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# OXIDATION AND DECHLORINATION OF CHLOROPHENOLS IN DILUTE AQUEOUS SUSPENSIONS OF MANGANESE OXIDES: REACTION PRODUCTS

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**Abstract**—Some monomeric and dimeric oxidation products of para- and/or ortho-chlorinated phenols in dilute (1 mmol/L phenol), acidified, aqueous suspensions of manganese oxide (Na-buserite) were identified by MS, Fourier-transform IR spectroscopy and UV/visible spectroscopy. The para-chlorinated phenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-chloro-2-methylphenol) gave corresponding *p*-benzoquinones (benzoquinone, 2-chlorobenzoquinone, 2,6-dichlorobenzoquinone, 2-methylbenzoquinone) as the detectable water-soluble oxidation products. Dimeric products were present in the extracts obtained by washing the oxide with methylene chloride. Michael addition of phenolate to quinone seems to be the predominant mode of coupling. Chlorinated phenols without chlorine in the para-position (2-chlorophenol, 2,6-dichlorophenol) were more difficult to oxidize and afforded diphenoquinones as the only detectable water-soluble products. For all studied phenols, with the exception of 2,4,6-trichlorophenol, the amount of water-soluble products accounts only for a small fraction of oxidized phenol. The quinone and diphenoquinone products readily couple with phenols into humuslike materials.

**Keywords**—Chlorophenols Oxidation products Quinones Dechlorination Buserite

## INTRODUCTION

The reactions of chlorinated phenols at the surfaces of manganese oxides in aqueous suspensions have been shown to involve electron transfer from phenol to Mn(III/IV), resulting in manganese oxide reduction and dissolution [1]. The exact nature of these reactions and their products are not well understood. Product identification is necessary to deduce mechanisms of chlorinated phenol oxidation and coupling by manganese oxides in aqueous solutions. Product identification is also essential for assessing the importance of these reactions and the conditions under which they can occur in the environment. In addition, the oxidation of phenols by manganese oxides may provide an abiotic process in the treatment of waste water for the detoxification of toxic and bioresistant organic pollutants.

It is difficult to extract and identify products in dilute aqueous solutions because their concentrations are very low. Oxidation of most phenols by manganese oxides in dilute aqueous suspensions typically results in small amounts of unstable water-soluble products [2–4]. Increasing phenol concentrations to obtain higher conversion results in coupling reactions that would not occur under environmental conditions [5].

Recent studies have shown that 2,4,6-trichlorophenol can be dechlorinated at the para-position and oxidized to 2,6-dichloro-*p*-benzoquinone at the surface of manganese oxide [6]. This oxidation was very selective with high conversion to the benzoquinone product and very little coupling, as expected for phenol with both ortho-positions substituted [7]. A mechanism involving formation of an inner sphere surface complex between phenolate and manganese, followed with nucleophilic aromatic substitution by addition-elimination, has been proposed to account for the dechlorination and oxidation. The inner-sphere complex could explain why no radicals were detected by electron spin resonance in reacting suspensions and account for nucleophilic attack at the para-position only: ortho-positions in phenolate/manganese complex would be sterically hindered.

In the present study some monomeric and di-

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meric products of ortho- and/or para-chlorinated phenols in dilute acidic aqueous suspensions of manganese oxides have been identified.

## MATERIALS AND METHODS

All experiments were conducted at 22 ± 1°C. Phenols were analytical-grade reagents, obtained from Aldrich Chemical Co. (Milwaukee, WI) (2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol) and Eastman Kodak Co. (Rochester, NY) (2,4-dichlorophenol, 4-chloro-2-methylphenol), and were used as received. Methylene chloride was Fisher Scientific (Fair Lawn, NJ) spectranalyzed. Buserite in Na-saturated form was synthesized by method of Giovanoli et al. [8] and characterized as described elsewhere [6].

