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Electroreduction of Hexachlorobenzene in Micellar Aqueous Solutions of Triton-SP 175

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The electrochemical reduction of hexachlorobenzene (HCB) has been studied in micellar aqueous solutions using Triton-SP 175 which, unlike conventional surfactants, is acid-labile. At pH < 3, the hydrophobic residue cleaves from the hydrophilic chain, leaving a solution without surface-active properties and allowing recovery of the electrolysis products from the solution. A micellar solution containing 0.1% v/v Triton-SP 175 and 1% v/v heptane as cosolvent was indefinitely stable in the presence of 0.05 M sodium sulfate as an environmentally friendly supporting electrolyte. Electrolytic dehalogenation to less chlorinated benzenes was studied at a wide variety of cathodes; in all cases a quantitative material balance of phenyl residues was achieved. Lead was the preferred cathode in terms of both the degree of dechlorination achieved and the current efficiency.

Introduction

Chlorinated aromatic compounds such as polychlorinated benzenes and polychlorinated biphenyls (PCBs) owe their environmental persistence to their low chemical and biological reactivity. Aqueous waste streams or leachates containing these compounds are both recalcitrant to conventional biological treatment and toxic to the microorganisms in the biological reactor. Electrochemical technologies show promise for treating these materials due to the relative simplicity of the equipment, environmental friendliness, and the possibility of high-energy efficiency as compared with thermal and photochemical processes (1–3).

The low-chemical reactivity of chlorinated aromatic compounds is reflected in very negative potentials for reduction and very positive potentials for oxidation. The potential for dehalogenation of chlorinated benzenes in aprotic solvents such as dimethylformamide, dimethyl sulfoxide, and acetonitrile becomes increasingly negative with successive removal of chlorine substituents (4). This observation suggests that practical technologies should limit electrolysis to partial dechlorination to afford a product that is less toxic and more amenable to biological treatment; this approach contrasts with that of Petersen et al. (5), who exhaustively electrolyzed chlorinated benzenes to maximize dechlorination.

Electrolytic reduction of polychlorobenzenes requires two one-electron transfers for each chlorine atom removed as

chloride ion (6, 7, 8). An intermediate radical anion ($\text{ArCl}^{\cdot-}$) formed in the first step expels Cl^- to give an aryl radical (Ar^{\cdot}). This rapidly accepts a second electron to yield the reduced species Ar^- , protonation of which completes the reduction to ArH .

Our goal in this research was to evaluate electrolytic methods for the removal of hexachlorobenzene (HCB, a pesticide intermediate) from aqueous waste streams. We previously showed that HCB could be sequentially dechlorinated to penta-, tetra-, tri-, and dichlorobenzenes in methanol solution, using a mercury pool cathode and tetraethylammonium chloride as the supporting electrolyte (8). A quantitative material balance was obtained, and a current efficiency of 60% was achieved in the most favorable case. We now report that we have overcome three of the remaining obstacles to developing a practical electroreduction technology. First, solutions of practical interest are aqueous, but HCB is poorly ($\sim 10^{-8}$ M) soluble in water. Second, mercury is inappropriate for use as a cathode, as shown by experience in the chlor-alkali industry (9). Third, tetraethylammonium chloride is too costly to use as a supporting electrolyte and would give Cl_2 in the anodic reaction.

Experimental Methods

Chemicals. Chlorinated benzenes were obtained from Aldrich, and their purities were checked by HPLC and GC–MS. Tetraethylammonium chloride (TEACl) and sodium sulfate were used as supporting electrolytes (0.05 M TEACl and 0.05 M Na_2SO_4). HPLC-grade solvents were obtained from Fisher. Triton-SP 175 was supplied by Union Carbide. Microemulsions containing 0.1% Triton-SP 175 and 1% heptane as cosolvent were prepared using Millipore water and were sonicated for at least 4 h.

