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Electrochemical Oxidation of Chlorinated Phenols

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Electrochemical oxidation has been proposed as a remediation method for chlorinated phenols but is hampered by anode fouling. In this work we explore the mechanism of anode fouling by chlorinated phenols, compare structure vs reactivity for phenols differing in the extent of chlorination, and relate the efficiency of oxidation to the mechanism of oxidation at different electrode types. Linear sweep voltammograms at a Pt anode at several concentrations, sweep rates, and pH were interpreted in terms of deposition of oligomers on the anode surface. Chronopotentiometry at Pt showed that the oxidation potentials of the chlorinated phenol congeners ranged from +0.6 to +1.3 V vs SHE in the pH range 2−12; four electrons are transferred for mono- and trichlorophenols and two for pentachlorophenol. Passivation increased in parallel with the uncompensated resistance of the solution and occurred only at potentials at which water is oxidized, suggesting that the formation of the oligomer film involves attack of hydroxyl radicals on electrochemically oxidized substrate. Seven chlorinated phenols were electrolyzed at PbO_2, SnO_2, and IrO_2 anodes. Relative reactivities of congeners were anode-dependent, due to different mechanisms of oxidation: direct electron-transfer oxidation at PbO_2 and hydroxyl radical attack at SnO_2 and IrO_2. At current densities < 0.1 mA cm^{-2}, current efficiencies $> 50\%$ could be achieved with 4-chlorophenol at all three anodes.

Introduction

Aqueous wastes containing chlorinated aromatic compounds are recalcitrant toward remediation and toxic toward the microorganisms in conventional biological treatment reactors. Electrochemical technologies offer the prospect of relatively simple equipment, environmental friendliness, and the possibility of high energy efficiency by comparison with thermal treatment, whose public image is negative (*1*). Electrolysis can be used as a “front-end” technology ahead of biological treatment, with the objective of detoxifying contaminant(s), rather than mineralizing them completely (*2*).

Although electrochemical treatment can involve either reduction or oxidation, the only report on electrochemical reduction of a chlorinated phenol involved sequential dechlorination of a 50 ppm solution of pentachlorophenol at a carbon fiber cathode (*3*), and the current efficiency was low. Direct anodic oxidation of chlorophenols (*4*−*6*) has been postulated to involve formation of a chlorophenol radical cation that readily deprotonates. Subsequent reactions include further oxidation to a benzoquinone derivative and ring-opening to acids such as muconic, maleic, and oxalic, and ultimately CO_2 (*7*−*9*). In these reactions the anode may behave either as a sink for electrons from the substrate or function electrocatalytically by generating reactive hydroxyl radicals at its surface. Regardless of the mechanism, it should have a high overvoltage for generating O_2 by electrolysis of water.

Although organic wastes in general can be oxidized at numerous electrode materials (*10*), phenols cause inactivation of the anode, reportedly through the deposition of oligomers (*9*−*11*) that form when phenoxy radical attack unreacted substrate. Oxide-based anodes appear to be less prone to fouling than metals. Phenol was oxidized faster at PtO_2 than Pt (*10*, *12*), graphite (*12*), or Ni (*12*) with less adsorption of products onto the electrode surface. Success has also been obtained with dimensionally stable anodes (DSA), which are prepared by thermal deposition of a thin (a few micrometers) layer of metal oxide(s) (e.g., SnO_2, IrO_2, RuO_2), on a base metal such as Ti, Zr, Ta, or Nb (*9*). Both disappearance of phenol and loss of total organic carbon (TOC) were more efficient at a Sb-doped SnO_2/Ti anode than at Pt (*7*).

This study was undertaken to increase our knowledge of the electrochemical oxidation of chlorinated phenols, the ultimate aim being evaluation of electrochemical oxidation as a treatment technology. The specific objectives were to explore the mechanism of anode fouling by chlorinated phenols, to compare structure vs reactivity for phenols differing in the extent of chlorination, and to relate the efficiency of oxidation to the mechanism of oxidation at different electrode types.