### *Product extraction and identification*

*Water-soluble products.* The phenol ($10^{-3}$ M, 200 ml) and Na-buserite (1 g) were placed in a 220-ml cylindrical glass reaction container, protected from light with aluminum foil and equipped with a magnetic stirring bar. The pH was adjusted to 2.5 with 0.2 M HCl. The suspension was stirred until the maximum intensity of yellow color in the supernatant was achieved (usually 10–15 min). The suspension was then filtered through a 0.2-μm Nuclepore® (Pleasanton, CA) membrane filter, and the filtrate was extracted with methylene chloride, dried over anhydrous sodium sulfate, and concentrated to 5 ml by evaporation. The entire extraction procedure was performed with protection from light.

The UV/visible spectra of filtered reacted aqueous suspensions were recorded on a Perkin Elmer (Norwalk, CT) Lambda 4C spectrophotometer. Phenol concentrations in filtrates were obtained from the absorption intensity at $\lambda_{max}$ of each phenol after baseline adjustment. All experiments were performed in triplicate and the average values are reported.

*Insoluble products.* The above reaction mixture was centrifuged to separate the oxide from aqueous solution. The oxide was briefly shaken with 20 ml of methylene chloride. The extract was dried over sodium sulfate and concentrated to 1 ml by evaporation.

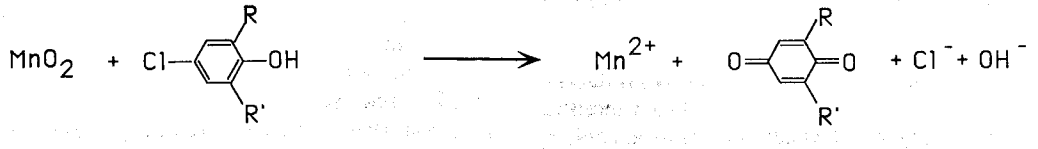
*Gas chromatography–Fourier transform infrared spectroscopy–mass spectroscopy (GC-IR-MS).* The analysis of products was performed by GC-IR-MS. The GC was a Hewlett Packard (Avondale, PA) 5890 Series II with a DB-5 fused-silica capillary column (J & W Scientific, Folsom, CA) of 30-m length and 0.25-mm i.d., with 0.25-μm film thickness for MS, and of 25-m length and 0.3-mm i.d. for IR. Injection port and transfer line were held at a temperature of 280°C. Helium was used as a carrier gas. The splitless mode was used for analysis of water-soluble extracts and the split mode for analysis of extracts obtained by washing the oxide with methylene chloride. The temperature was programed from 100 to 260°C at 10°C/min with a solvent delay of 4 min. The temperature of the IR light pump was held at 280°C. The IR detector was a Hewlett Packard 5965A Fourier-transform instrument acquiring interferograms at the rate of three scans per second with a resolution of 4 $cm^{-1}$. The mass spectral detector (MSD) was a Hewlett Packard 5970. It was set to acquire scans at 1/s over a range of $m/z$ 40 to 550. The ionization voltage of MSD was 68 eV, with a 220-mA emission current from an ion source at 220°C. Data acquisition was handled by two Hewlett Packard 9000 Series 300 computers with accompanying acquisition and processing software.

Nonvolatile extracts were evaporated to dryness in the air, compressed into KBr pellets, and analyzed by a Fourier-transform Perkin Elmer 1720-X spectrometer with 2 $cm^{-1}$ resolution.

## RESULTS AND DISCUSSION

### *Phenols with chlorine in para-position*

Four para-substituted phenols (1a–d) gave *p*-benzoquinones (2a–d) as the only detectable water-soluble products:




**1a,2a**: R=R'=H
**1b,2b**: R=Cl,R'=H
**1c,2c**: R=R'=Cl
**1d,2d**: R=$CH_3$, R'=H

The decrease in phenol concentration for a reaction time of 5 min in unbuffered and buffered suspensions is shown in Table 1. In unbuffered suspensions, pH increased during reaction by 0.5 to 1 pH units. Except for 2,4,6-trichlorophenol, for which almost complete conversion to 2,6-dichloro-*p*-benzoquinone was obtained [6], quinones in the aqueous solution accounted for only a small amount of oxidized phenols. It is well-known that phenols with no substituents or just one substituent in the ortho-position give a complex mixture of branched products that are likely to be insoluble in acidic aqueous media.