Chromatography. HPLC analyses were performed on a Waters system containing a model 486 tunable absorbance detector, U6K injector, and 600 E system controller. The system was computer controlled using Millennium 2010 chromatographic software. Absorbances were monitored at $\lambda = 227$ nm. Analytical separations were performed on a Waters μ Bondapak C_{18} , 3.9×300 mm column, which was eluted with 90/10 methanol/water at flow rate of 2 mL/min. Solvents used were HPLC grade and were filtered under vacuum before use through 0.45 μm Nylon 66 membranes to remove microparticulates.

Reference Electrodes. An internal Ag/AgCl reference electrode was used when TEACl was the supporting electrolyte. For experiments with Na_2SO_4 as the supporting electrolyte, an external reference electrode was used (saturated Ag/AgCl or SCE). All potential data were corrected to the standard hydrogen electrode (SHE) as a common point of reference.

Working Electrodes. The anode was composed of Ti/IrO₂ and had an area of 27 cm². The mercury pool cathode had an area of 6 cm² (1.7 mL) and almost filled the cathodic compartment of the cell. The glassy carbon (GC) electrode was prepared from a plate that was sealed in epoxy resin and polished using 0.3 μm alumina. Other metallic cathodes were prepared from the relevant metal wire (2 m \times 0.5 mm). For the experiments involving lead cathodes with large surface area, the most successful material was obtained by cathodic deposition of ~ 4 g of lead on a lead wire support, using 0.015 M $\text{Pb}(\text{NO}_3)_2$ and 0.15 M sodium citrate at pH 6.5. Lead was deposited in the form of long bright needles.

Exhaustive Electrolyses. These were performed using a sandwich-type flow-through cell that was previously de-

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scribed (8). The cells were constructed from high-density polypropylene or Plexiglas; they were mounted horizontally for use with the Hg pool cathode and vertically for use with solid cathodes for a better removal of hydrogen gas that forms during electrolysis. The anode and cathode compartments of the cell had volumes of 3.3 mL and were separated by a Nafion 417 membrane; the distance between the electrodes was ~ 0.1 cm. The cell was controlled by a EG&G model 273 potentiostat/galvanostat.

Continuous Flow Experiments. Experiments were carried out under amperostatic polarization, with the various cathode materials compared at the same current density. A 30-mL sample of 3×10^{-5} M HCB in Triton-SP 175 microemulsion/0.05 M Na_2SO_4 was continuously recirculated through the cathodic compartment by a peristaltic pump at flow rate of 2.5 mL/min, and 25 mL of electrolyte (microemulsion/0.05 M Na_2SO_4) was pumped through the anodic compartment. Before applying any current, the solutions were recirculated for 1 h, and samples were collected during this time to ensure that no degradation of the starting material occurs under open circuit conditions. The catholyte was deaerated by purging with argon for 30 min before electrolysis, and a slow Ar flow was maintained throughout the experiment. In order not to break the microemulsion by evaporating the heptane, one drop of heptane was added periodically to the catholyte, and the contents of the flask were mixed for a few minutes. Later, it was discovered that the electrolyses could be carried out without loss of efficiency even in the presence of air. The experiments were analyzed by HPLC, after removing 1.0-mL aliquots of microemulsion from the catholyte, breaking the emulsion with dilute hydrochloric or sulfuric acid, and partitioning the products into heptane. Lower chlorinated benzenes were formed, and a quantitative material balance ($>98\%$) was achieved. The yields were corrected for the change in volume due to removal of aliquots during electrolysis.

Single Flow Experiments. A microemulsion containing 3×10^{-5} M HCB/0.05 M Na_2SO_4 was pumped from a 0.5-L flask through the cathodic compartment at 0.4 mL/min, and the output from the cathode was directed to waste. Approximately 25 mL of electrolyte (microemulsion/0.05 M Na_2SO_4) was continuously circulated through the anodic compartment. The catholyte was deaerated by purging with argon for 30 min before electrolysis. Electrolysis was carried out under amperostatic polarization for 30 min before any samples were collected for analysis to achieve a steady state. The analytical procedure was similar to that used in continuous flow experiments. Measured potentials were corrected for IR drop by the current interrupt method.

