Articles

Effects of Humic Acid on the Light-Induced Degradation of Chlorophenols

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Abstract

The effects of humic acid (HA) on the oxidative degradation of chlorophenols (CPs) by irradiation with visible light ($\lambda > 370$ nm) are described. The photodegradation of CPs was observed in the absence of HA. However, the rate of degradation was increased in the presence of HA. The degree of acceleration of CP degradation increased with increasing degree of humification of the HAs. In general, the amount of free radicals, such as semiquinone radicals, increase with increasing humification of HA. This tendency suggests that the quinone content of the HA is related to the observed difference in degradation rate. In addition, it has been reported that hydroxyl radicals (HO·) can be generated from the degradation of H_2O by photosensitized quinones. Therefore, the enhancement in the light-induced degradation of CPs in the presence of HAs can be attributed to HO·; generated via photosensitized quinones in HA. The contribution of HO· to the degradation of CPs was supported by the detection of higher levels of hydroxylation byproducts, such as quinones and catechols.

Introduction

The fate and behavior of persistent organic pollutants (POPs) in the aquatic and soil environment are largely related to the abiotic and biotic processes. In particular, abiotic processes that involve sunlight are known to be important degradation pathways of POPs in the surfaces of aquatic and soil environments (Cooper et al., 1989). The photosensitization of humic substances (HSs), which are widely distributed in the environment, can yield a variety of active species, such as singlet oxygen (Frimmel et al., 1987), hydrated electrons (Zepp et al., 1987) and H_2O_2 (Cooper and Zika, 1983, Fukushima and Tatsumi, 1999). Hydrated electrons play a significant role in the photoreduction of POPs, including trichloroethylene, chloroform and nitrobenzene (Zepp et al., 1987). In contrast, active oxygen species, such as singlet oxygen and hydroxyl radicals (HO·), play a role in the oxidative degradation of POPs. In particular, photo-Fenton processes, which involve both HSs and iron, have been examined, as a major factor in HO· generation in the environment. Zepp et al. (1992), Fukushima et al. (2000, 2001a and 2001b) and Tanaka et al. (2003) reported that the oxidative degradation of POPs, such as nitrobenzene, aniline, pentachlorophenol and bisphenol A, via photo-Fenton processes are enhanced by the addition of HSs and iron species.

On the other hand, the direct photolysis of POPs has mainly been examined from the standpoint of irradiation by uv light. Frimmel (1994) reported that the direct photolysis of a pesticide (*e.g.* atrazine) at wavelengths above 254 nm was inhibited by HSs. In the environment, the wavelength range of sunlight, which has a strong intensity, is mainly in the visible region above 370 nm (Leifer, 1988). Since POPs absorb visible light poorly, the direct photolysis may

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not occur in the environment. However, brown colored HSs absorb visible light, and the resulting photosensitized HSs may lead to the light-induced degradation of POPs. Nevertheless, the effects of HS on the light-induced degradation of POPs have not been investigated in the visible region. In the present study, we report on the effects of HS on the light-induced degradation of chlorophenols (CPs) under irradiation by visible light ($\lambda > 370$ nm). In addition, the degradation kinetics and nature of the byproducts produced were investigated to explain the oxidation characteristics of CPs. CPs were selected as model POPs, since they are listed as prior pollutants by USEPA (Keith and Telliard, 1979). Moreover, commercial and peat humic acids (HAs) were used as models of HSs in the environment.

