

## Effect of chloride ions on 4-chlorophenol photodegradation in the absence and presence of titanium silicalite-2

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### Abstract

The effect of  $\text{Cl}^-$  ions on the photodecomposition of 4-chlorophenol (4-CP) was investigated with and without titanium silicalite-2 (TS-2) catalyst as a function of pH by absorption spectroscopy. In the absence of TS-2, chloride ions enhance the photodegradation of 4-CP in acidic and neutral solutions under UV illumination, with a faster photodegradation in acidic solutions. In the presence of TS-2, however, chloride ions enhance the photodegradation only in acidic solutions. The results reveal that chloride ions should be in close proximity to 4-CP in order to enhance photodegradation. The enhancement can be attributed to the reaction of chloride ions with chloride radicals that are abstracted from 4-CP either by absorption of the light or by reaction with hydroxyl radicals. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Photodecomposition; 4-chlorophenol; TS-2; Chloride ion

### 1. Introduction

In recent years, the photocatalytic degradation of pollutants using semiconductors under ultraviolet light has attracted considerable attention for application to environmental clean up [1–12]. Photonic energy higher than the band gap of a semiconductor generates photoinduced conduction band electrons and valence band holes in the semiconductor. The photodegradation of pollutants is initiated by the attack of the photogenerated holes or subsequently produced hydroxyl radicals on the surface of semiconductor particles [7–18]. Many studies [18–25] suggest that highly-oxidizing hydroxyl radicals are produced in two ways: (1) oxidation of hydroxide ions or water molecules adsorbed on the surface of semiconductor particles by photogenerated holes, and (2) through a series of redox reactions resulting from the trapping of photogenerated electrons by oxygen [26].

Recent studies [27,28] reveal that photocatalytic activity toward the decomposition of phenol is improved with a mixed oxide of  $\text{TiO}_2/\text{SiO}_2$  as opposed to  $\text{TiO}_2$  alone. The enhancement of the decomposition is attributed to the presence of a Ti-O-Si phase at the  $\text{TiO}_2/\text{SiO}_2$  interface, with the  $\text{SiO}_2$  providing better adsorption sites in the vicinity of  $\text{TiO}_2$ . Furthermore, titanium silicalites (composites of  $\text{TiO}_2$  and  $\text{SiO}_2$ ) [29–32] including titanium silicalite-2 (TS-2) are

reported to exhibit photocatalytic reactivities in the reduction of NO and aromatic pollutants with aqueous hydrogen peroxide. The nature of the environment of the cavity in TS-2 in regard to its reactivity as a catalyst, however, needs to be further investigated.

A common feature of photocatalytic reactions occurring on semiconductor catalysts suspended in aqueous solution is dependence of the reaction rates on pH change. The surface charge and band edge positions of the catalysts are strongly influenced by pH [33]. Above the point of zero charge (PZC) of a catalyst, the catalyst surface is negatively charged and repels negative ions, and thus can interfere with the action of hydroxyl radicals on the photodegradation of pollutants. Below the PZC, the positive charge on the catalyst surface attracts anions.

Domestic and industrial wastewater usually contain not only organic pollutants, but also considerable concentrations of common inorganic ions, such as perchlorate, nitrate, sulfate, chloride and phosphate. The effects of common inorganic anions [34–36] on the rates of photodegradation of pollutants on irradiated  $\text{TiO}_2$  have been examined by monitoring the rate of  $\text{CO}_2$  evolution from salicylic acid, aniline and ethanol. It is reported that perchlorate and nitrate exerted very little effect on the photodegradation rates, but sulfate, chloride and phosphate were rapidly adsorbed on the catalyst and reduced the photodegradation rate by 20–70%. These observations suggest that inorganic anions may compete with the pollutants for surface active sites, and block the photodegradation of the pollutants [37].

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Studies on the effects of chloride ions on the photodegradation rates of pollutants on irradiated TiO<sub>2</sub> are inconclusive. Some researchers [38] report that the photodegradation rate of 2,4-dichlorophenol is little affected by the addition of  $2.0 \times 10^{-4}$  M NaCl at pH 6.4, whereas others report that the photodegradation efficiency of pollutants decreases due to blocking active sites of TiO<sub>2</sub> by absorbed Cl<sup>-</sup> ions for the photodecomposition of dissolved organic nitrocompounds in saline solution [18], 2,4-dichlorophenol [39], and HCOOH solutions [40].