Linear Sweep Voltammetry. These experiments were performed using 3×10^{-5} M HCB in microemulsion/0.05 M Na_2SO_4 without prior deoxygenation of the solutions. Several different cathode materials were used, each with an area of 0.1 cm^2 . A scan rate of 10 mV/s was used.

Results and Discussion

Solubility. The solubility of HCB in water is very low ($\sim 10^{-8}$ M), but in methanol, concentrations of up to 10^{-3} M can be attained (8). We attempted to increase the solubility of HCB by the use of methanol/water mixtures, reasoning that methanol is inexpensive and is also nontoxic toward microorganisms in subsequent biological treatment of partly dechlorinated HCB. Differential pulse voltammograms (DPV) were recorded on a sessile drop Hg electrode, starting with 0.1 mM HCB/0.05 M TEACl in methanol and gradually adding water/0.05 M TEACl. DPV were recorded after each such addition (Figure 1). The diminution of the peak height was greater than can be explained simply because of diluting the solution with water/TEACl (compare the peak heights at 95% and 100% methanol in Figure 1). Precipitation of HCB began

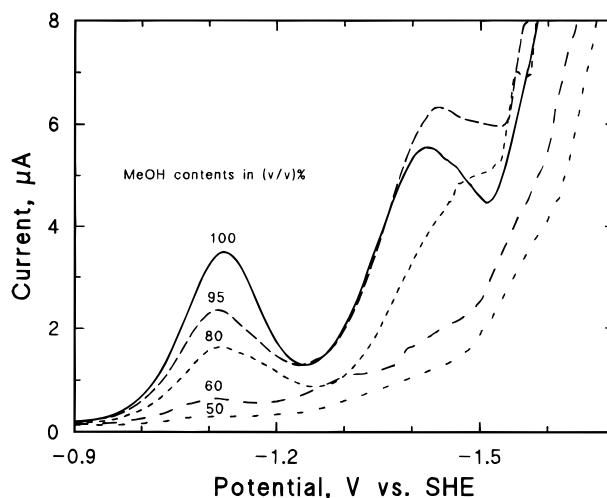


FIGURE 1. Differential pulse voltammograms of 0.1 mM HCB in MeOH/water mixture using a sessile drop Hg electrode.

when the ratio of methanol/water was 70/30 (v/v), and at a 50/50 methanol/water ratio, the recorded DPV closely resembled that of the electrolyte alone. These experiments made clear that it was impractical to raise the aqueous concentration of HCB by adding small amounts of methanol as a cosolvent.

Surfactant media have previously been used to increase the solubility of hydrophobic chloro compounds in water (10–13). Surfactants with a single hydrophobic chain, such as cetyltrimethylammonium bromide, afford conventional microemulsions. Those with two hydrophobic chains, such as didodecyl dimethylammonium bromide, give lamellar solutions in water or salt solutions. In homogeneous mixtures of oil and water, didodecyl dimethylammonium bromide gives interweaved strands of continuous aqueous and organic phases, known as bicontinuous microemulsions. The organic phase not only increases the solubility of the hydrophobic chloro compound but also brings the substrate into close proximity with the cathode. A difficult problem has been to find a method to break the microemulsion and to quantitatively recover the electrolysis products from this medium; recently, it has been found that the reaction products can be separated by passing the product mixture twice through silica gel columns and evaporating the solvent (14).

The recent introduction of the Triton-SP series of surfactants by Union Carbide offered a prospective novel solution to the problem of breaking the emulsion. These nonionic surfactants consist of a proprietary hydrophobe attached to a polyethoxylate hydrophilic chain. The significant advance is that the hydrophobe can be cleaved from the polyethoxylate chain by brief treatment with dilute acid ($\text{pH} < 3$), upon which the cleaved Triton-SP 175 loses its surfactant properties irreversibly and becomes compatible with subsequent biological treatment (15).