The detection of monomeric *p*-benzoquinone products by GC-IR-MS analysis was possible if the starting phenol was not present in the extract. In the GCs of the extracts containing unreacted phenols, the *p*-benzoquinones were present in trace quantities or were not detected at all (with exception of 2c), although they were present in the aqueous solutions (Table 2) before extraction. Because such extracts usually did not contain volatile products, the loss of quinone monomers must have occurred by polymerization during concentration of the extract.

The monosubstituted *p*-benzoquinones (2b, 2d) were unstable and very light sensitive in aqueous suspensions of manganese oxides, and were therefore particularly difficult to extract. Figure 1a shows the total ion chromatogram of the methylene chloride extract of a filtered 2,4-dichlorophenol aqueous solution after reacting with buserite. At low pH (<3.5), low 2,4-dichlorophenol concentrations (<1 mmol/L), high oxide quantities (5 g/L), and short reaction times (10 min), almost all 2,4-dichlorophenol was reacted. The only products found in the methylene chloride extract were chloro-*p*-benzoquinone (*m/z* 142) and chloro-*p*-hydrobenzoquinone (*m/z* 144). The occurrence of the M + 2 peak corresponding to chloro-*p*-hydrobenzoquinone may be the result of 2b reduction in GC-MS during analysis [9]. Longer reaction times resulted in loss of the yellow color of the aqueous solution and disappearance of the quinone 2b UV absorbance band.

In an attempt to identify other insoluble reaction products of 1b, the oxide was separated from the aqueous solution and washed with methylene

Table 2. Absorption characteristics of aqueous phenol solutions

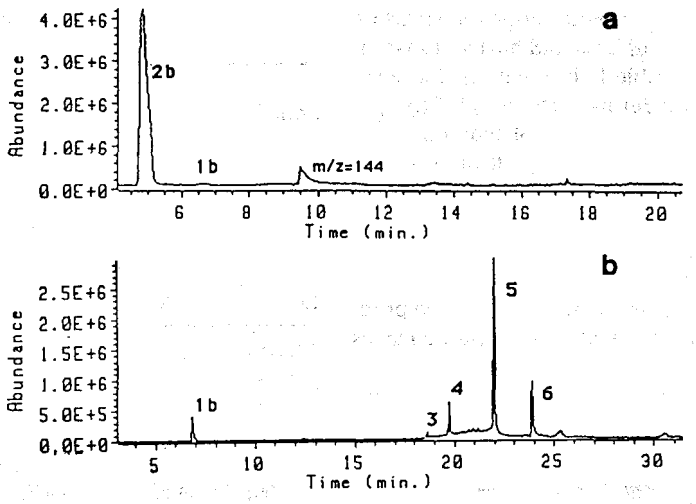
| Phenol | $\lambda_{max}$ (nm) | New bands appearing after oxidation[a] |
|---|---|---|
| 1a | 278 | 245 |
| 1b | 284 | 254 |
| 1c | 293 | 270, 345 |
| 1d | 279 | 228, 249, 327 |
| 1e | 272 | 264[b], 412 (0.55)[c] |
| 1f | 281 | 275, 331, 433 (0.37)[c,d] |
| 1g | 269 | 245, 253, 263, 398 (0.56)[c] |

[a]Reaction conditions as in Table 1; absorption maxima correspond to the products listed in Table 1.
[b]Observed only at pH 2.2.
[c]Number in parentheses is the maximum absorbance obtained at pH 2.2.
[d]Reported absorbance (nm) and ε (1/M cm) for 9a: 261 (5,390), 273 (4,520), 283 (3,470), 435 (71,800) in chloroform [15]; 427 (73,000) in acetonitrile [19].

