. While various brands and/or preparation of anatase $TiO_2$ can result in different reactivities [7], the influences of solution pH are not expected to produce such drastically different observations. Significantly different trends have also been reported in degradation studies of substituted phenols (i.e. a decrease in the reactivity of nitrophenols with increasing pH [8] and a relative constant increase from pH 2 to 12 in the degradation of 2-chlorophenol [4]). Our intention was to carefully evaluate the effects of pH over a wide range on the photo-oxidation of phenol, to help clarify the differences among previous reports and address the pronounced influence which solution pH can have in $TiO_2$ photocatalysis. We report the effects of solution pH on the initial reaction rates, apparent kinetic parameters and extent of $TiO_2$ photocatalytic degradation of phenol.

## 2. Experimental details

### 2.1. Chemicals

Phenol and chloroform obtained from Fisher Scientific (Purified grade and Certified ACS respectively) were used without further purification. Solutions were prepared with deionized water and the solution pH was adjusted with HCl or NaOH. The photocatalyst, Degussa P25 $TiO_2$ lot number RV2186 (surface area 50 $m^2\ g^{-1}$, average primary particle size 30 nm, X-ray structure primarily anatase) with an isoelectric point at pH 6.6, as reported on the technical data sheet, was used throughout the investigations.

*SSDI* 1010-6030(95)04103-6

### 2.2. Apparatus

Samples were irradiated simultaneously in a Rayonet Photochemical Chamber (reactor model RPR-100 from Southern New England Ultraviolet Company) fitted with 16 "Black Light" phosphor (350 nm) lamps, a Rayonet Merry-Go-Round (model RMA-500) and a cooling fan. The operating temperature inside the reactor was $40 \pm 2$ °C. Each sample was magnetically stirred throughout irradiation; a magnetic stirrer was placed inside the reactor and an $8 \times 13$ mm$^2$ Teflon stirring bar inside each 50 ml reaction vessel (screw-capped, round-bottomed Corex tube). The intensity of the incident light, $1.6 \times 10^{16}$ photon s$^{-1}$ cm$^{-3}$, was measured by means of a potassium ferrioxilate actinometer [9].

### 2.3. General procedure

Aqueous stock solutions of phenol were prepared for each pH studied. A 50 ml aliquot of deionized water of the desired pH was placed in the round-bottomed Corex tube; a determined volume of this water was removed and replaced with an equal volume of the appropriate aqueous stock solution to achieve the desired concentration. $TiO_2$ (0.1 g l$^{-1}$) was added and the mixture sonicated (43 kHz) for 5 min to achieve a homogeneous suspension. The mixture was cooled to 22 °C with an iced water bath while stirring, before removing a 5.0 ml aliquot for analysis ($t = 0$ min). The 5.0 ml aliquot of the mixture was filtered through a 0.45 mm polytetrafluoroethylene (PTFE) acrodisc into a 40 ml extraction vial (borosilicate clear glass with open-topped phenolic caps and PTFE septa). Two 5.0 ml aliquots of deionized water of pH 3.0 were filtered consecutively to rinse the syringe and acrodisc and the filtrate was adjusted to pH 3.0 with HCl or NaOH as required. The filtrates, 10.0 ml of deionized water, 5.0 ml of $CHCl_3$, and an internal standard were added to the extraction vial. The extraction vials were shaken in an Orbit Shaker (Lab-Line Instruments) for 3 min at 300 rev min$^{-1}$ and the $CHCl_3$ layers transferred with disposable pipettes into amber autosampler vials for analyses.

Samples were taken at 0, 5, 10, 15 and 30 min of irradiation for the kinetic analysis and the control mixtures were sampled at 0, 15, 30, 60, 120 and 240 min. The control reactions were carried out over the entire pH range to evaluate the effect of $O_2$, direct photolysis and dark adsorption.

### 2.4. Analysis

The disappearance of phenol was monitored using a Hewlett–Packard Gas Chromatograph 5890 equipped with an FID detector and a J&W Scientific DB-1 ($30 \text{ m} \times 0.25$ mm, 0.25 $\mu$m) column. The temperature program started at 40 °C for 5 min with an increase of 20 °C min$^{-1}$ to 220 °C and a final time of 5 min. The temperatures of the injector and detector were 200 and 250 °C respectively. The head pressure was 14.1 lbf in$^{-2}$; the purge was off at 0 min and on at 1.5 min. The gas flows were 375 ml min$^{-1}$ for air, 30 ml min$^{-1}$ for nitrogen plus helium (carrier) and 30 ml min$^{-1}$ for hydrogen. The amounts of phenol left after irradiation were quantified with a standard calibration curve using toluene as the internal standard.