Concentrations of HCB up to at least $50 \mu\text{M}$ were attainable in 0.1% Triton-SP 175 with cosolvent 1% heptane: the solutions were milky white and stable toward breaking the emulsion for (at least) weeks. Our objective was to employ aqueous media with the minimum of additives. HCB could not be solubilized in Triton-SP 175 alone, even at 1% surfactant, and a stable emulsion was not formed below 0.05% surfactant. The use of 0.1% surfactant and 1% cosolvent offered a successful compromise. HCB was successfully reduced in 0.1% Triton-SP 175 at the mercury pool cathode in a recirculating flow-through cell under amperostatic conditions that closely duplicated our previous experiments in methanol (8) (Figure 2A). Penta-, tetra-, and trichlorobenzenes were formed, as in methanol, and a quantitative material balance ($>98\%$) was achieved.

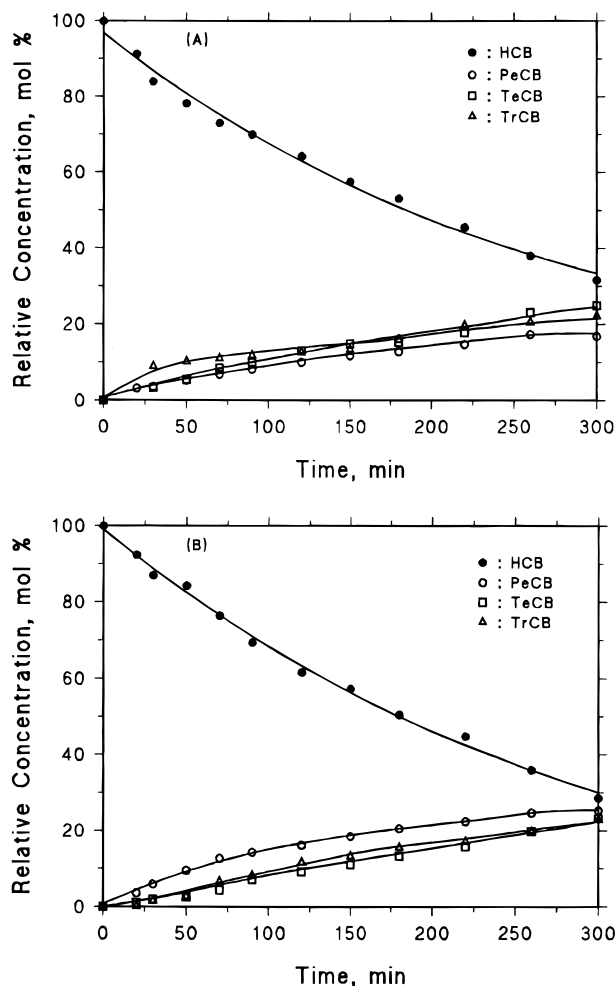


FIGURE 2. Electrolysis of 3×10^{-5} M HCB in microemulsion using continuous flow, $F = 2.5$ mL/min, current density = 2.5 mA/cm², Hg pool: (A) 0.05 M TEACl; (B) 0.05 M Na₂SO₄.

Supporting Electrolyte. The experiment reported in Figure 2A employed TEACl as the supporting electrolyte, but this has already been noted as unsuitable for practical technology. We considered sodium sulfate to be an ideal supporting electrolyte for this application because sodium ions and sulfate ions are neither electroactive nor pose an environmental threat (no limits are placed on their concentrations in aqueous discharges).

The Triton-SP 175 microemulsion (Triton-SP 175:heptane:water = 0.1:1:98.9, v/v) was stable in the presence of 0.05 M Na₂SO₄. No significant reduction or oxidation current was observed by DPV in the potential range -2.0 to 1.4 V vs SHE, showing that this medium had suitable electrochemical properties for the purpose of reducing HCB (it could presumably also be useful for electrooxidations). Electrochemical reduction of HCB with Na₂SO₄ as supporting electrolyte gave the same dechlorination products and occurred with similar current efficiency as with tetraethylammonium chloride (Figure 2B). In our previous work in methanol, the efficiency of electrolysis was lower when NaCl replaced TEACl as the supporting electrolyte (8). The latter effect was ascribed to preferential adsorption of TEA⁺ ions at the surface of the cathode, thereby altering the electrical double layer so as to increase the useful potential range of the electrode (16). We speculate that in the microemulsion the surfactant itself is the chief adsorbent to the cathode surface. All subsequent experiments were carried out using 0.05 M Na₂SO₄ as the supporting electrolyte.