Experimental Methods

Voltammetry. Voltammetry and chronopotentiometry were performed in unstirred solutions with a platinum bulb (0.3 cm^2) as the working electrode. The counter electrode was a platinum sheet (3 cm^2); the reference electrode was external saturated Ag/AgCl, connected to the cell by a 0.1 M Na_2SO_4 salt bridge. The potentiostat was an EG&G Princeton Applied Research Model 273 operated by M270 software. All potentials are reported against a standard hydrogen electrode (SHE); voltammograms were performed in triplicate to ensure reproducibility. Solutions were in equilibrium with air at pH $\sim$ 6 unless noted otherwise; changes in pH were made by adding NaOH or H_2SO_4.

Bulk Oxidation. Substrates were phenol, 2-chlorophenol (2-MCP), 3-chlorophenol (3-MCP), 4-chlorophenol (4-MCP), 2,4-dichlorophenol (DCP), 2,4,5-trichlorophenol (TCP), and pentachlorophenol (PCP), as its sodium salt which, unlike PCP, is freely soluble in water. Chemicals were obtained from Aldrich (3-MCP, 4-MCP, PCP), Sigma (TCP), Acros (DCP), and Fisher Scientific (2-MCP, hydroquinone, benzoquinone). Galvanostatic electrolyses were carried out using a flow-through, sandwich type cell constructed from Plexiglas. The anode and cathode compartments (each 2.5 mL) were separated by a Nafion - 417 membrane. Anolyte and catholyte solutions were delivered from 60 mL glass reservoirs, using a peristaltic pump at 7 mL min^{-1}, with upward flow to facilitate removal of gas bubbles. LFL-Tygon was used at the pump; Teflon tubing was used for connections between the pump and the reservoirs. Anodes (10−30 cm^2) were constructed from PbO_2 or “class-1” DSA materials. The PbO_2 electrodes were either cut from a new automotive battery or

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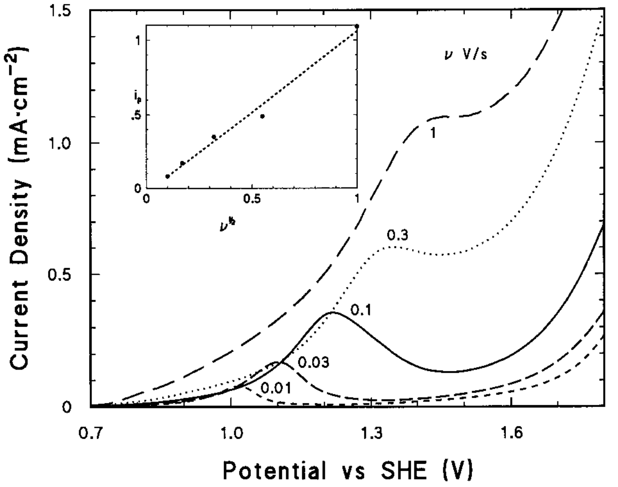

FIGURE 1. Linear sweep voltammograms (Pt anode, pH 6) for the oxidation of 1 mM 4-chlorophenol at scan rates 0.01−1 V/s.

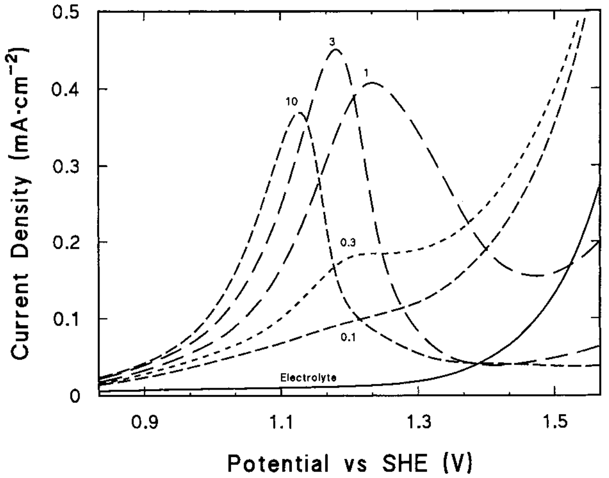

FIGURE 2. Linear sweep voltammograms for the oxidation of different concentrations (0.1−10 mM) of 4-chlorophenol at a Pt anode and pH 6.