This paper aims to elucidate the effect of Cl<sup>-</sup> ions on the photodecomposition of 4-chlorophenol (4-CP) using the TS-2 catalyst. To this end, the photodecomposition of 4-CP was investigated as a function of solution pH in the presence of Cl<sup>-</sup> ions. The experimental results were interpreted in terms of adsorptivities of 4-CP and Cl<sup>-</sup> ions to the TS-2 catalyst based on electrostatic interaction. 4-CP is a common pollutant in industrial wastewater that may originate from petroleum refining, coal conversion, fiberboard production, and the production of dyes, drugs, and fungicides. The irradiated solution of 4-CP was analyzed by UV absorption spectroscopy. The kinetics of the photodegradation of 4-CP on TS-2 were analyzed according to the Langmuir–Hinshelwood equation.

## 2. Experimental

### 2.1. Preparation for TS-2

TS-2 was crystallized by hydrolysis of tetraethylorthosilicate (TEOS) and tetrabutylorthotitanate (TBOT) using tetrabutylammonium hydroxide (TBAOH) as a template. This synthetic route is very similar to that developed by Thangaraj et al. [41]. The chemical composition of the initial TS-2 gel was 0.03 TiO<sub>2</sub>:SiO<sub>2</sub>:0.36 TBAOH:20 H<sub>2</sub>O. In a typical preparation, a desired amount of TEOS was hydrolyzed in 20% TBAOH aqueous solution under vigorous stirring for about 30 min. Then, the required amount of TBOT in about 5 ml of isopropyl alcohol was slowly added under stirring for 30 min in order to complete the hydrolysis of TEOS and TBOT. The resulting gel was slowly heated to about 80°C and kept at that temperature for 2 h under stirring to remove isopropyl alcohol followed by the addition of an appropriate amount of Milli-Q water. It was then transferred into a 35 ml Teflon flask, placed in a static autoclave and crystallized under autogenerative pressure at 175°C for 24 h. The crystallized TS-2 was recovered by filtering, washed several times with Milli-Q water, and dried overnight in an oven at 110°C. Finally, the TS-2 was calcined to remove occluded TBA<sup>+</sup> cations from the TS-2 pores at 500°C for 5 h.

### 2.2. Characterization of TS-2

X-ray powder diffraction patterns were obtained by using a Macscience M03XHF<sup>22</sup> diffractometer at room tempera-

ture utilizing Ni filtered Cu K $\alpha$  radiation with 40 kV, 30 mA at 0.02° width and 4°/min scan speed. IR spectra were obtained by a Bomem, Hartman & Braun MB-series spectrometer utilizing KBr pellets. UV reflectance spectra were obtained on a Varian CARY-5G spectrophotometer. Surface area was calculated using the BET equation with a Micromeritics ASAP 2010 instrument. Atomic concentration of Ti in TS-2 was analyzed with a Perkin-Elmer OPTIMA 3000XL ICP spectrometer.

### 2.3. pH dependence of distribution coefficient

To understand the interaction between the TS-2 cavity and 4-CP, the distribution coefficients of 4-CP were measured from pH 1 to 12. The pH was controlled with HCl and KOH, and measured by a Horiba pH meter F-13 with a glass electrode. For the pH dependence of the distribution coefficient of 4-CP between TS-2 and aqueous medium, 1 g/l TS-2 was added into flasks containing  $1.0 \times 10^{-4}$  M 4-CP at different pHs. After reaching equilibrium under stirring for 1 h, TS-2 was filtered at 3500 rpm with a Hanshin Medical HC-16A centrifuge. The concentration of the solution was measured by UV absorption spectroscopy using a Hewlett Packard 8453 diode array spectrophotometer.

