

Electrochemical Hydrodehalogenation of Chlorinated Phenols in Aqueous Solutions

I. Material Aspects

H. Cheng,^a K. Scott,^{a,*,z} and P. A. Christensen^{b,*}

^aDepartment of Chemical and Process Engineering and ^bDepartment of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne, Northumberland NEI 7RU, United Kingdom

Pentachlorophenol (PCP) and 2,4-dichlorophenol (DCP) have been hydrodehalogenated by electrochemical reduction in aqueous solutions at ambient and elevated temperatures. Galvanostatic and/or potentiostatic hydrodehalogenation (HDH) was carried out in conventional H-cells or solid polymer electrolyte cells operated in batch or/and batch-recycle modes. The processes were monitored by both chloride ion analysis and high performance liquid chromotography product analysis. The effect of the cathode, separator, and cell type on the rate and efficiency of HDH of 1 mM DCP and 0.071 mM (saturated) PCP in 0.05 M Na₂SO₄/H₂SO₄ (pH 3) and/or pure water are reported. Several types of cathodes, *e.g.*, Fe gauze and foil, Pd/Fe gauze, Pd/Fe foil, carbon cloth, and Pd/carbon cloth, were tested. Palladized cathodes showed high catalytic activity and long term stability for the HDH processes. Both cation and anion exchange membranes were employed to separate the divided H-cells and solid polymer electrolyte cells. Complete HDH of 1 mM DCP with a current efficiency of 70% and an energy consumption below 20 kWh/kg DCP, was realized in an H-cell with a Pd cathode at ambient temperature. Similar results were obtained for HDH of 0.071 mM PCP but with lower current efficiency, *e.g.*, 16% and higher energy consumption, *e.g.*, 80 kWh/kg PCP. The cell gave a current efficiency of 15% and an energy consumption of 11.6 kWh/kg DCP for complete HDH of 1 mM DCP in pure water solution. For complete HDH of 0.071 mM PCP in the SPE cell, current efficiency and energy consumption were 10% and 90 kWh/kg PCP.

Manuscript received June 11, 2002. Available electronically December 23, 2002.

Halogenated liquid wastes are routinely produced in industrial processes, *e.g.*, approximately 1 million tonnes of such wastes are generated annually in the U.K.¹ Until very recently, the disposal practice for these wastes was landfill for short-chain chlorinated organics, incineration for resistant and intractable compounds such as polychlorobiphenyls (PCBs) and pesticides, and use as a fuel supplement in cement kilns where a high calorific value of the organic made this a practical proposition. Disposal to landfill is now virtually precluded by the Environment Agency. Incineration has a number of serious drawbacks, such as high capital costs of plant, processing, and transport, production of harmful substances, *e.g.*, dioxin and adverse public reaction. Therefore, other routes have been explored, such as bioremediation,² chemical and electrochemical dehalogenation.²⁻⁴

Bioremediation has been applied to dehalogenate a wide variety of halogenated compounds using the metabolism of microorganisms.² Bioremediation greatly depends on the ability of microorganisms to survive in an environment containing halogenated compounds. A more challenging issue is that the products of bioremediation are often toxic and, in some cases, may be more harmful to human health than the parent compounds.⁴ Microorganisms can evolve relatively quickly to develop biochemical traits but in some cases, long-term operation is necessary, *e.g.*, months for the bioremediation of PCBs.⁵

Hydrodehalogenation (HDH) was considered as a low-waste technology for detoxifying organic halogenated waste and regeneration of the initial raw materials.⁶ Chemical dehalogenation has been developed as an alternative to incineration for disposal of halogenated organic compounds, which can proceed several ways, *e.g.*, catalytic and reactive procedures. The reactive dehalogenation involves the use of relatively expensive chemicals, such as LiAlH₄ or NaBH₄, as hydrogen donors, and is therefore considered only for preparative synthesis.⁷ Catalytic HDH of organic halogenated compounds is accepted as a practical choice at the moment and can be carried out in the gas⁸ or liquid phase.⁹ As there are harsh conditions in catalytic HDH, *e.g.*, high temperature (above 400°C in most cases),¹⁰ there are requirements for thermal, mechanical, and chemical stability of catalytic reactor components. More severely, catalytic

HDH often takes place at a gradually decreasing rate through progressive poisoning of the catalyst in some cases. This is accompanied by a rapid deactivation of the catalyst. Low-temperature catalytic HDH of bromobenzene was performed, *e.g.*, at 40°C, but the results and other reaction conditions are unacceptable for industry.⁷