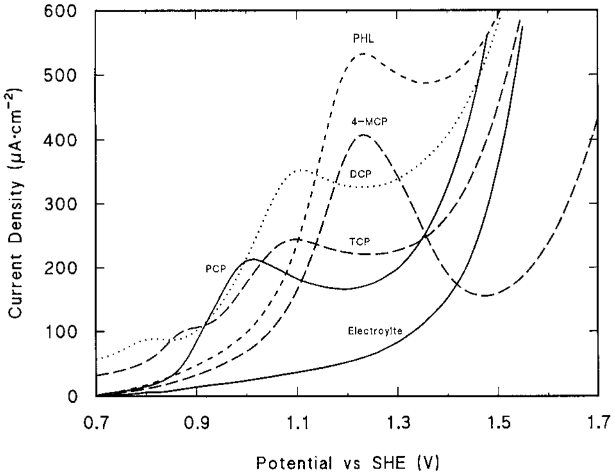

FIGURE 3. Linear sweep voltammograms for the oxidation of several chlorophenols (1 mM) at pH 6.

prepared in our laboratory by anodic oxidation of solid Pb in 30% H_2SO_4 at 10 mA cm^{-2} for 1 h. The DSA electrodes consisted of either IrO_2 or doped SnO_2 (the latter provided by ELTECH Systems Corporation, specification EC420). The IrO_2 anode (oxide coating ~1 mg/cm^2) was prepared by repeated immersion of Ti metal in H_2IrCl_6 solution and annealing at 500−550 °C. The counter electrode was either Pt or Ti (10 cm^2). The supporting electrolyte was normally 0.1 M Na_2SO_4 in Millipore Milli-Q water; experiments in which the solution was buffered employed 0.05 M disodium hydrogen phosphate, adjusted to pH 6.7 with phosphoric acid. The anode potential was measured vs external Ag/AgCl, which was connected to the anode compartment by Teflon tubing containing electrolyte solution. Electrolyses were carried out amperostatically, using a Pine RDE4 potentiostat.

HPLC. Aliquots (150 μL) of anolyte were removed at appropriate times and separated using a Rheodyne injector with a 20 μL sample loop, Waters 501 pump, 25 cm × 4.6 mm reverse-phase C18 stainless steel column, and Waters 440 UV absorbance detector (254 nm) at flow rates of 0.5−1.0 mL min^{-1}. Data were downloaded into a microcomputer and analyzed using Peaksimple II software, detection limits < 10^{-5} M. Mobile phases employed HPLC grade solvents (Fisher): 60:40 (v/v) MeOH:H_2O for phenol and MCPs, 80:20 (v/v) MeOH:H_2O for DCP, TCP, 90:10 (v/v) CH_3CN:H_2O for PCP.

Results and Discussion

Linear Sweep Voltammetry. Linear sweep voltammograms for 1 mM 4-MCP at a Pt anode showed an oxidation peak that increased in amplitude and moved to more positive potentials with increased sweep rate (ν), typical of an irreversible reaction (Figure 1). The dependence of the peak current i_p on $\nu^{1/2}$, as predicted by the Randles-Ševčik equation (*15*), shows that oxidation is diffusion controlled at this concentration (inset).

At fixed scan rate (0.1 V/s), the peak current for 4-MCP was not proportional to concentration above 1 mM and shifted to less positive potentials as concentration increased. Simultaneously, the oxidation of water shifted to more positive potentials (Figure 2). This behavior is consistent with previous observations of anode fouling during bulk electrolyses of phenols (*9*−*11*). We construe Figure 2 in terms of anodic inactivation once a certain amount of substrate has been oxidized; a faster sweep rate (Figure 1) or a lower concentration (Figure 2) allow more positive potentials to be reached before fouling occurs. The current drops due to deposition of oxidized material on the anode, which increases its resistance (discussed later), whereupon a higher potential must be applied to oxidize water.