### 2.4. Photodegradation

The photodegradation of  $1.5 \times 10^{-4}$  M 4-CP on TS-2 was carried out with 1.0 g/l TS-2 and  $1.0 \times 10^{-2}$  M chloride ions. Since the surface charge of TS-2 and the predominant species of 4-CP are dependent upon pH of the solution, the reaction rate was investigated as a function of pH. The pH was adjusted with HCl and NaOH. Stock solution containing a desired concentration of 4-CP (Aldrich) was prepared with Milli-Q water. A photochemical reactor was made of Pyrex glass with a plain quartz window and a water circulating jacket. The reactor contained 50 ml of the stock solution, TS-2 in suspension, and Cl<sup>-</sup> ions. Irradiation was carried out through the quartz window with a 250 W xenon lamp (Ilctec Co.) in the air when the adsorption equilibrium was reached under stirring for 1 h. After the irradiation, the powder catalysts were filtered at 3500 rpm with a Hanshin Medical HC-16A centrifuge. The photodegradation rate of 4-CP was monitored by measuring absorption spectra of the filtered solutions using a Hewlett Packard 8453 diode array spectrophotometer.

## 3. Results and discussion

### 3.1. Basic characteristics

The XRD spectrum of a xerogel, before crystallization in a static autoclave, showed that the xerogel was completely amorphous having no peaks related to TS-2. After crystallization, however, characteristic peaks of TS-2 at  $2\theta=7.9$ ,

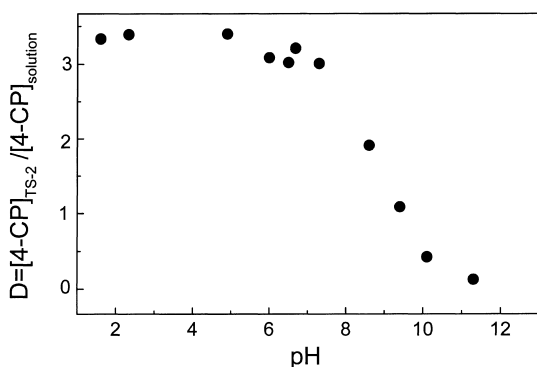


Fig. 1. Change in the distribution coefficient of 4-CP as a function of pH.

8.8, 23.2 and 24.0 were observed [41]. The IR spectrum of TS-2 presented a band at  $960\text{ cm}^{-1}$ , which has been assigned to the stretching vibration of Si-O-Ti, arising from  $\text{SiO}_2$  units linked to Ti atoms. The presence of the band suggests that Ti atoms are effectively incorporated into the  $\text{SiO}_2$  lattices [42].

Absorption edge of the UV reflectance spectra is calculated to be about 300 nm for TS-2 and 380 nm for  $\text{TiO}_2$  by the Kubelka–Munk function

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

where  $R$  is the measured reflectance. The blue shift of the absorption edge of TS-2 with respect to  $\text{TiO}_2$  indicates that  $\text{TiO}_2$  in TS-2 is isolated with tetrahedral coordination [43,44]. Ti atomic concentration in TS-2 was found to be about 3% from an analysis by ICP spectrometry. The surface areas of the prepared TS-2 particles and Degussa P-25  $\text{TiO}_2$  were 550 and  $58\text{ m}^2/\text{g}$ , respectively.

The distribution coefficient ( $D$ ) of 4-CP measured as a function of pH is shown in Fig. 1. The  $D$  value is given by

$$D = \frac{\text{Concentration adsorbed in TS-2}}{\text{Concentration remaining in aqueous solution}} \quad (2)$$

The TS-2 cavity is negatively charged at pH above the PZC of TS-2. The PZC of  $\text{TiO}_2$  is known to occur at pH 6.3 [45]. Since  $\text{SiO}_2$  is more acidic than  $\text{TiO}_2$ , the PZC of TS-2 is expected to occur below pH 6.3. If pH is higher than 9.34, the  $\text{pK}_a$  of 4-CP, the deprotonated 4-CP predominates and, thus, is repelled from the negatively charged TS-2, explaining the rapid decrease in the  $D$  value at pH above the  $\text{pK}_a$ . In acidic solutions below pH 6, the  $D$  values are nearly identical due to the same interaction between 4-CP and positively-charged TS-2. With the increase in pH above 6, the  $D$  value gradually declines because neutral 4-CP molecules adsorb less on the negatively-charged TS-2.