Materials and Methods

Materials

Commercial HAs were purchased from Aldrich (AHA) and Wako Pure Chemicals (WHA). These compounds were purified using methods approved by the International Humic Substances Society (IHSS) (Swift, 1996). In addition, a peat HA was also isolated from a Shinshinotsu peat soil (SHA) by the same method. Elemental analyses and absorption coefficient data (e) are summarized in Table 1. For the measurement of e, absorption spectra of the aqueous solutions of HAs (pH 7, 50 mg L^{-1}) were measured using a JASCO V-550 type uv/vis spectrophotometer with a quartz cell (10 × 10 mm). The e value can be calculated from the absorbance, using Eq. (1):

$$e\,(\mathrm{L\,cm^{-1}\,g^{-1}\,C}) = \frac{\text{Absorbance}}{[\mathrm{HA}\,(\mathrm{g\,L^{-1}})]\times\%\mathrm{C}/100} \qquad (1)$$

where [HA (g L^{-1})] and %C denote the concentrations of HAs and the percentages of carbon in the HAs, respectively.

The CPs used in the present study were *o*-chlorophenol (*o*-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TrCP). These reagents were purchased from Wako Pure Chemicals. Stock solutions of CPs were prepared by dissolving these compounds in acetonitrile. However, for the analysis of byproducts, the stock solution of *o*-CP was prepared by dissolving it in pure water. The acetonitrile and methanol used in the analyses were HPLC grade (Kanto Chemicals).

Light irradiation

The pH of solutions containing CPs (50 μM) and HAs (50 mg L^{-1}) was adjusted to 7 by the addition of aqueous NaOH and H_2SO_4. A 20 mL aliquot of the test solution was placed in a quartz reactor (20 × 20 × 80 mm). The solution was then irradiated with a 500W Xenon short arc lamp (Ushio Denki) with a UV-37 glass filter ($\lambda > 370$ nm). The temperature of the solution was maintained at 25.0 ± 0.3°C during the irradiation.

Chlorophenol analysis

After irradiation, a 30 μL aliquot of the test solution was injected into a HITACHI L-6000 HPLC system. A mixture of water and acetonitrile was used as the mobile phase, where the mixing ratios (v/v) were 7:3 (*o*-CP) and 1:1 (2,4-DCP and 2,4,6-TrCP), and the flow rate was 1.0 mL min^{-1}. An Inertsil PH column (150 mm × 4.6 mm i.d., GL Sciences Inc.) was used. The CPs were detected at 210 nm using an L-4200 type uv-vis absorption detector (HITACHI).

Byproduct analysis

To investigate the degradation pathways, a test solution containing *o*-CP was irradiated and the resulting byproducts were analyzed. A 20 mL aliquot of the test solution at pH 7, which contained *o*-CP only or both *o*-CP (500 μM) and AHA (50 mg L^{-1}), was irradiated for 24 h. After irradiation, AHA in the test

Table 1. Results of elemental analyses and measurements of absorption coefficients.

HAs	Elemental analysis (%)					Atomic ratio		Absorption coefficients (L cm^{-1} g^{-1} C)		
	C	H	N	O	S	H/C	O/C	e_{400}[a]	e_{600}[a]	$\log e_{400}/e_{600}$
AHA	42.32	3.98	0.61	50.35	2.74	1.12	0.89	16.9	1.86	0.96
SHA	51.22	4.86	2.89	40.20	0.83	1.13	0.59	8.89	0.77	1.06
WHA	48.33	3.24	1.14	46.66	0.63	0.80	0.72	26.5	5.20	0.71

[a] Absorption coefficient at 400 or 600 nm.

solution was eliminated by passing the solution through an ultrafiltration filter (molecular weight cut off of 5000, Millipore Ultrafree CL filters). A 20 μL aliquot of the filtrate was injected into a JASCO PU-980 type HPLC system. For the analysis of phenol derivatives, a reversed-phase column (Waters Cosmosil 5C18- MS column, 4.6 mm i.d. × 250 mm) was used for the separation, and a mixture of methanol and a 0.08% aqueous solution of H_3PO_4 was used as the mobile phase. The following methanol gradient was employed: 20% for 10 min, 20 – 45% for 5 min and 45% for 8 min. The flow rate of the eluent and the column temperature were set at 1.0 mL min^{-1} and 50℃, respectively. For the analysis of organic acids, an ion-exclusion column (Shodex KC-811 column, 8 mm i.d. × 300 mm) was used, and a mixture of acetonitrile and 4 mM aqueous $HClO_4$ (1:9, v/v) was used as the mobile phase, where the flow rate of the eluent was 1.0 mL min^{-1} and the column temperature was 50℃. For both HPLC analyses, the compounds were detected at 210 nm by means of an SPD-6D type uv-vis detector (Shimadzu). The concentration of Cl^- in the solutions was measured by a DX-120 type ion chromatograph (Dionex). Total organic carbon (TOC) content in the test solution was analyzed by a TOC meter (TOC-5000 type, Shimadzu).