The electrode could not be reactivated by washing with organic solvents; it had to be heated in a flame, consistent with inactivation being caused by oligomer deposition. This limited voltammetric studies to Pt, because the metal oxide coatings of DSAs are incompatible with regeneration in a flame.

Peak currents in the linear sweep voltammograms of more chlorinated phenols (1 mM, scan rate 0.1 V/s) shifted to less positive potentials (Figure 3), opposite to what might intuitively be expected, because highly chlorinated compounds are generally more resistant to oxidation. All begin to oxidize at anode potentials near +0.9V, but the current falls earlier in the voltammetric scan for the more highly chlorinated phenol congeners, which form more insoluble deposits. Figure 4 (linear sweep voltammograms for 4-MCP over the pH range 2−12) shows that the onset of oxidation shifted to lower potentials at higher pH, especially near the pK_a (9.2 for 4-MCP). This indicates that the phenolate is oxidized more easily than the neutral phenol (*11*).

Chronopotentiometry. Oxidation potentials of 4-MCP, TCP, and PCP were obtained by chronopotentiometry. Figure 5, for example, shows the oxidation of 4-MCP at pH 2; the oxidation potential of the substrate is obtained from the flat part of the curve at the lowest polarization currents after the anode has charged. The data for MCP, TCP, and PCP at

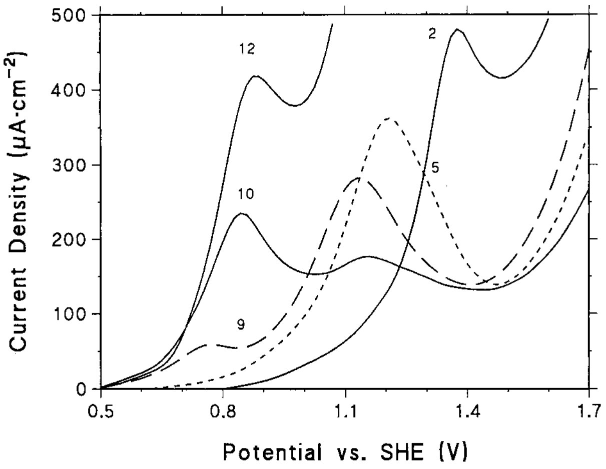

FIGURE 4. Linear sweep voltammograms for the oxidation of 1 mM 4-chlorophenol at different pH.

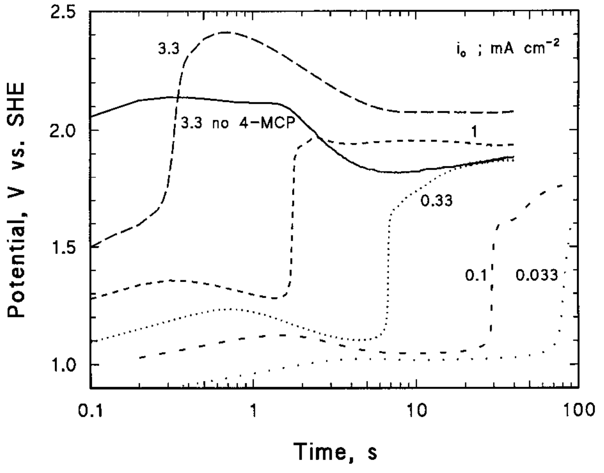

FIGURE 5. Chronopotentiometric oxidation of 10 mM chlorophenol on a platinum bulb at pH 2 with polarization currents i_0 ranging from 0.033 to 3.3 mA cm^{-2}.

TABLE 1. Oxidation Potentials of Chlorinated Phenols at Specified pH Values[a]

conditions	E_{ox} 4-MCP	E_{ox} TCP	E_{ox} PCP
acidic form	+1.1 V (pH 2)	+1.1 V (pH 7)	not determined
basic form	+0.6 V (pH 12)	+0.8 V (pH 9)	+0.9 V (pH 9)

[a] pK_a values are 9.4 for 4-MCP, 7.1 for TCP, and 4.9 for PCP.

different pH (Table 1) show that chlorophenols are oxidized at potentials close to +1 V; the phenolates are oxidized at less positive potentials than the corresponding phenols, but the extent of chlorination affects the oxidation potential only slightly. We associate the "humps" in the chronopotentiometric curves at higher current (Figure 5) with the onset of poisoning.