### 3.2. $\text{Cl}^-$ ion effect on direct photodegradation

The UV absorption spectra presented in Fig. 2 visually show that chloride ions certainly enhance the photodegradation of 4-CP in acidic and neutral solutions under UV

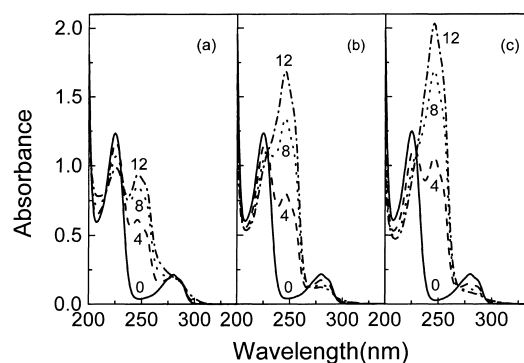


Fig. 2. Irradiation-time dependence of absorption spectra 4-CP: (a) in neutral solution; (b) 0.010 M NaCl at pH 5.7 and (c) 0.010 M HCl at pH 2.1. The numbers indicate the irradiation time in min.

illumination in the absence of TS-2. In 0.010 M HCl, the 4-CP photodegradation proceeds even faster than in 0.010 M NaCl.

These observations in Fig. 2 are graphically reproduced in Fig. 3 where the variations of relative concentration of 4-CP at 225 nm versus irradiation time are plotted in the initial stage of the photodecomposition reaction. It is summarized that the direct rate of 4-CP photodegradation decreases in the following order: 0.010 M HCl > 0.010 M NaCl  $\cong$  0.010 M  $\text{HClO}_4$  > neutral solution without  $\text{Cl}^-$ . Since perchlorate ions were expected not to influence direct photodegradation, the increased enhancement over the neutral solution of 4-CP appears to originate from the increased electron withdrawal of the protonated hydroxyl group of 4-CP. Contrary to the enhancement of the photodegradation in acidic and neutral solutions, there is no difference in the rates of the deprotonated 4-CP photodegradation irrespective of the presence of chloride ions in 0.010 M NaOH. Presumably, the electrostatic repulsion between the two negatively-charged species at pH 11.2 inhibits the catalytic activity of chloride ions observed at pH 5.7 and 2.1. At pH 11.2, 98% of 4-CP molecules exist as the deprotonated species. It is unreasonable to compare the rate of 4-CP photodecomposition in alkaline solution

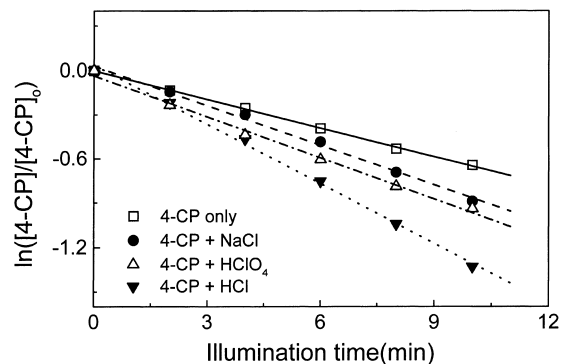


Fig. 3. Irradiation-time dependence of the relative concentration of 4-CP at 225 nm upon adding 0.010 M  $\text{Cl}^-$  or  $\text{ClO}_4^-$ .

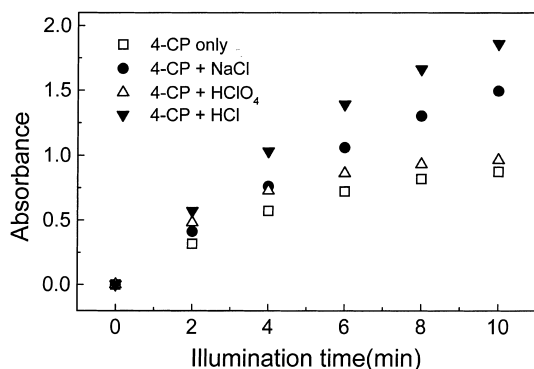


Fig. 4. Time-course of the absorbance at 246 nm of illuminated 4-CP solution upon adding 0.010 M  $\text{Cl}^-$  or  $\text{ClO}_4^-$ .

with that in neutral solution because the absorption spectrum of deprotonated 4-CP is shifted to the longer wavelength region with respect to that of 4-CP. It is obvious, however, that the photodegradation rate of deprotonated 4-CP is not influenced by the presence of chloride ions in alkaline solution.