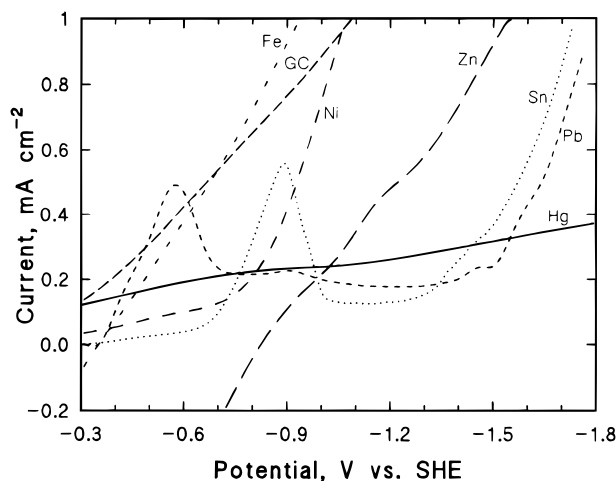


FIGURE 3. Linear sweep voltammograms of microemulsion/0.05 M Na₂SO₄ using various cathode materials.

Choice of Cathode. Because mercury is undesirable as an electrode for industrial processes, we investigated a series of other metals as possible cathodes for comparison against Hg. The most important property sought was a high overvoltage for hydrogen evolution, otherwise the current efficiency is severely reduced.

Voltammetry. As implied by Figure 1, the detection of reduction currents of HCB in mostly aqueous solutions is not possible. We examined the electrochemical properties of several cathode materials in 0.1% Triton-SP 175 with cosolvent 1% heptane and supporting electrolyte 0.05 M Na₂SO₄ using linear sweep voltammetry. A complication in these experiments was that the solubility of oxygen in the microemulsion is higher than in methanol and is at least 2 orders of magnitude larger than that of HCB. Complete removal of oxygen by purging with argon would require such a long purging time that it would also remove the heptane used as a cosolvent in the microemulsion. Consequently, Figure 3 portrays the performance of the cathode materials rather than the behavior of HCB at these cathodes. To interpret Figure 3, we note that the potential required for the first three dechlorinations of HCB are about -1.1 , -1.3 , and -1.6 V vs SHE (8) and that the anodic current is presented as a negative current. The objective was to find cathode materials that would exhibit only residual current (no hydrogen evolution) when the cathode was strongly negatively polarized.

Experimentally, Hg showed the largest cathodic range before hydrogen evolution commenced, but Pb and Sn also exhibited only residual current beyond the potential required for the first reduction of HCB. This suggested that Pb and Sn might be promising cathode materials for practical electroreductions of HCB. At Pb and Sn cathodes, current peaks were recorded at potentials of -0.5 and -0.9 V vs SHE, respectively. These were attributed to the reduction of metal oxide films formed during more anodic polarization or at no polarization (open circuit). (During bulk electrolysis, these oxide films would be reduced as soon as the cathode became negatively polarized.)

Metals such as iron and stainless steel, which have low overvoltage for hydrogen evolution, had very restricted ranges of usable potential. We had expected glassy carbon (GC) to be a useful material based on its behavior in methanol, in which GC performed almost as well as a sessile drop Hg electrode (Figure 4). In practice, GC had little usable potential range in the surfactant medium, showing a large current of hydrogen ion reduction at modestly negative potentials. We suggest that this phenomenon may be caused by the presence