The transition time τ is the time required to decrease the concentration of the chlorinated phenol at the electrode surface to zero at constant applied current (i_0); the potential increases sharply when the phenol is exhausted and water is oxidized. The theoretical relationship between τ and i_0 is given by the Sand equation (eq 1) (*13*).

$$\tau^{1/2} = \frac{\pi^{1/2} n F D^{1/2} c^{o}}{2 i_{o}} \tag{1}$$

The number of electrons (n) involved in the oxidation of the chlorophenols is obtained most reliably when poisoning of the anode is minimized, namely low chlorophenol concentration and high applied current, the conditions that minimize τ. Plots of ($i_0\tau^{1/2}$) vs i_0^{-1} should lie parallel to the abscissa if the Sand equation is followed (*14*), but in our experiments the plots were curved due to anode inactivation. To obtain n, we plotted ($2i_0\tau^{1/2}/\pi^{1/2}D^{1/2}Fc^{o}$) vs i_0^{-1} by evaluating constants and assuming $D = 5 \times 10^{-6}$ cm^2 s^{-1} (*15*). Figure 6 shows these data for 4-MCP at various concentrations and pH. The Sand equation was followed precisely for c_0 = 1 mM at pH 12, giving n = 4, i.e., a four-electron oxidation under these conditions. At lower pH and/or higher concentrations n = 4 was the limiting behavior as $i_0^{-1} \rightarrow$ zero, with deviation from the Sand equation increasing with i_0^{-1}. Similar experiments indicated a four-electron process for TCP but only a two-electron process for PCP. Macdougall (*11*) proposed that the formation of the polymer film from PCP at a graphite felt anode is a one-electron process and that the resistive layer could be removed by reversing the polarity. This was not observed in our experiments at Pt.

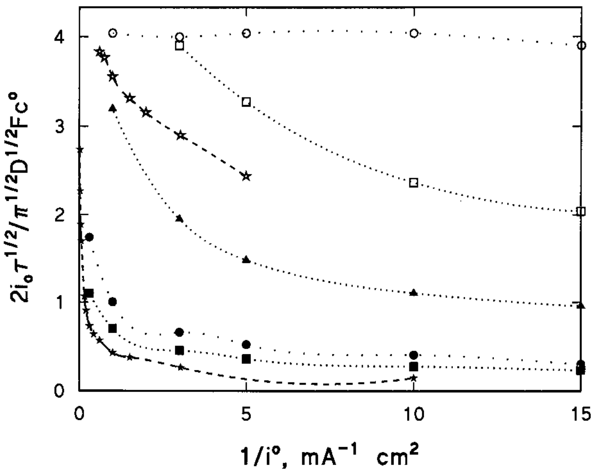

FIGURE 6. Plot of the apparent number of electrons for oxidation of 4-MCP as a function of concentration and pH (○ = 1 mM, pH 12; □ = 1 mM, pH 2; ☆ = 1 mM, pH 7; ▲ 2 mM, pH 2; ● = 10 mM, pH 12; ■ = 10 mM, pH 2; ★ = 10mM, pH 7).

The uncompensated resistance (R_u) of the solution is the resistance between the working electrode and the capillary tip of the reference electrode. R_u can be expected to increase when the passivating film develops on the anode. R_u was measured as the ratio uncompensated voltage/i_0, using the current interrupt technique (Model 273 Potentiostat, instruction manual). For 10 mM 4-MCP at pH 2, R_u increased from 15 to ~70 Ω after the transition time (Figure 7: the high concentration was chosen to give a large deviation from the Sand equation, cf. Figure 6), providing excellent evidence that passivation is caused by oligomer deposition on the electrode after the original oxidation of the substrate. The limiting value of R_u decreases as i_0 increases, possibly due to further, destructive, oxidation of the oligomer, but we have no direct evidence for this. At high pH however, R_u and i_0 increased in parallel. The increase in R_u after the transition time was similar in magnitude for 4-MCP and TCP but was considerably larger for PCP.