To support the rate of 4-CP disappearance, the appearance of benzoquinone (BQ), a primary reaction intermediate of direct photodegradation, was monitored by absorption spectroscopy and shown in Fig. 4. The concentration of BQ measured at 246 nm in the solution containing 0.010 M chloride ions certainly increases compared with that in the absence of chloride ions as a result of the faster photodegradation of 4-CP. The relative rate of BQ appearance is found to follow the same order as the rate of 4-CP disappearance, indicating that the faster the direct photodegradation of 4-CP, the faster the production of BQ in the early stages of 4-CP photodegradation.

### 3.3. $\text{Cl}^-$ ion effect with TS-2

To elucidate further the effect of chloride ions on the photodegradation of 4-CP in the presence of a catalyst, the rate of the 4-CP photodecomposition was investigated when adding TS-2 into the solution. Fig. 5 summarizes the variations of relative concentration of 4-CP measured at 225 nm and deprotonated 4-CP measured at 243 nm on the TS-2 catalyst versus irradiation time in the initial stage of the photodecomposition reaction with respect to changes in chloride ions and pH. The stability of TS-2 was evaluated by measuring  $D$  of 4-CP with the irradiated solutions containing TS-2. It was found that  $D$  in acidic at pH 2 and neutral solutions remained at the respective values up to 20 min of irradiation, revealing that TS-2 was stable under the experimental condition.

Although 4-CP direct photodegradation was enhanced by chloride ions in neutral solution, chloride ions do not influence 4-CP decomposition in the presence of TS-2 at pH 5.7. This result can be explained by assuming that the TS-2 cavity has a hydrophobic environment at the neutral pH.

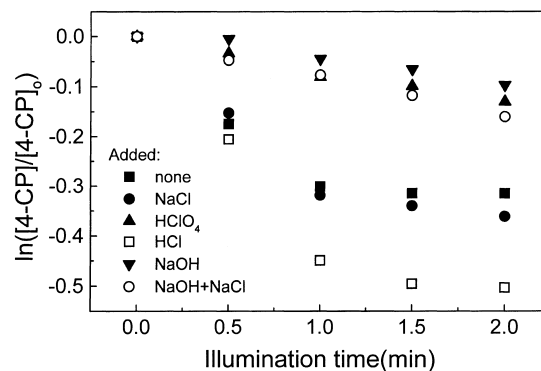


Fig. 5. Irradiation-time dependence of the relative concentrations of 4-CP at 225 nm and of deprotonated 4-CP at 243 nm with TS-2 upon adding 0.010 M  $\text{Cl}^-$  or  $\text{ClO}_4^-$ .

The hydrophobic surface of the TS-2 cavity strongly adsorbs 4-CP (cf. Fig. 1), but not chloride ions. Thus, most of the 4-CP molecules are present in the TS-2 cavity, whereas chloride ions are expected to be located outside of the catalysts. As a consequence, the photodegradation of 4-CP on the TS-2 catalyst is not affected by 0.010 M NaCl at pH 5.7.

In 0.010 M HCl, however, the environment of the TS-2 cavity becomes positively charged. The positively-charged TS-2 cavity adsorbs both 4-CP and chloride ions. The photodegradation of 4-CP in the presence of TS-2 is now expected to be catalyzed by chloride ions in an acidic solution of pH 2.1. The result in Fig. 5 indeed shows that the photodegradation of 4-CP on the TS-2 catalyst was enhanced by the added chloride ions at pH 2.1. The 4-CP photodegradation is catalyzed because 4-CP molecules and chloride ions can be positional close together in the TS-2 cavity. On the other hand, in 0.010 M  $\text{HClO}_4$ , 4-CP photodegradation is retarded compared with that in 0.010 M NaCl. These observations suggest that  $\text{ClO}_4^-$  ions may compete with the pollutant for the surface active sites of TS-2 and, thus, block the photodegradation of 4-CP, because  $\text{ClO}_4^-$  ions can be adsorbed on the positively-charged surface in the TS-2 cavity under acidic conditions. It is concluded that the apparent photodegradation rate of 4-CP in the presence of the TS-2 catalyst decreases in the following order: 0.010 M HCl > 0.010 M NaCl  $\cong$  neutral solution without  $\text{Cl}^-$  > 0.010 M  $\text{HClO}_4$ .