More competitive ways of chemical HDH have been developed based on zero-valent metals such as iron, known as dissolving metal reductions.^{2,3} Over the last few years, it has been shown that these metals can effect the HDH of a range of chlorinated organic compounds in contaminated groundwater.^{2,3,11,12} Chemical HDH using iron alone suffered from slow reaction rates, particularly for aromatic halogenated compounds, under ambient temperature and pressure.⁵ Partial HDH of PCBs by iron was only achieved under high-temperature and high-pressures, *e.g.*, 250°C, 10 MPa.¹³

Interestingly, the deposition of small amounts, *ca.* 0.05 wt %, of Ni or Pd onto the iron has been found to significantly enhance the rate of HDH, *e.g.*, one to two orders of magnitude for trichloroethylene (TCE), compared to the rate at Fe alone which extends the range of halogenated organic compounds amenable to treatment from TCE to polychlorinated biphenyls.^{14,15}

Recently, the electrochemical HDH of chlorinated organic compounds has been explored as another means to replace incineration for disposal of halogenated organic wastes.¹⁶⁻²¹ The cathode material has been found to have a major effect on the efficiency of the electrochemical HDH of organic halogenated compounds. A typical example is the HDH of 1,2,3,5-tetrachlorobenzene (TCB) and chlorobenzene (CB) in methanol or dimethylsulfoxide and acetonitrile (with 0.25 M tetraethylammonium bromide) at a cathode potential of -3.3 V vs. Ag/AgCl.¹⁷ More than 95% conversion of 12 mM CB was achieved with a current efficiency of 15-20% on the carbon cloth or Pb cathodes. On the other hand, Pt, Ti, and Ni cathodes only gave current efficiencies of *ca.* 5% and lower conversions.

The electrochemical dechlorination of 153 ppm 4-chlorophenol to phenol in 0.05 M sodium acetate-acetic acid solution has been reported. A conversion, up to 100% dechlorination, of 153 ppm 4-chlorophenol was achieved by using palladized carbon cloth or graphite cathodes after 15 h electrolysis.¹⁸

The majority of work examining the effect of cathode materials, even using Fe as a cathode, concentrated on mechanistic analysis rather than practical applications. Moreover, environmentally unac-

^z E-mail: k.scott@ncl.ac.uk

^{*} Electrochemical Society Active Member.

ceptable materials, such as Hg and Pb, have been used as cathode materials,^{17,19} which makes such techniques unattractive for industry.

Based on the above work on the HDH of halogenated organic compounds, the aim of the work reported in this paper is to find a technical way to effect the electrochemical HDH of halogenated organic compounds in aqueous solutions. The first stage focused on the HDH of 2,4-dichlorophenol (DCP) and pentachlorophenol (PCP) because of their importance in industrial waste-water treatment. In Europe, the acceptable level of PCP in wastewater is in the range of 0.1-1 ppm, and that of its reduction product, DCP, is 4 ppm.²⁰ In drinking water, the acceptable level is extremely low, *i.e.*, only 1 ppb.²¹ In common with many halogenated organic compounds, it is not possible to treat PCP and DCP routinely by common bioremediation techniques, due to their toxicity to the bacteria employed.⁵

One accepted approach to eliminate PCP from water is absorption using granulated activated carbon, which causes some technical and economic problems in the disposal of PCP-containing carbon materials.²¹ Anodic dehalogenation of PCP in aqueous solutions has been examined as an alternative to adsorption, via electrochemically initiated condensation reactions at high-surface-area carbon felt anodes. In the best case, a current efficiency of 100% for the electrochemical condensation process was achieved in the controlled potential electrolysis of 0.35 mM PCP in 1 M acetate buffer solutions. However, at potentials less than 0.79 V vs. RHE, PCP was only partially dehalogenated, and at higher potentials, *e.g.*, 1.9 V vs. RHE, the products were chlorinated compounds, *e.g.*, 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone and were essentially insoluble and caused anode passivation.²¹

Another option is electrochemical HDH of DCP and PCP

$$Cl_2C_6H_3OH + 4e^- + 2H^+ \rightarrow C_6H_5OH + 2Cl^-$$
 [1]

$$Cl_5C_6OH + 10e^- + 5H^+ \rightarrow C_6H_5OH + 5Cl^-$$
 [2]

The only reported work on the electrochemical HDH of PCP was using a flow-through cell with carbon fiber cathodes operated in a batch-type recycle mode.²⁰ The HDH was performed in 0.1 M Na₂SO₄/0.1 M NaOH solution at constant current densities. At 500 mA cm⁻², complete dehalogenation of the PCP to phenol and chloride ions was achieved. However, the current efficiency was very low, about 1%, and the energy consumption was high, about 400 kWh/kg PCP for 90% conversion. At lower current densities, PCP was only partially dehalogenated to tetrachlorophenol, dichlorophenol, or monochlorophenol, respectively.²⁰

The overall aim of the work reported in this paper was to develop a technical process for the dehalogenation of aqueous solutions containing chlorophenols, including PCP and DCP, based upon electrochemical HDH. This paper deals with the effect of cell materials, *e.g.*, cathode, and cell separator, on the efficiency of the HDH of PCP and DCP. The following paper examines the influence of operational parameters.