Because we could determine the uncompensated voltage only within ±1 mV, R_u could be measured only when $i_0 >$ 0.1 mA cm^{-2}. Under these conditions, τ is small (Figure 5) and oxidation of water occurs concurrently with oxidation of the substrate, again consistent with polymer formation being a two-step process involving both direct oxidation of the phenol and attack on the oxidized product by e.g. hydroxyl radicals. One possibility might be oxidation of 4-MCP to a quinone which traps hydroxyl radicals, leading eventually to

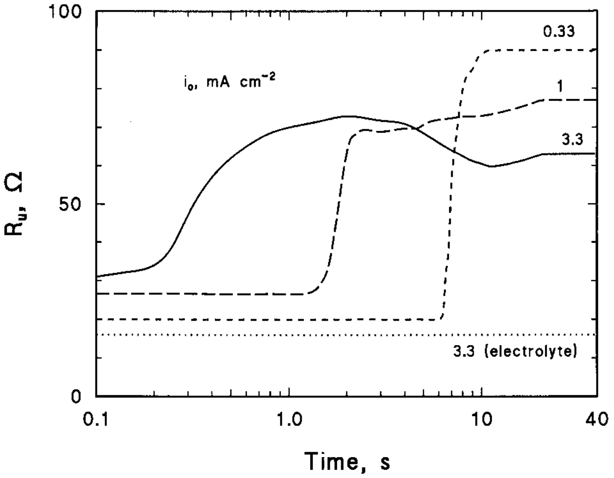

FIGURE 7. Uncompensated resistance as a function of time and polarization current during oxidation of 10 mM 4-chlorophenol on a platinum bulb at pH 2.

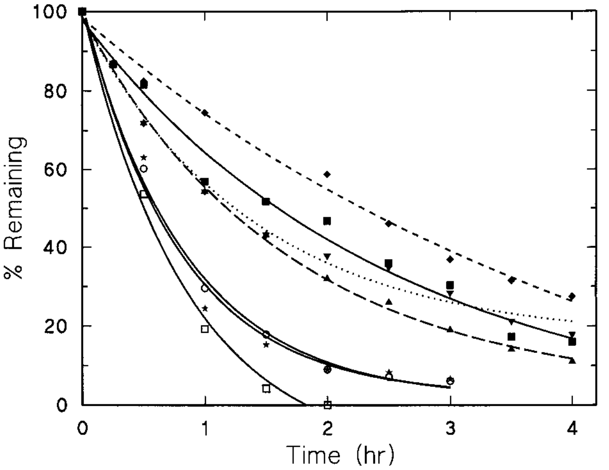

FIGURE 8. Oxidation of chlorophenols (◆ 3-MCP; ■ 4-MCP; ▼ PHL; ▲ 2-MCP; ★ DCP; ○ TCP; □ PCP) at a SnO_2 anode as a function of time (i = 85 mA).

oligomer formation; this is consistent with Gattrell's (*10*) conclusion that phenol (unsubstituted) undergoes diffusion-controlled oxidation to benzoquinone, with subsequent ring opening being adsorption controlled. Accordingly, 4-MCP oxidized less easily than hydroquinone ($E°_{ox} = 0.70$ V) (*15*) but much more easily than benzoquinone, which gave no oxidation current even in acetonitrile solution at +3 V vs SHE.

Electrolyses. We oxidized seven phenols (unsubstituted to pentachloro-) at PbO_2, IrO_2, and SnO_2 anodes at $i = 85$ mA (corresponding to 5−6.5 mA cm^{-2}). From literature data and our own voltammetric studies, we realized that electrode fouling would be a significant practical issue. With 10 mM solutions, anodes typically lost all their catalytic activity after only a few hours of use and could not be reactivated. This problem was minimized when the chlorophenol concentration was lowered to 1.0 mM, and the activity of a given anode was monitored by using the rate of electrolysis of 4-MCP as a benchmark. The data for SnO_2, which ultimately proved to be the most satisfactory, are illustrated in Figure 8; Table 2 summarizes the results at all three anodes on the assumption of pseudo-first-order kinetics; entries with a poor r^2 generally exhibited slow reaction rates that were close to zero-order in substrate.