Results and Discussion

Degradation kinetics of CPs

Figure 1 shows data on the kinetics of degradation of 2,4,6-TrCP in the absence and presence of AHA. In the dark (Fig. 1 ▲), no disappearance of 2,4,6-TrCP was observed after 180 min of stirring, even in the presence of AHA. This shows that the adsorption of 2,4,6-TrCP to AHA does not occur during the 180 min of the reaction period. In the absence of AHA (Fig. 1 ○), 30% of the 2,4,6-TrCP was degraded after 120 min of irradiation. Figure 2 shows the uv absorption spectrum of 2,4,6,-TrCP, the wavelength dependence on the transmittance of the glass filter and the intensity of the lamp. As shown in Fig. 2, the glass filter permits light above 350 nm to pass through, and 2,4,6-TrCP did not absorb in this wavelength range. However, light above 250 nm is produced by the lamp, and the absorption band of 2,4,6-TrCP is within this range. If 2,4,6-TrCP would not have absorbed light above 350 nm, this disappearance could not have been observed in the absence of HA under the conditions of the present study. The direct photolysis of 2,4,6-TrCP, shown in Fig. 1 ○, can be attributed to the fact that the glass filter cannot completely eliminate the uv components of the light from the lamp. On the other hand, in the presence of AHA (Fig. 1 ●), 60% of the 2,4,6-TrCP was degraded after 120 min of irradiation. These results show that the addition of AHA is effective in enhancing the light-induced degradation of 2,4,6-TrCP.

To quantitatively evaluate the effect of AHA on the degradation of CPs, we calculated the pseudo-first-order rate constants (k) from each kinetic curve. The rate constants were calculated based on the disappearance of CPs:

$$-dC_t/dt = kC_t \qquad (2)$$

where C_t and t denote the concentration of CPs at an arbitrary irradiation period and the irradiation time (s),

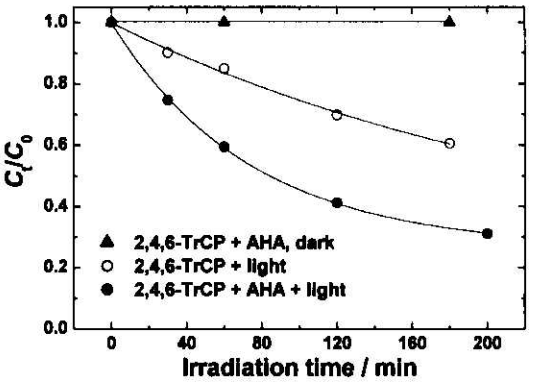


Figure 1. Kinetic curves of 2,4,6-TrCP degradation in the absence and presence of AHA. $[2,4,6\text{-TrCP}]_0$ = 50 μM, [AHA] = 50 mg L^{-1}, pH 7.