## 3. Results and discussion

Photoexcitation of the semiconductor $TiO_2$ promotes an electron from the valence band to the conductance band, creating an electron ($e^-$)–hole ($h^+$) pair. While the electron and hole can be trapped by the crystal lattice and absorbates [10], the primary reactive species will be referred to simply as holes and electrons for the purposes of this paper. The potential for reduction by the electron and oxidation by the hole exists at the surface of the photoexcited semiconductor. Oxidation can occur directly by electron transfer from the substrate to $h^+$ or indirectly by reaction with hydroxyl radicals. Substrates with the proper oxidation potentials can undergo direct oxidation, generating radical species [11–15]. In aqueous solutions, hydroxyl radical formation is considered to be a critical step for the mineralization of a variety of hazardous organics. Hydroxyl radical is formed from the oxidation of surface-adsorbed water molecules and/or hydroxyl ions and to a lesser extent from the reaction of peroxide formed as a byproduct in low quantities from the superoxide radical anion.

Competition for adsorption sites between the substrate and the $H_2O/{}^-OH$ species at various pH values is expected to influence reaction rates and pathways for the direct and indirect oxidative processes responsible for photodecomposition [4–6,16,17]. The effect of pH on semiconductor-catalyzed photo-oxidation has been studied on a variety of substrates under various experimental conditions [5,6,8,16–23]. Although the data suggest that reaction rates are moderately dependent on pH and changes of one order of magnitude have been observed, the mechanistic details are poorly understood.

The initial rates of phenol disappearance were determined from the first 10%–20% loss of phenol under saturated oxygen conditions. The reaction conditions among the runs were identical except for concentration and solution pH as specified. The initial rates obtained by plotting concentration vs. time are summarized in Table 1.

Under our experimental conditions the initial degradation rates are reasonably constant over the range from pH 3 to 9 and increase substantially with concentration. The initial degradation rates and concentration dependence were reduced at pH 1 and 11. A plot of initial rates as a function of solution pH (Fig. 1) shows significant decreases at pH 1 and 11.

Several groups have reported concentration and pH dependences on initial reaction rates [1,4–6,8,17,24]. Differences in our observations and among these previous studies may be the result of variations in the initial phenol concentrations. At relatively high concentrations, i.e. millimolar range, phenol adsorption and subsequent oxidation by both holes and hydroxyl radicals may be operative, whereas

Table 1
Initial phenol degradation rates as a function of concentration and solution pH

| Solution pH | Phenol concentration [a] × $10^5$ (M) / initial rate [b] × $10^5$ (M $min^{-1}$) |
|---|---|
| 1.0 | 45/0.21, 53/0.25, 71/0.26, 88/0.33, 170/0.45 |
| 3.0 | 36/1.4, 46/1.7, 63/1.7, 90/1.8, 180/2.4 |
| 5.0 | 44/1.6, 51/1.6, 52/1.7, 70/1.9, 86/2.0, 87/1.9, 120/2.2, 120/2.0, 172/2.5, 173/2.4 |
| 7.0 | 45/2.0, 55/2.1, 73/2.4, 91/2.4, 129/2.7, 180/3.1 |
| 9.0 | 46/1.9, 55/2.0, 72/2.1, 91/2.1, 130/2.4, 190/2.8 |
| 11.0 | 47/0.71, 55/0.66, 74/0.75, 93/1.1, 185/1.2 |
| 13.7 | 60/2.2, 81/2.4, 100/2.3, 141/2.7, 200/2.7, 203/2.8 |

[a] The concentrations were determined from a standardization curve. An error of ±2% was observed in the initial concentrations.

[b] The initial rates were reproducible within 4%, based on duplicate runs at several concentrations.

at lower concentrations, i.e. micromolar range, oxidation by hydroxyl-mediated pathways may be the only significant degradation pathway. A change in the degradation kinetics has also been reported at relatively high concentrations as a result of multilayer adsorption [25]. In our experiments, under moderate concentrations, multilayer stacking of solute molecules at the surface of $TiO_2$ does not appear to occur to an appreciable extent. Variations in the semiconductor-catalyzed initial photodegradation rates of phenol with different types of $TiO_2$ are presumably the result of differences in morphology and texture, individual surface acid–base properties and pretreatment conditions among the various investigations.