Table 1. Oxidation of phenols with Na-buserite

| | Phenol concn. ($c/c_0$)[a] | | | | |
|---|---|---|---|---|---|
| | Unbuffered[b] | | Buffered[c] | Products[d] | |
| Phenol | pH 2.2 | pH 3.2 | pH 4.7 | *p*-Benzoquinone | Diphenoquinone |
| 1a | 0.12 | 0.55 | 0.76 | 2a | |
| 1b | 0.09 | 0.43 | 0.75 | 2b | |
| 1c | 0.08 | 0.57 | 0.68 | 2c | |
| 1d | 0 | – | – | 2d | |
| 1e | 0.52 | 0.88 | 0.96 | | 8 |
| 1f | –[e] | 0.71 | 0.87 | | 9 |
| 1g | 0.14 | 0.82 | 0.85 | 2a | 10 |

[a]Reaction time is 5 min, $c_0 = 6.4 \times 10^{-4}$ M, 0.6 g/L buserite.
[b]pH adjusted with HCl.
[c]$2.0 \times 10^{-3}$ M Na-acetate.
[d]Water-soluble products; conversions are <10%, except for 1c (see [6]).
[e]Could not be measured because of interference of products in solution.




Mass spectral data for dimers formed from 2,4-dichlorophenol.

| Product | m/z | number of chlorines | MS peaks (intensities) |
|---|---|---|---|
| 3 | 302 | 3 | 302(15),267(100),239(38),173(3),145(4),113(9) |
| 4 | 322 | 4 | 322(55),287(5),252(100),223(7),177(2),160(5) |
| 5 | 304 | 3 | 304(89),268(8),234(100),205(7),146(16),130(34) |
| 6 | 322 | 4 | 322(80),324(100),295(3),252(3),223(31),159(5),161(7) |

Fig. 1. Total ion chromatogram of methylene chloride extract of oxidation products of 2,4-dichlorophenol: (**a**) extract of filtered aqueous solution and (**b**) extract obtained by washing the oxide.

chloride. The yellow extract was analyzed by GC-IR-MS, and the chromatogram is shown in Figure 1b. The first peak corresponds to the starting compound, 1b. The other peaks correspond to the dimeric products similar to the dimers obtained from 1b by incubation with the enzyme, phenol oxidase [10]. It is possible that the extract contained oligomers and polymers that were not volatile enough to be detected by GC-IR-MS. The peaks with *m/z* 302 (3, three chlorines), 324 (4, four chlorines), 304 (5, three chlorines), and 324 (6, four chlorines) were identified as one of the isomers of the structures shown in Figure 2. Compound 3 most likely forms by Michael addition of 2,4-dichlorophenolate to 2b. The extent of coupling is probably very small in dilute suspensions over a short time. Coupling may be greater at the oxide surface, where the dissociation of the phenolic OH group might be promoted. The concentration of products at the surface is likely greater than in the bulk solution, as well. The product 3 is similar to a previously described dimer 7 that formed by Michael addition of 2,4,6-trichlorophenol to 2,6-dichloro-*p*-benzoquinone [6]. The formation of 7 [6] was probably more difficult then the formation of 3 because it required the dechlorination of quinone. Compound 5 corresponds to reduced 3 (M + 2 peak), the reduction very likely being an artifact of the analytical procedure [9]. Ortho-C—C coupling occurred to a very small extent to give dimer 4. It has been shown that in Cu(II) catalyzed oxidations of 2,4-disubstituted phenols, ortho-C—C coupling occurs by an intramolecular process involving two adjacent phenoxy ligands at a single copper center [11]. If formation of 4 in the present study requires such coordination on the manganese oxide surface, it would have low probability because it is unlikely that two phenols would coordinate to the same surface manganese. Thus the amount of 4 formed would be low, in agreement with the weak peak for 4 in the ion chromatogram. The dimer 4 could also form by coupling between two free phenoxy radicals, which would again afford a low conversion, because free chlorinated phenoxy radicals are very short lived in acidic aqueous solutions.