In addition, Fig. 5 shows the chloride ion effect on deprotonated 4-CP photodegradation on TS-2 at pH 11.2. The surface of the TS-2 cavity is negatively charged at pH higher than the PZC of TS-2, and 4-CP is predominantly deprotonated at pH higher than the  $\text{pK}_a$  of 4-CP. The negatively charged surface of the TS-2 cavity likely repels both deprotonated 4-CP and chloride ions. Deprotonated 4-CP and chloride ions are located outside of the TS-2 cavity, and, thus, the photodegradation rate of deprotonated 4-CP should not be affected by TS-2. As a result, TS-2 is no longer a good photocatalyst for 4-CP in aqueous solutions at a pH

higher than the  $pK_a$  of 4-CP irrespective of the presence of  $Cl^-$  ions.

### 3.4. The role of chloride ions

The data presented here indicate that chloride ions enhance the direct photodegradation of 4-CP in neutral and acidic solutions. With the TS-2 catalyst, chloride ions enhance 4-CP photodegradation only in acidic solutions. At a pH higher than the  $pK_a$  of 4-CP and the PZC of TS-2, however, chloride ions are found not to be influential in 4-CP photodecomposition regardless of the presence of TS-2. The results are best explained by assuming that chloride ions should be in close proximity to 4-CP molecules when 4-CP photodecomposition is enhanced. In the absence of a heterogeneous catalyst, chloride ions can approach close to 4-CP in acidic and neutral solutions at pH lower than the  $pK_a$ , whereas they are apparently repelled from deprotonated 4-CP in alkaline solutions. In particular, 4-CP photodecomposition is found to be faster in a HCl acidic solution at pH 2 than in neutral solutions. In the acidic solution, there presumably exists a protonated 4-CP species. As a result, additional contributions to 4-CP photodegradation become feasible. The protonated hydroxyl group of 4-CP now possesses an increased electron withdrawing ability due to the C–Cl bond. This increased ability results in a weakening of the C–Cl bond followed by the relatively easy breaking of the bond.

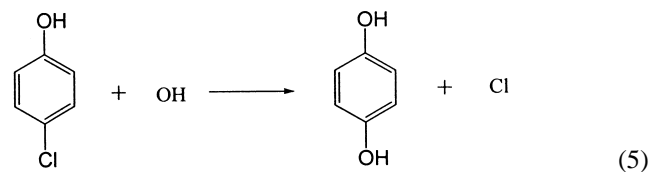
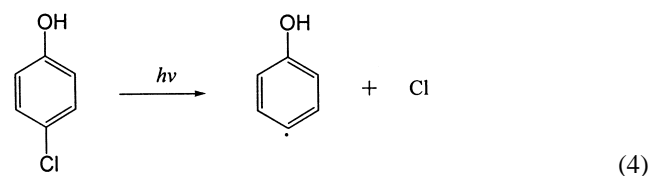
In the presence of the TS-2 catalyst, chloride ions are observed to enhance 4-CP photodegradation only in HCl acidic solutions. Under such conditions, most of the reactant molecules and chloride ions are likely present in the tiny volume of the TS-2 cavity. Therefore, 4-CP photodegradation is enhanced due to the proximity of chloride ions to the reactant molecules and to the increase in the electron withdrawing ability as discussed above. In addition, hydronium ions can react with the photogenerated electrons to form hydrogen atoms



This reaction reduces the recombination between the charge carriers, which enables more holes to participate in the 4-CP photodecomposition. In alkaline solution, chloride ions and deprotonated 4-CP are most likely repelled from the negatively charged TS-2, making the catalyst indifferent to the influence of chloride ions on 4-CP photodecomposition. At pH 5.7, chloride ions are not favorably adsorbed on the TS-2 surface, whereas 4-CP is a strongly adsorbed on the catalyst. This difference in the adsorptivity makes the influence of chloride ions insignificant.

The reasons for chloride ion enhancement of the 4-CP photodegradation are speculative at the present time. Further investigated anions in the solution at neutral pH include nitrate, sulfate, chlorate, thiocyanate, perchlorate, and dihydrogenphosphate; none of them appreciably changed 4-CP

photodecomposition as chloride ions did. This result indicates that the effect of chloride ions on 4-CP photodecomposition is not caused by a change in the bulk properties of the solution, but by a specific interaction related to chloride ions. One possibility is that chloride ions react with chloride radicals to form  $Cl_2^-$  ions. Cl radicals can be generated by the abstraction reactions (4) and (5) below. Reaction (4) directly occurs upon absorption of light. The OH radicals in reaction (5) are produced by the interaction of water with photogenerated holes originating from the TS-2 catalyst. The Cl abstraction is a key step in 4-CP degradation to yield primary intermediates such as BQ or hydroquinone (HQ).