TABLE 2. Pseudo-First-Order Rate Constants for Electrolysis of Chlorinated Phenols at Different Anodes at 5 mA cm^{-2}

	IrO_2		PbO_2		SnO_2	
substratae	k, h^{-1}	r^2	k, h^{-1}	r^2	k, h^{-1}	r^2
phenol	0.971	0.942	4.16	0.996	0.717	0.995
2-chlorophenol	0.278	0.974	5.45	0.997	0.484	0.993
3-chlorophenol	2.08	0.848	0.113	0.991	0.209	0.993
4-chlorophenol	0.785	0.963	0.466	0.971	0.396	0.985
2,4-dichlorophenol	0.265	0.969	0.413	0.971	1.16	0.986
2,4,5-trichlorophenol	0.828	0.978	0.134	0.968	1.17	0.996
pentachlorophenol	3.86	0.991	0.980	0.987	1.18	0.996

The pH of the analyte decreased from 6 to 2 during the electrolyses, due to competing oxidation of water ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). Electrolyses with pentachlorophenol were carried out in buffered solution (pH 6.7) because this substrate is insoluble at low pH; in other cases, the pH of the solution in the reservoir was readjusted to ~7 with NaOH after removing each aliquot for HPLC analysis.

At a PbO_2 anode (20 cm^2; 5 mA cm^{-2}) prepared from a commercial lead/acid battery, phenol reacted substantially faster than its chlorinated analogues, but no obvious structure−reactivity trend was evident. The order of reactivity was phenol > PCP > 2- and 4-MCP > 3-MCP, 2,4-DCP, and 2,4,5-TCP; the rate of disappearance of 4-MCP was 2.7 × faster at a PbO_2 anode prepared in our laboratory than at the commercial material, using the same (nominal) current density.

At the DSA materials, the ease of oxidation increased with increasing chlorination of the substrate. Electrolysis at the SnO_2 anode (13 cm^2; 6.5 mA cm^{-2}) was more efficient than at IrO_2 (20 cm^2; 5 mA cm^{-2}) for most substrates, and the reactions followed first-order kinetics much more closely; however, the IrO_2 anode was more resistant to poisoning.

The performance of an anode material could not be evaluated by testing a single substance; the reactivity of phenol was in the order $PbO_2 > SnO_2 > IrO_2$; for monochlorophenols it was $PbO_2 \sim SnO_2 > IrO_2$, while the more heavily chlorinated phenols followed the order $SnO_2 > IrO_2 > PbO_2$. Comparisons in the literature are limited to phenol as the substrate; phenol was oxidized 8× faster at SnO_2 than at PbO_2 at a current density of 5 mA cm^{-2} (*16*) and at similar rates at Pt and SnO_2 (20 mA cm^{-2}) (*8*). Such observations are difficult to evaluate because the efficiency of oxidation depends on the method of preparing the electrodes and because we have no information about whether the results were affected by electrode fouling.

The variation in substrate reactivities with the anode material suggests changes in the reaction mechanism. Physical organic studies on chlorinated aromatics show that the chlorine substituent is very weakly deactivating in processes that lead to a build-up of positive charge on the aromatic ring ($\sigma^+ = 0.035$ (*17*)), consistent with the near independence of oxidation potentials among the chlorinated phenols in Table 1. Nevertheless, the rate of oxidation at the PbO_2 anodes decreased with increasing chlorination of the substrate (Table 2). Direct electron transfer from the substrate to the anode is unlikely to be relevant to electrolyses at DSAs, which function by generating electrophilic hydroxyl radicals at their surfaces (*2, 18*). Two mechanisms for oxidation at DSAs have been advanced, both of which postulate electrochemical oxidation of the surface metal oxide to a higher oxidation state [MO_{x+1}]. The first (M1) is that [MO_{x+1}] reacts with water to form hydroxyl radicals which are adsorbed, at least initially, at the surface of the electrode [$MO_x \cdot (OH^*_{ads})$] before oxidizing the target substrate, competitively with disproportionation to O_2. The second (M2) is that [MO_{x+1}] oxidizes the substrate directly, returning the metal oxide to the lower oxidation state (*2*). Comninellis (*19*) has indicated that DSAs based on SnO_2 are more likely to undergo M1, while IrO_2-based DSAs are more likely to undergo M2.