Since the models generally employed to evaluate the kinetic parameters for heterogeneous photocatalysis assume saturation-type kinetics at or near the semiconductor surface [26], the effects of pH must be critically evaluated. The rates of chemical reactions can be affected by electrostatic interactions between the semiconductor surface, solvent molecules, substrates and charged radicals formed throughout the reaction process [14,16,23].

The Langmuir–Hinshelwood (L–H) kinetic model has been used to describe semiconductor photocatalysis [24,26,27]. In using this model, it is assumed that the reaction rate is dependent on two processes: the equilibrium adsorption coefficient ($K$) and the rate of reaction of the adsorbate ($k'$). The L–H kinetic parameters $K$ and $k'$ can be determined from the slope ($1/k'$) and intercept ($1/Kk'$) of a linear plot of inverse rate vs. inverse concentration.

In our studies a well-mixed oxygen headspace was maintained and constant dissolved oxygen is assumed. Initial reaction rates were determined at low substrate conversions to minimize competitive adsorption between substrate and product. Except for the initial solution pH, experimental conditions remained constant among the various trials. The reciprocal plot for all the solution pH values investigated is shown in Fig. 2.

While the L–H model is consistent with reaction kinetics involved in heterogeneous photocatalysis, Turchi and Ollis

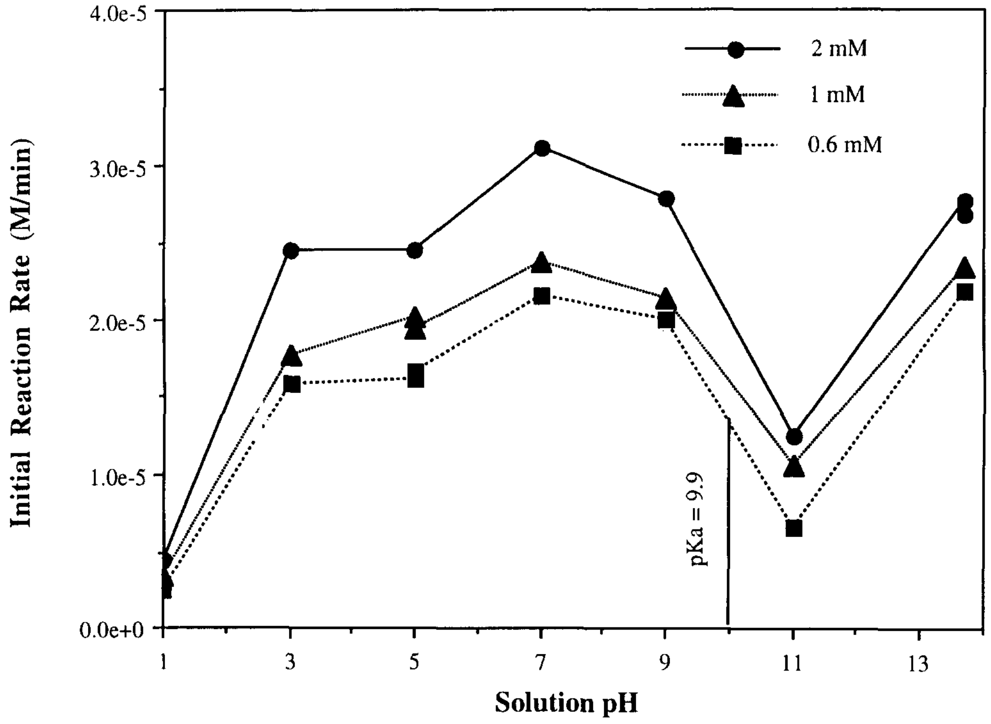

Fig. 1. Initial reaction rates for $TiO_2$-catalyzed photodegradation of phenol as a function of solution pH.