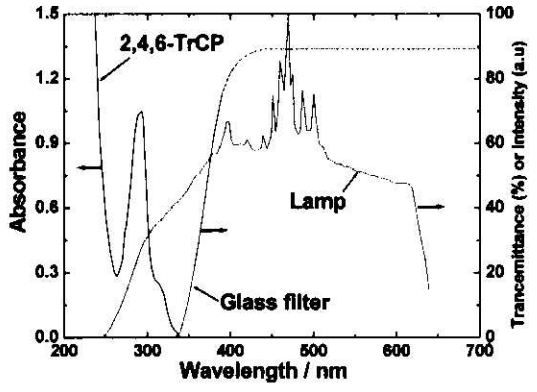


Figure 2. Uv absorption spectrum of 2,4,6-TrCP, wavelength dependence on transmittance of the glass filter and intensity of the lamp. [2,4,6-TrCP] 500 μM, pH 6.

respectively. The integrated form of Eq. (2) can be written as:

$$C_t/C_0 = \exp(-kt) \qquad (3)$$

where C_0 denotes the initial concentration of CPs. The k values can be calculated by the non-linear least square curve-fittings of the data points in the kinetic curves to the Eq. (3). Table 2 shows the k values in the absence (k_0) and presence (k_{HA}) of AHA. The k_{HA}/k_0 ratio in Table 2 represents the degree of acceleration, as the result of adding AHA. In all CPs, the light-induced degradation was accelerated in the presence of AHA. Such acceleration is probably due to the production of active species via the photosensitized HA.

Table 2. Comparison of pseudo-first-order rate constants for the light-induced degradation of CPs in the absence and presence of AHA.

CPs	k_0 / s^{-1}	k_{HA} / s^{-1}	k_{HA}/k_0
o-CP	11.7	17.5	1.50
2,4-DCP	29.7	52.2	1.76
2,4,6-TrCP	46.0	109	2.36

Influence of HA type

To investigate the influence of the type of HA, the degradation kinetics of 2,4,6-TrCP were compared in the presence of three different HAs. The kinetic curves are shown in Fig. 3. After 120 min of irradiation, 28%, 39% and 88% of 2,4,6-TrCP were degraded in the presence of SHA, AHA and WHA, respectively. The pseudo-first-order rate constants for each HA are summarized in Table 3. The k_{HA} were significantly varied by HA types, and the order of k_{HA}/k_0 was WHA > AHA > SHA. In the dark, the disappearance of 2,4,6-TrCP was not observed in the presence of WHA and SHA as well as of AHA. These results show that the photosensitization of HA contributes to the degradation of 2,4,6-TrCP.

To clarify what species parameters of HAs are re lated to the k_{HA}/k_0 ratios, the visible absorption characteristics of the HAs were investigated. The absorption spectra (e vs. wavelength) for each HA are shown in Fig. 4. The order of the absorption coefficient above 370 nm was WHA > AHA > SHA. This order is similar to that for the k_{HA}/k_0 ratio. In addition, the $\log e_{400}/e_{600}$, H/C and O/C are related to the degree of humification (Kuwatsuka et al., 1978, Tsutsuki and Kuwatsuka, 1978, Kumada, 1955). From these

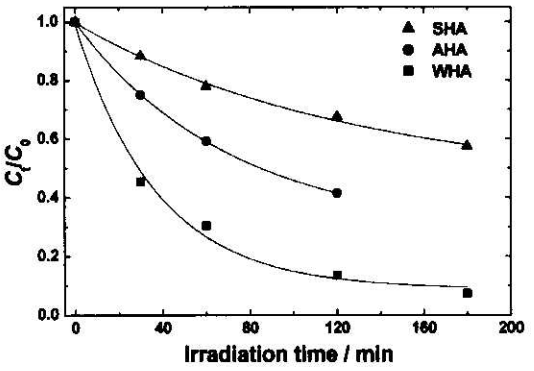


Figure 3. Kinetic curves of 2,4,6-TrCP degradation in the presence of three different HAs. $[2,4,6\text{-TrCP}]_0$ = 50 μM, [HA] = 50 mg L^{-1}, pH 7.

Table 3. Comparison of pseudo-first-order rate constants for the light-induced degradation of 2,4,6-TrCP in the presence of three HAs (k_0 = 46.0 s^{-1}).