For reaction (6) to occur efficiently, chloride ions should be available near the site of Cl abstraction. Reaction (6) certainly facilitates the photodegradation of 4-CP according to the Le Chatelier principle.

Quantitative data related to the role of chloride ions on 4-CP photodegradation in the presence of the TS-2 catalyst were obtained by utilizing the Langmuir–Hinshelwood equation. The rate of photocatalytic degradation of 4-CP is a function of the initial concentration of 4-CP. This rate can be evaluated using the apparent reaction rate constant ( $k_a$ ), adsorption coefficient ( $K$ ), and initial concentration of 4-CP by the inverse of the equation.

$$-\frac{dt}{d[4\text{-CP}]} = \frac{1}{k_a} + \frac{1}{k_a K [4\text{-CP}]} \quad (7)$$

Plots of the inverse of the initial rate of 4-CP photodegradation were obtained as a function of the reciprocal initial 4-CP concentration. The  $k_a$  and  $K$  constants can be derived from the intercept and slope of these straight lines. The results are summarized in Table 1. The values of  $k_a$  are consistent with the results presented above. That is, 4-CP photodegradation is enhanced in HCl acidic solutions, and the decrease in  $k_a$  under basic conditions is due to the electrostatic repulsions between chloride ions and both negatively-charged TS-2 and deprotonated reactant. The adsorption constants are found to be the same below the  $pK_a$  of 4-CP, indicating that under such conditions, the adsorptivity of 4-CP on TS-2 is almost identical. However, in alkaline

Table 1

The apparent reaction rate constant ( $k_a$ ) and the adsorption coefficient ( $K$ ) of 4-CP with the TS-2 catalyst

Solution <sup>a</sup>	$k_a$ (mmol/h)	$K$ (l/mmol)
4-CP	30	1
4-CP+NaCl	30	1
4-CP+HCl	50	1
4-CP+NaOH	20	3
4-CP+NaOH+NaCl	15	5

<sup>a</sup> Concentration:  $1.0 \times 10^{-4}$  M 4-CP;  $1.0 \times 10^{-2}$  M  $\text{Cl}^-$ ;  $1.0 \times 10^{-2}$  M NaOH.

solutions, the reactant is expected to be repelled from the negatively-charged TS-2, and, thus, the  $K$  values appear to be meaningless.

It is worth mentioning that the relative absorbance near 290 nm with the TS-2 catalyst differs from that without TS-2. The species responsible for the absorbance is HQ. HQ and BQ are known two primary intermediates of the 4-CP photodegradation. Fig. 2 indicates that in the absence of TS-2, BQ is a major intermediate in the direct photolysis of 4-CP. In the presence of TS-2, however, HQ can be produced via reaction with OH radicals. Absorbance near 290 nm arising from HQ in the presence of the TS-2 catalyst was observed to increase compared with that in Fig. 2 [45].

#### 4. Conclusion

The effect of  $\text{Cl}^-$  ions on the photodecomposition of 4-CP was investigated with and without the TS-2 catalyst as a function of pH by absorption spectroscopy. In the absence of TS-2, chloride ions enhance the photodegradation of 4-CP in acidic and neutral solutions under UV illumination, with a faster photodegradation in acidic solution. Contrary to the enhancement of photodegradation in acidic and neutral solutions, there is no difference in the rates of deprotonated 4-CP photodegradation irrespective of the presence of chloride ions in alkaline solution because of the electrostatic repulsion between the two negatively-charged species. In the presence of TS-2, however, chloride ions enhance the photodegradation only in acidic solutions. Decomposition is not influenced by chloride ions with TS-2 in neutral and alkaline solutions, since chloride ions and 4-CP are present outside and in the cavity of TS-2, respectively, in neutral solutions and since both chloride ions and deprotonated 4-CP are electrostatically repelled from TS-2 in alkaline solutions. These results reveal that chloride ions should be in close proximity to 4-CP in order to enhance the photodegradation. The enhancement can be attributed to the reaction of chloride ions with chloride radicals to form  $\text{Cl}_2^-$ . The chloride radicals are abstracted from 4-CP either by absorption of light or by reaction with hydroxyl radicals.

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