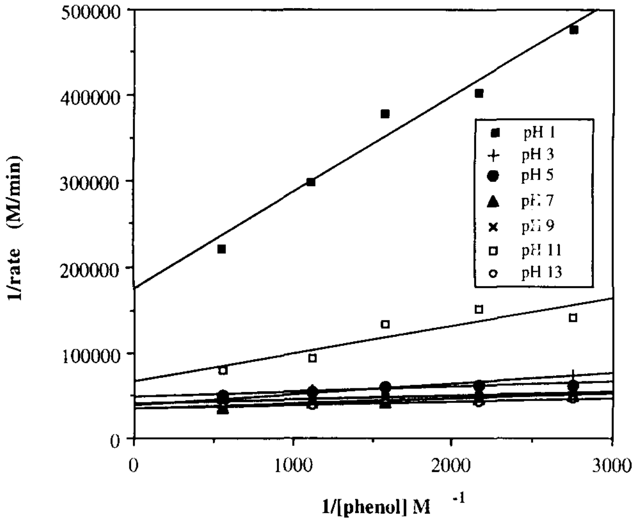

Fig. 2. Langmuir–Hinshelwood plots (reciprocal initial rate vs. reciprocal initial concentration) for $TiO_2$-catalyzed photodegradation of phenol as a function of solution pH.

Table 2
Langmuir–Hinshelwood kinetic parameters as a function of solution pH

| Solution pH | Fit [a] | $k' \times 10^5$ ($M\ min^{-1}$) | $K \times 10^{-3}$ ($M^{-1}$) |
|---|---|---|---|
| 1.0 | 0.985 | 0.58 | 1.29 |
| 3.0 | 0.943 | 2.68 | 2.90 |
| 5.0 | 0.935 | 2.80 | 2.83 |
| 7.0 | 0.981 | 3.47 | 2.93 |
| 9.0 | 0.978 | 2.95 | 3.59 |
| 11.0 | 0.901 | 1.52 | 1.62 |
| 13.7 | 0.900 | 3.05 | 4.21 |

[a] The correlation coefficient $r$ for the best least-squares line representing the experimental data.

suggest that the parameters obtained represent apparent kinetic information [26]. These apparent kinetic parameters $k'$ and $K$ can be used to compare the reactivities of different substrates under the same experimental conditions or of a compound, phenol in our case, at different initial solution pH values.

The apparent kinetic parameters determined from the slope and intercept of the reciprocal plots for each solution pH are summarized in Table 2. Although there is a slight deviation at high pH, the correlation between the L–H model and the experimental data appears to be consistent over the range of solution pH studied. The L–H kinetic parameters are similar over the range of solution pH from pH 3 to 9. At pH 1 and 11 substantial decreases in the initial reaction rates and the Langmuir–Hinshelwood kinetic parameters $K$ and $k'$ are observed. The smallest values for the constants $K$ and $k'$ were observed at pH 1, while relatively large constants were observed at pH 13.7. The increase in the kinetic parameters at pH 13.7 is surprising, since substrate adsorption is generally considered to be critical for substrate degradation and the phenol exists as the negatively changed phenoxide [28], which is expected to result in minimal adsorption.

Although there is only a moderate difference among the initial rates and the L–H kinetic parameters from pH 1.0 to 13.7, there are some rather peculiar changes as a function of pH. At pH 1.0 the reaction is significantly retarded. This retardation has been observed not only in studies of phenol [5,6] but also with 4-chlorophenol [2] and chlorobenzene [19], which suggests that at low solution pH the semiconductor surface changes and there is either an inhibition of substrate adsorption or in the formation of oxidative species such as $^{\bullet}OH$, or both. Consistent with our observations is the suggestion that under acidic conditions a higher local pH near or at the interface can have a pronounced effect on product yields [6]. It is also possible that competing reactions and adsorption of $Cl^-$ from the acidification procedure may become predominant under the experimental conditions [2].

It has been suggested that the initial rates should increase at higher pH owing to a greater extent of surface coverage by $HO^-$ ions, which in turn can be oxidized to $^{\bullet}OH$ and ultimately lead to the degradation of phenol [4,5]. In our studies, similar initial reaction rates for phenol degradation in the pH range from 3.0 to 9.0 were observed, suggesting that the variation in $H_3O^+$ and $HO^-$ ions has a relatively minor influence on the overall degradation in this range. The lack of significant acceleration in the initial reaction rates at higher pH may also be the result of competition between hydroxide ions and phenoxide species for adsorption sites [5,8] and the relative rates of the subsequent oxidative reactions, but analogous observations in the degradation of chlorobenzene, where there is no special competition for adsorption sites or strong electrostatic repulsions [19], indicate that this explanation has limited applicability.