HAs	k_{HA} / s^{-1}	k_{HA}/k_0
AHA	109	2.36
WHA	340	7.39
SHA	50.2	1.09

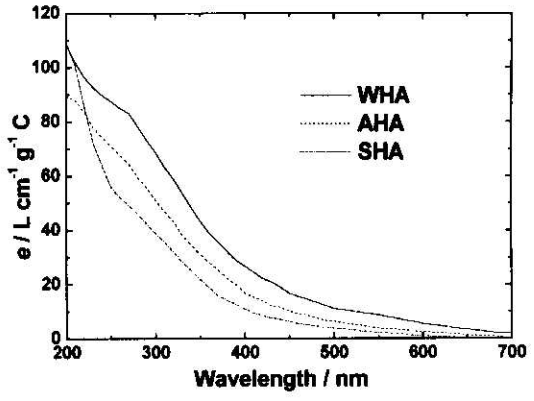
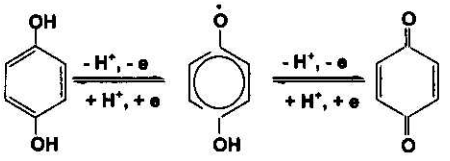


Figure 4. Uv-vis absorption spectra of three HAs. [HAs] 50 mg L^{-1}, pH 6.

values in Table 1, the order of humification degree was estimated as: WHA > AHA > SHA. These results suggest that the degree of humification of HA can be related to the rate of light-induced degradation of 2,4,6-TrCP.

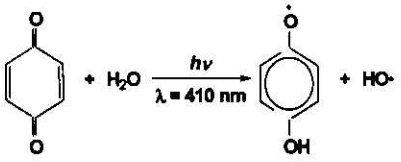
A previous study, using electron resonance spectroscopy (Schnitzer and Levesque, 1979), showed that the amount of free radicals in HS increased with increasing degree of humification. The free radicals

in HSs are known to be mainly semiquinone radicals. Such radical species can readily be oxidized to quinone, as shown in Eq. (4):



(4)

Therefore, the amounts of quinone in HS can also increase with increasing humification. According to Ononye and Bolton (1986) and Chen and Pignatello (1997), the photosensitization of 1,4-benzoquinone in aqueous solution yields a semiquinone radical and HO·, as shown in Eq. (5):



(5)

The semiquinone radical can be subsequently converted to 1,4-hydroquinone and hydroxy-1,4-benzoquinone. In addition, a semiquinone radical can automatically be oxidized to 1,4-benzoquinone again. Thus, the redox couple of 1,4-benzoquinone / semiquinone radical can play an important role in the photocatalytic generation of HO·. This suggests that HO·, which can be generated from photosensitized quinones in HA, contributes to the light-induced degradation of CPs. Thus, the differences in the k_{HA}/k_0 ratio may depend on the amounts of quinone moieties in the HAs.

Another possible pathway for HO· generation is the direct photolysis of H_2O_2 ($\lambda < 400$ nm), generated by the reduction of dissolved O_2 via photosensitized HSs (Chen and Pignatello, 1997). To examine this possibility, we examined the influence of dissolved O_2 on the light-induced degradation of 2,4,6-TrCP in the presence of AHA. As shown in Fig. 5, the rate of degradation of 2,4,6-TrCP under aerobic conditions (air saturated) was similar to that under anaerobic conditions (N_2 saturated). These results indicate that the contribution of dissolved O_2 to the light-induced degradation of 2,4,6-TrCP is not very significant. Therefore, the enhancement in the light-induced degradation of CPs in the presence of HA can be attributed to HO·, generated from the degradation of H_2O by photosensitized quinones in HA , as written in Eq. (5).