Finally, washing the oxide with methylene chlo-

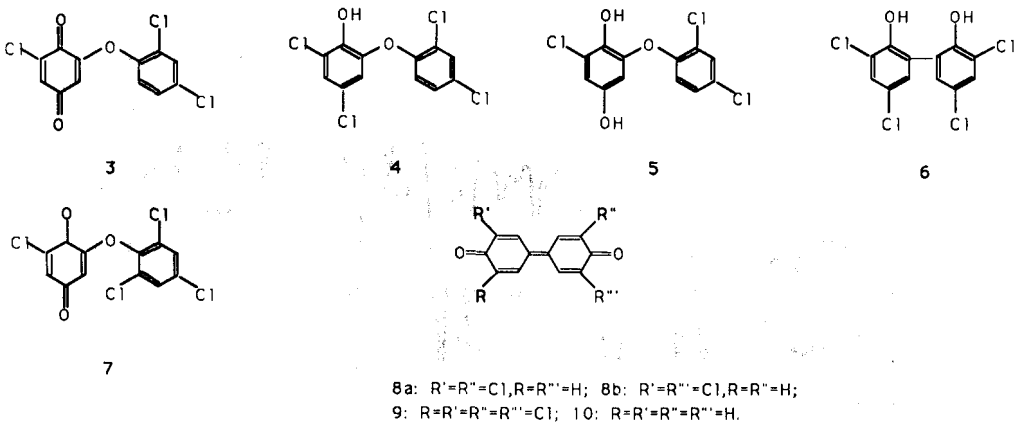



Fig. 2. Dimers identified as oxidation products of 1b (3–6), 1c (7), 1e (8a,b), 1f (5, 9), and 1g (10). The C—O-coupled dimers may be coupled at different positions.

ride after longer reaction times resulted in a nonvolatile, oily, green-yellow extract. The IR spectrum of this humuslike polymer (Fig. 3) contains absorption bands associated with the bonds C—Cl (794 $cm^{-1}$), C=O (1,646, 1,696 $cm^{-1}$), and C—C of the quinoid ring (1,624 $cm^{-1}$). The spectrum also contains a number of bands (1,445, 1,331, 1,235, 1,187, 1,073, 943 $cm^{-1}$) that occur in the vapor-phase IR spectrum of 3, inferring that the polymeric material contains C—O-coupled quinones and phenols.

Oxidation and coupling of a 4-chloro-2-methylphenol (1d) proceeded faster than that of 2,4-dichlorophenol, resulting in a number of water-soluble dimeric and oligomeric products (*m/z* 282, 318, 330), some of which contained no chlorine. The peak with *m/z* 282 is an ortho-C—C-coupled 1d, analogous to dimer 4. The higher reactivity of 1d is probably due to the activating effect of the electron-donating methyl group. The methyl substituent might have stabilized the phenoxy radical, enabling some free radical reactions. The monomeric quinone 2d was even less stable than 2a and could not be extracted from the aqueous solution for GC-IR-MS analysis.

*Phenols with no para-chloro substituents.* In contrast with 1a-d, the phenols 1e (2-chlorophenol) and 1f (2,6-dichlorophenol), having no chlorine substituent in the 4-position, did not give quinones 2b and 2c in detectable quantities under mild experimental conditions. The decrease in the concentration of phenols 1e and 1f occurred to a smaller extent (Table 2) than for mono- and dichlorinated phenols with chlorine in the para-position.

Reaction with buserite in acidified aqueous suspensions resulted in water-soluble products with strong absorption bands at 412 and 433 nm for 1e and 1f, respectively. The strong absorption in this region of the visible spectrum is characteristic of diphenoquinones (Table 2). These products were unstable and disappeared from solution within 10 to 15 min.

The compound 1e most likely C—C coupled at the para-position to give 8a and/or 8b (Fig. 2). No reports were found in the literature on the spectra and properties of the *n,n'*-dichlorophenoquinones. Attempts to extract 8a,b for GC-IR-MS analysis were unsuccessful, probably due to its high reactivity and formation of nonvolatile high-molecular-weight products. The reduction of 8a,b with zinc dust resulted in a UV absorption maximum at 264 nm. The expected reduction product of 8a, 3,3'-dichloro-4,4'-biphenyldiol, has been reported to absorb at 264 nm ($\epsilon$ = 23,000 [12]).