At pH 11, despite a relatively high concentration of hydroxide, a sharp decrease in the kinetic parameters and moderate deviation from the L–H model are observed. The decrease in the initial reaction rate is attributed to repulsion between the negatively charged $TiO_2$ particle and phenoxide which inhibits adsorption and thus reactions occurring near or at the surface of the $TiO_2$ particle, leading to slower initial rates and moderate deviation from the L–H model.

Several experiments were run to access the role and contributions of direct photolysis reactions (Fig. 3). The degradation of phenol over the pH range from 3.0 to 9.0 as result of direct photolysis is negligible. Direct photolysis requires oxygen and probably involves the formation of superoxide and phenoxyl radical. Reactions conducted under a nitrogen atmosphere in the presence of $TiO_2$ showed a significant decrease in the efficiency of phenol removal under our experimental conditions. It is generally accepted that oxygen acts as an electron trap and is required for photodegradation to occur, thus explaining the decrease in the rate and extent of degradation in the absence of oxygen. The moderate degradation of phenol in nitrogen-purged solutions may be the result of residual oxygen adsorbed on the semiconductor surface or direct oxidation of phenol by photogenerated holes at the surface of the $TiO_2$. No color developed in the reaction solutions purged with nitrogen at extended irradiation times.

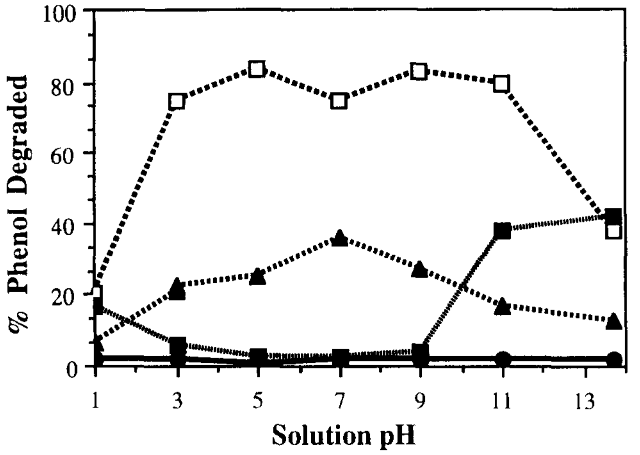

Fig. 3. Photodegradation of phenol in aqueous media after 4 h of irradiation (350 nm) under various experimental conditions: □, $TiO_2/O_2$/light; ▲, $TiO_2/N_2$/light; ■, no $TiO_2/O_2$/light; ●, $TiO_2/O_2$/no light.

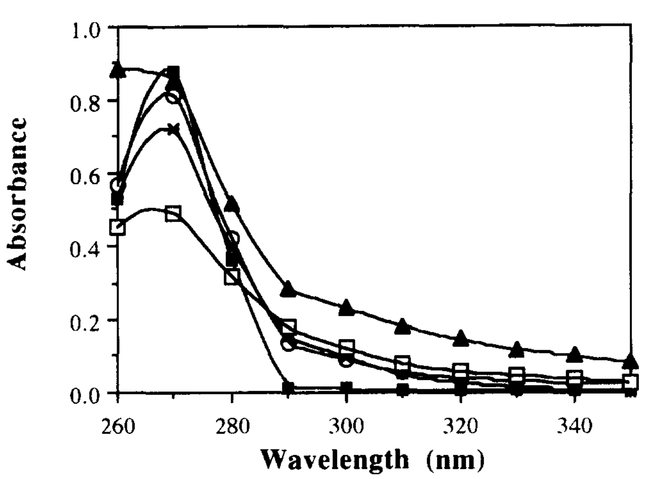

Fig. 4. UV–visible spectra of solutions resulting from photolysis (350 nm) of phenol in presence and absence of $TiO_2$ as a function of time under acidic conditions, solution pH 1: ■, initial solutions prior to irradiation ($t = 0$ h); ○, $TiO_2/O_2$/light at 4 h; ×, $TiO_2/O_2$/light at 8 h; □, $TiO_2/O_2$/light at 20 h; ▲, no $TiO_2/O_2$/light at 20 h.