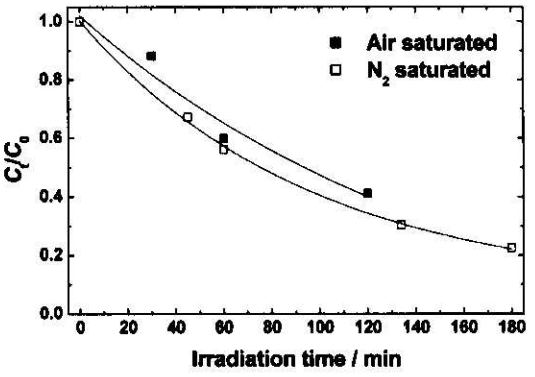


Figure 5. Comparison of kinetic curves of 2,4,6-TrCP degradation under aerobic (air saturated) and anaerobic (N_2 saturated) conditions. $[2,4,6\text{-TrCP}]_0$ = 50 μM, [AHA] = 50 mg L^{-1}, pH 7.

Byproduct patterns

To better understand the degradation pathway of CP, we analyzed the byproducts in the solution after irradiation. In this study, TOC in the test solution should be measured, in order to determine the extent of mineralization to CO_2 as a final product. However, acetonitrile was used as a co-solvent of CPs in the kinetic study, which resulted in a higher background carbon in measuring TOC. Because several-ten mg L^{-1} levels of carbon are required for the measurement of TOC, it is necessary to dissolve large amounts of CPs in the test solution without acetonitrile. Thus, in this study, we selected *o*-CP because of its higher water solubility.

When a solution containing *o*-CP (500 μM) and AHA (50 mg L^{-1}) was irradiated for 24 h, 36% (180 μM) and 56% (280 μM) of the *o*-CP was degraded in the absence and presence of AHA, respectively. Figures 6 a and b show the reversed-phase HPLC chromatograms of the test solutions before and after irradiation. In the presence of AHA, catechol, chlorohydroquinone and 3-chlorocatechol were detected as byproducts. However, in the absence of AHA, no detectable byproducts were observed by reversed-phase HPLC. The formation of such byproducts supports the contribution of HO· to the light-induced degradation of CPs.

On the other hand, Cl^- analyses by ion chromatography showed that, after 24 h of irradiation, 180 and 200 μM of Cl^- were released from *o*-CP in the absence and presence of AHA, respectively. These concentrations of chlorine in the absence and pres-

ence of AHA correspond to 100 % and 70% of the concentrations of degraded *o*-CP. The sum of the concentrations of 3-chlorocatechol and chlorohydroquinone were only 3% of the degraded *o*-CP. Thus, 27% of the chlorine species produced in the presence Moreover, the release of chlorine from *o*-CP implies that further oxidized byproducts, such as organic acids and CO_2, can be produced. An analysis of organic acids by ion-exclusion chromatography showed that maleic and fumaric acids were produced as a result of irradiation (data not shown). Such organic acids may be further oxidized to CO_2. The percentages of mineralization to CO_2, calculated from TOC values, were 30% and 50% of the degraded *o*-CP in the absence and presence of AHA, respectively.

Possible pathways for the degradation of *o*-CP are summarized in Fig. 7. The HO•, generated via the photosensitized quinone moieties in HA, can attack the anionic species of *o*-CP (*o*-CP$^-$) to yield hydroxycyclohexadienyl radicals (Buxton, G. V. et al., 1986). These radicals can be converted to chlorophenoxy radicals (*o*-CP•), quinones and catechols. It has been reported that polymerized compounds are produced via the oxidative coupling of chlorophenoxy radicals, such as *o*-CP•. In addition, ring cleavage in quinones and catechols may yield organic acids, such as maleic and fumaric acids. Such acids can be further mineralized to CO_2 by oxidation by HO•.