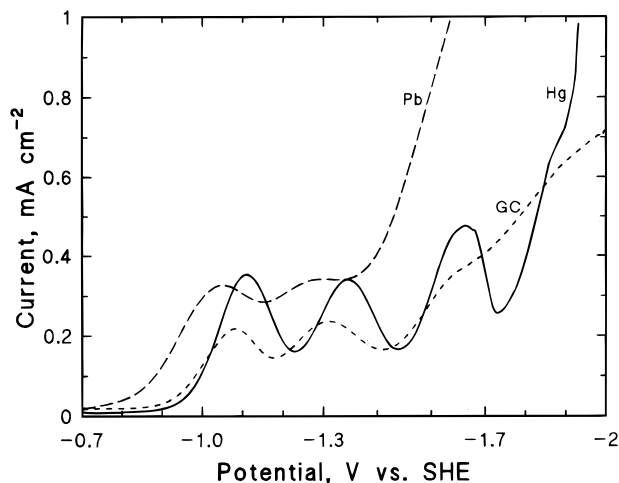


FIGURE 4. Differential pulse voltammograms of 1 mM HCB in methanol/0.05 M Na₂SO₄ at Hg, lead, and glassy carbon cathodes.

TABLE 1. Pseudo-First-Order Rate Constants of 30 μ M HCB in Microemulsion/0.05 M Na₂SO₄ (Continuous Flow Electrolysis, $F = 2.5$ mL/min)

electrode	k (s ⁻¹) $\times 10^6$		
	0.5 mA/cm ²	2.5 mA/cm ²	6.7 mA/cm ²
Hg		65	
Pb	53	55	72
Zn	48	43	63
Sn	48	37	48
Cd	42	43	
SS		37	48
Fe		32	42
Ni		28	32
GC			23

of surfactant on the electrode, causing the GC to lose its high overvoltage for hydrogen evolution.

Bulk Electrolysis. Bulk electrolyses were carried out in the flow-through cell with amperostatic polarization (see Table 1). Unlike our previously reported experiments in methanol (8), which were always deoxygenated, the electrolyses described in this paper could be carried out in the presence of air. In all cases a quantitative material balance, based on phenyl residues, was observed throughout the reactions. Most of the cathodes gave distributions of the electrolysis products similar to those recorded in Figure 2B, but dehalogenation was more efficient at the Pb cathode, at which trichlorobenzene was the major product (Figure 5A). The order of usefulness of the different cathodes generally followed that expected from the voltammetric experiments; lead, zinc, and tin (with mercury as a reference point) showed the largest overpotentials for hydrogen evolution in this medium (cf. Figure 3) and also had greater efficiencies for electrochemical degradation of HCB by the crude measure of the pseudo-first-order rate constant for its disappearance. (We note that toxic metals such as lead and cadmium may be employed as cathodes because there is no tendency for them to oxidize under these conditions to soluble M²⁺ species.) Glassy carbon was the least effective cathode material, again consistent with its voltammetric behavior.

These amperostatic experiments were carried out at current densities (0.5–6.7 mA cm⁻²) at which hydrogen evolution was copious. The overall current efficiency was very low (~1%), and the rate of reduction scarcely increased with increasing current density on account of competing evolution of hydrogen.

Single flow experiments with amperostatic polarization were carried out using lead, zinc, tin, and mercury cathodes