TABLE 3. Current Efficiencies[a] for Oxidation of 4-Chlorophenol at Different Anodes and Current Densities

anode	85mA [~5mA cm^{-2}]	10mA [~0.6mA cm^{-2}]	1mA [~0.06mA cm^{-2}]
IrO_2	1.8% [1.9V]	19% [1.5V]	54% [1.4V]
PbO_2	2.1% [1.9V]	21% [1.5V]	77% [1.3V]
SnO_2	2.8% [2.4V]	29% [1.9V]	61% [1.5V]

[a] Current efficiency defined as the ratio of charge required to oxidize 4-chlorophenol (assuming a four-electron oxidation) to total charge passed through the cell. Values in brackets are the measured potentials at the anode under the specified conditions.

We found that highly chlorinated phenols were the most reactive at DSAs. Although this reactivity order is incompatible with the rate-determining step being the attack of OH (which is highly electrophilic) on the phenolic substrate, it does not exclude a hydroxyl radical mediated reaction: the reactivity profile could also be consistent with increasingly easy expulsion of $Cl^\bullet$ from the cyclohexadienyl intermediate formed when $OH^\cdot$ adds to the chlorophenol.

Current Efficiency. The current efficiency at each anode was calculated at different current densities using 1 mM 4-MCP as the substrate and assuming the four-electron oxidation determined by chronopotentiometry, corresponding to transformation of the phenol to a quinone (Table 3). Experimentally, HPLC and GC/MS supported the formation of benzoquinone as a product from phenol and monochlorophenols. Current efficiencies were calculated for the first 1 h of oxidation at 5 and 0.6 mA cm^{-2} and the first 3 h of oxidation at 0.06 mA cm^{-2}, when the loss of substrate was approximately linear with time. The values in brackets show the approximate measured potential of the anode during electrolysis. Calculations were corrected for volume changes due to withdrawal of aliquots for analysis.

The current efficiency was consistently higher at low current densities, because the positive polarization of the anode inevitably increases in parallel with current density, and so more of the charges passed will cause the unproductive electrolysis of water. All anodes exhibited current efficiencies > 50% at low current density, a promising result in terms of our ultimate goal of developing an electrochemical remediation technology for chlorophenols. The progressive loss of TOC from the solution during electrolysis suggests that the current efficiency is actually higher than this; for example, 20−45% TOC was lost during the first 2 h of electrolysis of 4-MCP at a SnO_2 anode, during which time 60% of the 4-MCP reacted. Thus, some fraction of the electrolysis always proceeds to CO_2, perhaps by hydroxyl radical attack on the quinones (*20*, *21*). DeSucre (*1*) had previously observed a loss of TOC during the electrolysis of phenol at a PbO_2 anode.

The lack of electrode materials that combine high current efficiency with freedom from fouling continues to be an obstacle to developing technology for anodic remediation of chlorinated phenols. Two opposing factors must be considered. At directly oxidizing anodes such as Pt and PbO_2, passivation would be inhibited by minimizing hydroxyl radical production. At DSAs, oxidation is believed to involve hydroxyl radical chemistry, suggesting that less polymer is formed when hydroxyl radicals attack unreacted chlorophenol than preoxidized material. In that case, the goal for optimum design of a DSA would be to maximize hydroxyl radical chemistry at the expense of direct oxidation. However, hydroxyl radical formation cannot be increased indefinitely without compromising current efficiency due to self-quenching of the radicals.

Acknowledgments

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