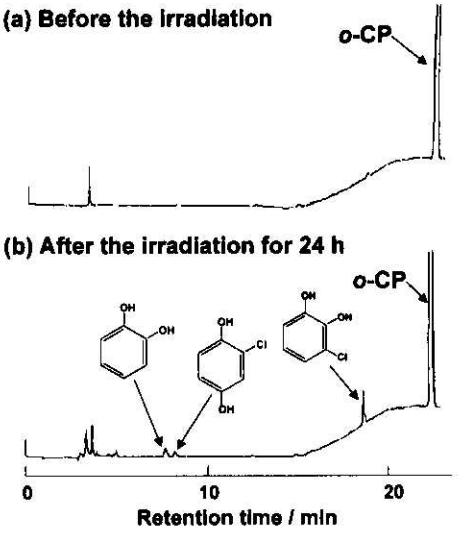


Figure 6. Reversed-phase HPLC chromatograms of test solutions containing *o*-CP and AHA before (a) and after (b) irradiation. $[2,4,6\text{-TrCP}]_0$ = 500 μM, [AHA] = 50 mg L^{-1}, pH 7, irradiation time: 24 h.

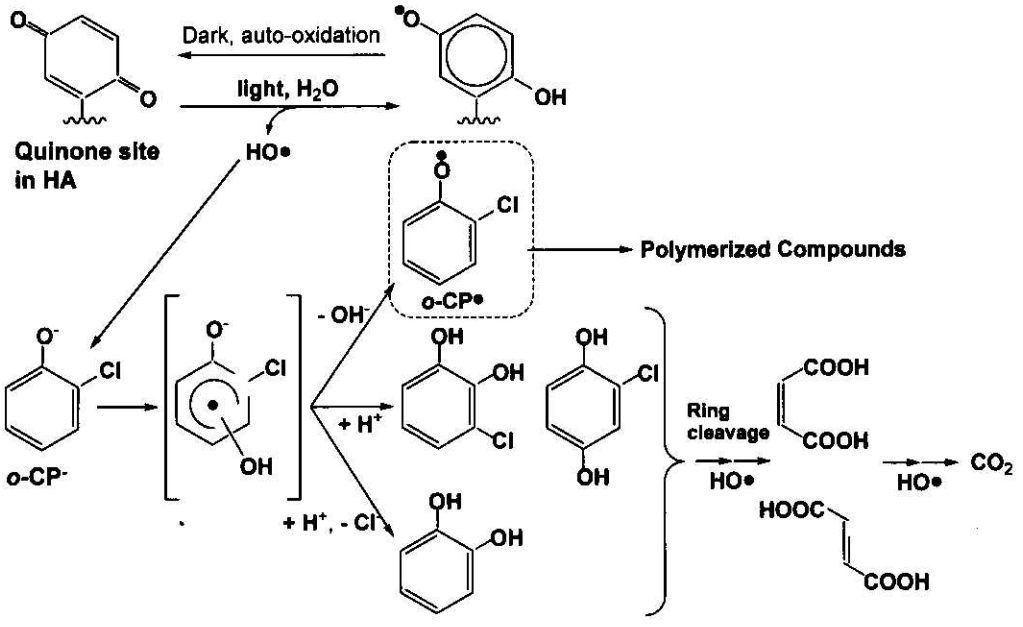


Figure 7. Possible reaction pathways of *o*-CP.

Conclusions

The present study shows that the light-induced degradation of CPs is accelerated in the presence of HAs. In particular, the degree of acceleration is related to the degree of humification of the HAs. The enhancement in the degradation of CPs can be attributed to HO·, generated from the degradation of H_2O by photosensitized quinones in the HAs. The contribution of HO· is also supported by the detection of additional hydroxylation byproducts, such as chlorohydroquinone, catechol and 3-chlorocatechol. For the degradation of pollutants by HO· in the environment, the photo-Fenton reaction is known to be an important process in the natural attenuation of POPs (*e.g.* Zepp et al., 1992). However, the generation of HO· via the photosensitization of quinone moieties in HSs also plays a significant role in the oxidative degradation of organic pollutants in the environment.

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