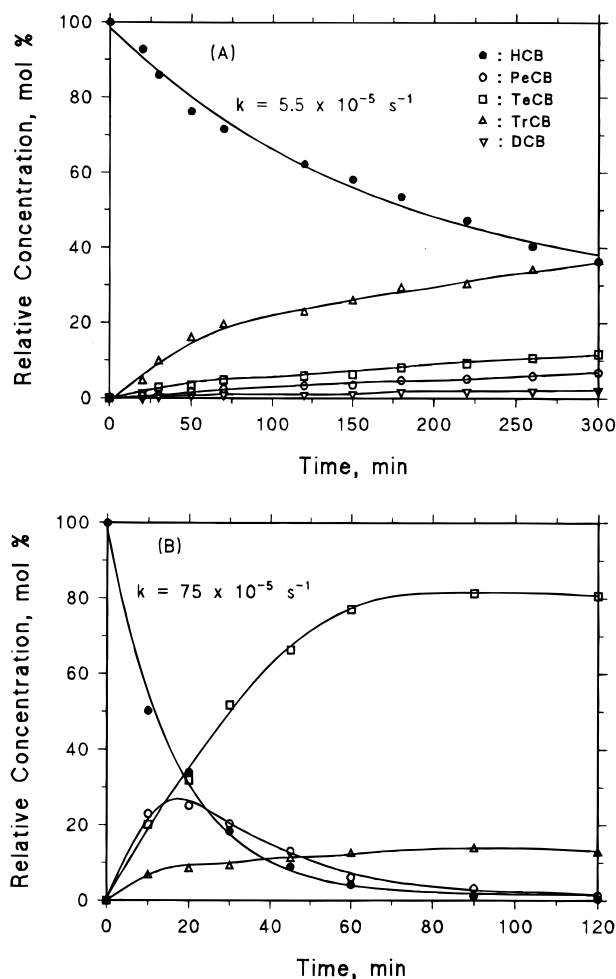


FIGURE 5. Electrolysis of 3×10^{-5} M HCB in microemulsion/0.05 M Na₂SO₄ (continuous flow, flow rate = 2.5 mL/min, current = 75 mA, Pb cathode): (A) wire with area 30 cm²; (B) ~4 g of Pb deposited on wire frame.

in the flow-through cell. In the case of Pb and Sn cathodes, an initial period of cathodic polarization was required for oxide film reduction before steady-state conditions were attained (compare Figure 3). Current efficiencies of electrolysis for these cathode materials are presented in Figure 6 as a function of applied current density. Table 2 records the experimental conditions for electroreduction corresponding to the best current efficiency as well as the product distributions observed for each cathode material. Lead was the best choice of cathode, in terms of both current efficiency (~5%) and extent of dechlorination. Its superior performance can be explained because the potential of -1.4 V vs SHE was achieved at very low current density, allowing the successive reduction of HCB to penta-, tetra-, and trichlorobenzenes. The optimal current efficiencies were achieved at the lowest current densities to minimize the extent of cathodic polarization and hence limit the production of hydrogen.

We showed, using different lengths of the Pb wire cathode at equal current densities, that the rate of reduction of HCB was directly proportional to the surface area of the electrode (data not reported). Knowing that the current efficiency is optimized at low current density, we concluded that practical dechlorination technology will require the cathode to have the largest possible surface area to achieve rapid reduction at the same time as passing a high current through the solution. Large area Pb cathodes were prepared in three ways: by depositing Pb from solution on to spongy iron, by using a piece of an automotive battery, and by depositing Pb

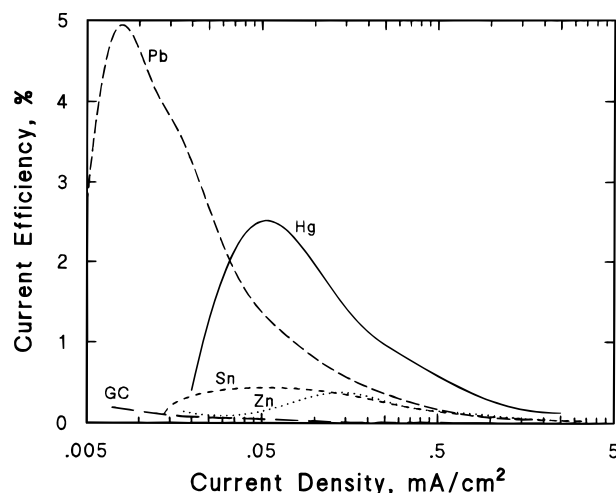


FIGURE 6. Current efficiency of HCB reduction in microemulsion/0.05 M Na₂SO₄ as a function of applied current density.