The methylene chloride extract of aqueous solution of 1f, analyzed by GC-IR-MS revealed only the unreacted compound, and trace quantities of 2,6-dichloro-*p*-hydroquinone (*m/z* 178). The extract obtained by washing the oxide with methylene chloride had 3,3',5,5'-tetrachloro-4,4'-biphenyldiol (9a, *m/z* 322, four chlorines) as its major volatile component. A small quantity of another product detected by GC-IR-MS was identified as 5 (*m/z* 304, three chlorines.

The mass spectrum of the product 9a was identical with the one reported in the literature [13,14]. The 3,3',5,5'-tetrachlorodiphenoquinone (9a) is thermally reduced during GC-MS analysis to give

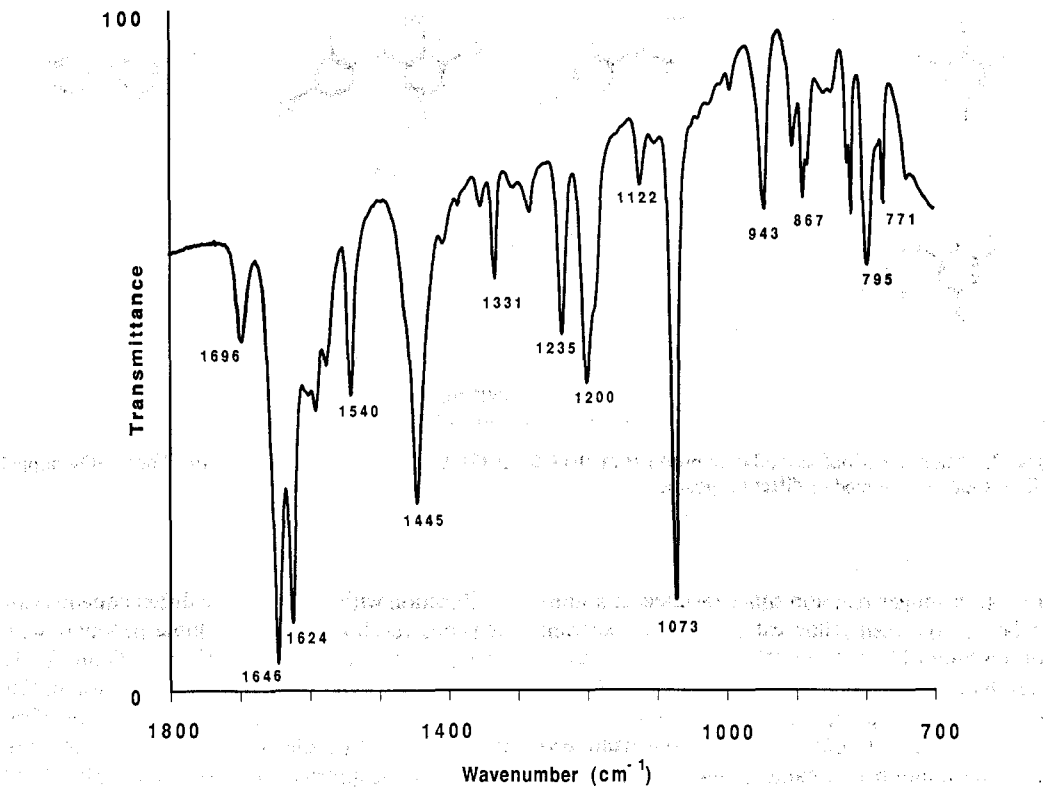



Fig. 3. The Fourier transform IR spectrum (KBr) of nonvolatile product obtained by washing the oxide with methylene chloride after reacting with aqueous 2a for 4 h. Compare with the vapor-phase data for product 3 [$cm^{-1}$ (%T)]: 1,706 (61), 1,662 (40), 1,628 (69), 1,587 (46), 1,445 (29), 1,344 (77), 1,280 (69), 1,236 (0), 1,187 (78), 1,114 (75), 1,067 (95), 939 (76), 897 (81), 878 (80), 776 (77).

biphenyldiol (M + 2 peak) [14]. The tetra-substituted diphenoquinones are less readily polymerized in solution than the unsubstituted and possibly disubstituted ones, such as 8 [15]. However on evaporation they tend to undergo polymerization into nonvolatile products [13].