Similar decreases in phenol concentration with the formation of a yellow solution in both the presence and absence of $TiO_2$ were observed at pH 1 (Fig. 4). These results suggest that the phenol does not significantly react by $TiO_2$-mediated photocatalysis but in fact undergoes direct photolysis with the probable formation of polyhydroxylated oligomers. Such oligomers have been observed previously when phenols were irradiated at 254 and 296 nm in aqueous media [29].

A substantial decrease in the concentration of phenol was observed at pH 11.0 and 13.7; a significant amount appears to be the result of direct photolysis with the production of reddish-colored solutions which turned yellow upon acidification. In the presence of the semiconductor the color rapidly faded upon continued irradiation.

At pH 13.7, where electrostatic repulsion between the phenoxide and the $TiO_2$ surface is expected to be significant, the initial degradation rate dramatically increases relative to the rate of pH 11.0, while the removal efficiency after 4 h of irradiation was low compared with reactions carried out in solutions of lower pH. Such acceleration of pH values higher than 12.0 has previously been attributed to the increased number of hydroxyl ions at the semiconductor surface [4,5], but this does not adequately explain our observations at pH 11. An increase in the initial degradation rates of chlorobenzene at pH $\geqslant$ 12.0 after remaining constant from pH 6.0 to 11.0 has also been observed [19]. These observations indicate that the $TiO_2$-mediated photodegradations at pH 11 and 13.7 involve different mechanisms.

We propose that the rate enhancement observed above pH 12 results from the formation of a different oxidizing species, either oxide radical anion or an analogous surface-adsorbed species. At sufficiently high solution pH the unprotonated hydroxyl radical $^\cdot O^-$ has been observed in homogeneous solution; this reacts in a different manner from $HO^\cdot$ ($pK_a = 11.8$) [30], thus affecting the initial rate of disappearance and the L–H kinetic parameters. It has been reported that in homogeneous aqueous media the reaction of the oxide radical anion with the phenoxide species has a rate constant $k$ equal to $6.5 \times 10^8$ l mol$^{-1}$ s$^{-1}$, which produces the phenoxyl radical [31], a neutral species:

$$^\cdot O^- + C_6H_5O^- + H_2O \longrightarrow 2HO^- + C_6H_5O^\cdot \qquad (1)$$

Formation of the oxide anion radical at pH 13.7 provides an additional and/or alternative pathway which is not readily accessible at solution pH less than 11.8 and may enhance the initial rate of degradation of phenoxide. The resulting phenoxyl radical should react at or near the semiconductor surface to a greater extent than phenoxide because of the reduced level of electrostatic repulsion. The competition for adsorption between phenoxide and the products of degradation appears to inhibit the extent of phenol disappearance [4]. Likely products are carboxylate ions which may form complexes with the $TiO_2$ surface and inhibit the adsorption of the phenol species. While degradation of the $TiO_2$ under strongly alkaline conditions may inhibit phenol degradation, experiments performed at pH 13 without any deactivation of the catalyst have been reported [32]. These studies suggest that pH effects on the degradation process are not only the result of changes in the concentration of hydroxide but also of the competitive adsorption and operative oxidative pathways at a given pH.

## 4. Conclusions

The influence of solution pH on the initial degradation rates and L–H kinetic parameters for $TiO_2$-catalyzed photo-oxidation of phenol was investigated. While the initial reaction rates and kinetic parameters are relatively constant from pH 3 to 9, changes at pH 1 and 11 are attributed to competitive adsorption and electrostatic repulsion between the solutes, solvent molecules and $TiO_2$ particles. While the acceleration in degradation rates at significantly high pH has been attributed to the increased concentration of hydroxide and competitive adsorption [4–6,32], our results are not adequately explained by these hypotheses. Hence we proposed a change in the reaction mechanism at pH $\geqslant$ 12 and the involvement of oxide radical anion to explain our observations and those reported in previous investigations. Additional discrepancies in our studies and among previous reports can be rationalized in terms of concentration effects. At higher concentrations, additional oxidative pathways may become operative, such as direct hole-mediated oxidation of the substrate [33]. Additional studies are under way to confirm the involvement of oxide radical anion and concentration effects and to establish the effect of carboxylate products on the initial rates and overall removal efficiency of phenol as a function of solution pH. Such studies will help clarify the importance of solution pH and competitive adsorption in photocatalytic degradation.

## Acknowledgements

This work was supported by the National Science Foundation RIMI Program (Grant HRD-9253014) and the Petroleum Research Fund (Grant ACS-PRF#26875-GB4).

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