TABLE 2. Relative Current Efficiencies for Various Cathode Materials (Reference Point: Pb Cathode with Current Efficiency ~5%)

electrode	current density (mA/cm ²)	-E (V vs SHE)	HCB:PeCB:TeCB:TrCB (mol %)	relative current efficiency
Hg	0.06	1.47	87.0:5.7:5.2:2.1	53
Pb	0.01	1.40	85.3:0.6:4.8:9.3	100
Zn	0.15	1.25	81.0:2.8:7.8:8.4	10
Sn	0.05	1.58	91.8:2.1:3.7:2.4	10

from solution on to Pb wire. The last of these was the most successful, although we were unable to measure the surface area of the cathode so prepared. Figure 5 compares the rate of reduction of HCB in continuous flow electrolysis at 75 mA on plain Pb wire of area 30 cm² (panel A) with the corresponding experiment on Pb deposited from citrate solution (panel B). Reduction at the cathode of larger surface area occurred an order of magnitude faster. One difference noted was in product distribution: whereas the major product at plain Pb wire was trichlorobenzene, the reaction at lower current density proceeded only to the tetrachlorobenzene stage because the lower current density caused the cathode to be less negatively polarized.

The literature contains numerous reports of reductions (17–20) and oxidations (21, 22) that can be carried out by “mediated” electrolysis. The principle underlying mediated electrolysis is that the mediator is a substance having one-electron redox properties. In the case of mediated reduction, for example, the electrochemical stage of the reaction is the reduction of the mediator (Med) to Med^{•-} at the cathode, followed by chemical reduction of the substrate by Med^{•-} in the bulk solution, with concomitant regeneration of Med. Rusling and co-workers have described the mediated electroreduction of polychlorinated biphenyls at impressive current efficiency in surfactant media using zinc phthalocyanine (ZnPc) as the mediator (12); however, high concentrations of ZnPc were needed relative to the concentration of the reducible substrate. In the micellar systems employed in the present work, we were able to achieve only micromolar concentrations of ZnPc, and no increase in the rate of reduction was observed by comparison with solutions not containing ZnPc. We also explored the use of Cr(III) as a water-soluble mediator, in which case the active reductant

would be Cr(II). The use of CrCl₃ was unsuccessful due to reduction of Cr³⁺ directly to the metal, and so the EDTA complex of Cr(III) was used. The reduction of the Cr(III) complex was easily observed by the discharge of its purple color, and no deposition of metallic Cr occurred, but the rate of reduction of HCB was not enhanced as compared with experiments in which Cr(III)–EDTA was absent. Due to account of the lack of success in these preliminary experiments and toxicity concerns in the specific case of chromium salts as mediators, we abandoned further exploration of mediated electrolysis in our system.

Finally, we examined the effect of temperature on the rate of electrodehalogenation using the Pb cathode. No change in current efficiency was observed when the micellar solution was electrolyzed at 40 and 50 °C, compared with room temperature, at a current density of 2.5 mA/cm². Experiments at higher temperature were tried (60 and 70 °C), but under these conditions the microemulsion was not stable. From the practical perspective, these observations show that the efficiency of dechlorination is indifferent to temperature.

In conclusion, we have achieved the three goals stated in the introduction of this paper. We have shown that practically useful concentrations of HCB can be obtained in aqueous solution using 0.1% Triton-SP 175 and 1% heptane as surfactant and cosolvent. Electrolytic dehalogenation of HCB can be achieved at a variety of cathodes, of which lead was the best under our conditions. The electrolysis products can be recovered following mild acid hydrolysis of the surfactant. We contrast our approach with the studies of Rusling et al. (13, 19) on the electrochemical dechlorination of PCBs using lamellar solutions containing water, oil, and didodecyl ammonium bromide, the latter acting as both surfactant and supporting electrolyte. The latter system, with high concentrations of hydrocarbon phase, is well suited to the remediation of PCB–mineral oil mixtures. Since our objective was to remediate aqueous streams or leachates containing HCB, we sought conditions that required minimal additives to the water phase. Our use of a nonionic surfactant requires an added supporting electrolyte: in our case, the environmentally friendly Na₂SO₄. So far, the current efficiency we have achieved is an order of magnitude poorer than that attained in methanol (8); however, the latter experiments employed a much larger concentration of HCB and were carried out in the absence of O₂, reduction of which will undoubtedly worsen current efficiency. It is also clear that higher current efficiency is achievable by operating at the smallest practical current density, although with some reduction in the overall extent of dechlorination. To achieve both high efficiency and rapid rate of reaction in practical remediations, cathodes must be developed having the maximum possible surface area.

Acknowledgments

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