The oxidation of unsubstituted phenol (1g) produced both diphenoquinone (10) and *p*-benzoquinone (2a) as the water-soluble oxidation products. In the previous study of oxidation of 1g [3] it was found that higher oxide quantities and low phenol concentration resulted in increased production of *p*-benzoquinone.

The diphenoquinones could form by a free radical mechanism or by coupling of phenoxy radicals coordinated to two adjacent surface manganese ions. The latter mechanism is more likely because free radicals are very short lived at low pH and were not detected by electron spin resonance. Further studies or molecular orbital calculations are needed to explain the lower reactivity of 1e compared to 1f. One possible explanation is the stronger polarization of 1f by the field effect of two chlorines. The $pK_a$ value for 1f is lower than it is for 1e, which makes formation of phenolate easier. Oxidation of phenolate requires significantly lower potential than the oxidation of phenol [16].

## CONCLUSIONS

The comparative study of the oxidation products of various ortho- and/or para-chloro-substituted phenols in aqueous manganese oxide suspensions shows that reaction rates and products of oxidation are largely dependent on whether chlorine or hydrogen is para- to the phenolic hydroxyl group. When chlorine is in the para-position, *p*-benzoquinone formation is facilitated in two ways. First, the ad-

dition of hydroxyl to para-carbon and elimination of chlorine does not require electron transfer, whereas the elimination of hydrogen requires a two-electron transfer from the aromatic ring. Thus, the transformation of any *p*-chlorophenol to *p*-benzoquinone is formally a two-electron oxidation. The transformation of phenol with hydrogen in the para-position to *p*-benzoquinone requires a four-electron oxidation. Second, the electron-accepting chlorine substituent activates the ring to nucleophilic aromatic substitution by the field effect [17]. With hydrogen in the para-position, the oxygenation of phenol appears to be more difficult and the reaction mechanism for *p*-benzoquinone formation is likely to be different. Compared to the unsubstituted phenol, 2- and 2,6-chlorinated phenols, 1e and 1f were more difficult to oxidize and did not form *p*-benzoquinones. Thus the chlorine substitution in the absence of para-chlorine had a deactivating effect on phenol oxidation.

All of the studied para-chlorinated phenols showed fairly high selectivity for dechlorination and hydroxylation at the para-position. This is consistent with a previously proposed mechanism for dechlorination and oxidation involving formation of a surface manganese/phenolate complex followed by nucleophilic aromatic substitution by addition of hydroxyl (or water) and elimination of chlorine [6]. When phenolate is coordinated to surface manganese, the ortho-positions are sterically inaccessible to hydroxylation.

The predominant mode of coupling seems to be the Michael addition of phenols to quinones. The para-C—O-coupled phenolic products were not detected, which is expected for phenol oxidations in acidic media, in which the phenoxy radical remains complexed to the metal [18]. Phenols without chlorine in the para-position C—C coupled to give diphenoquinones. The para-C—C coupling was obviously hindered by the presence of chlorine in the para-position, because no diphenoquinones or 4,4′-biphenyldiols were formed from phenols with chlorine in the para-position.

The studied phenols and monomeric *p*-benzoquinones have relatively high water solubilities and therefore are expected to be quite mobile in soils, sediments, and ground water. Thus the kinetics of oxidation and quinone formation and coupling should be studied in an open flow-through system. The reaction rates in such a system may be faster as a result of product removal.

The dechlorination and oxidation of phenols by manganese oxides may be important for detoxification and removal of these compounds from the environment, as they can result in dechlorinated, less toxic products that can then be biodegraded at a faster rate. The quinone products are also likely to be immobilized by coupling with phenols and incorporation into insoluble humuslike materials. The oxidation and coupling of phenols catalyzed by manganese oxides may also play an important role in the analysis of water samples for phenolic pollutants. For example, extraction of natural water samples containing manganese by U.S. Environmental Protection Agency (EPA) Method 625 has been shown to give very low recoveries of phenols due to oxidation of phenols by manganese oxide [4].

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