Experimental

Materials and chemicals.—The following materials were all used as received: Iron gauze (99%, BDH), iron wire (diameter 0.25 mm, 99.9%, Aldrich), iron foil (99.5%, 2.5×2.5 mm, Aldrich), mild steel mesh (wire diameter 0.15 mm, open area 35%), stainless steel mesh (AISI 304, wire diameter 0.25 mm, open area 37%, Goodfellow) or foil (AISI 316, thickness 0.25 mm, Goodfellow), Ti mesh (99.6%, open area 37% wire diameter 0.2 mm), carbon cloth (GC-14, E-TEK Inc.), iron powder (99.0%, maximum particle size 60 μ m, Goodfellow), palladium-charcoal (5% or 10% Pd, BDH), and palladium activated carbon powder (30% Pd, Aldrich). Reagents were K₂PdCl₆ (99%, Aldrich), PdCl₂ (99%, Aldrich), pentachlorophenol (PCP, 98%, Aldrich), 2,4-dichlorophenol (DCP, 99%, Aldrich), 4-chlorophenol (CP, 99%, Lancaster Synthesis), phenol (99.9%, Aldrich), Na₂SO₄ (97%, Aldrich), KCl (99%, Aldrich), and NaCl (99%, Aldrich), NaBH₄ (99%, BDH), FeSO₄ (99%, Aldrich),



Figure 1. Flow circuit for the electrochemical reductive HDH using a solid polymer electrolyte reactor in the batch recycle mode. 1. Power supply. 2. Catholyte reservoir. 3. Cell. 4. Thermostatic bath. 5. Catholyte. 6. Magnetic stirrer. 7. Pump. 8. Cathode. 9. Membrane. 10. Anode. 11. Anolyte.

 $(NH_4)_2SO_4$ (99%, Aldrich), NiSO_4 (98%, Aldrich), H₃BO₃ (99%, BDH), NaOH (AnalaR, BDH), HCl (37%, BDH), H₂SO₄ (98%, AnalaR, BDH), Nafion solution (5%, Aldrich), CH₃OH (HPLC-grade, Fisons), and acetic acid (99.9%, Aldrich).

All solutions were prepared using water with a resistance of 18.2 $M\Omega$ cm obtained from a Millipore-Q system. Due to the very low solubility of PCP in acidic and neutral aqueous solutions, the concentrated PCP solutions, above the saturated concentration, were prepared by dissolving the desired amount of PCP in methanol first and then diluting that to the required concentration. PCP solutions with less than 1% methanol, above the saturated concentration, were in the form of emulsions.

Two types of membranes were used in this work: Nafion 117 membrane (DuPont) and FuMATech FT-FKE-S membrane (FuMATech). Pretreatment of the Nafion 117 membranes is detailed elsewhere.²² The FuMATech FT-FKE-S membranes were used after immersion in water for at least 2 h.

Cells and apparatus.-Two cells were used, an H-cell and a solid polymer electrolyte zero gap flow cell. The H-cell, used for voltammetric measurements and the electrochemical HDH of PCP and DCP, consisted of two compartments, each with a volume of 80 cm³. Nafion 117 membrane, FuMATech FT-FKE-S membrane, or a glass frit was employed as the separator between the cell compartments. Nitrogen was bubbled through the catholyte of the H-cell at the start of the voltammetric experiments. The solid polymer electrolyte cell, operated in a batch recirculation mode for the electrochemical HDH of PCP and DCP, was made from either stainless steel or graphite blocks with machined flow channels. The flow circuit of the solid polymer electrolyte cell, as shown in Fig. 1, consisted of a laboratory scale two-electrode cell, two pumps (H. R. Flow Inducer, England), two reservoirs (1 dm³ in volume each) for anolyte and catholyte, respectively, and thermostatic baths (B-480 Waterbath, Buchi, Switzerland) for temperature control.

In operation, the catholyte and anolyte, each with a volume of 100 cm^3 , were pumped through the cell and then returned to the reservoirs for recycling. All electrolyses were carried out under gal-vanostatic control, ranging from 5 to 100 mA cm⁻², for a period between 30 min and 20 h. The concentrations of chloride ion were measured with an ion analyser and the concentrations of reactant, intermediates, and products were monitored using HPLC. The data was used to determine the process efficiency, as a function of time.

Various materials, *i.e.*, iron gauze, iron wire, iron foil, mild steel mesh or sheet, stainless steel mesh or plate, Ni foam, nickel, palladium, and nickel-palladium on Ti mesh, Pd/carbon cloth, Pd-Ni/carbon cloth, and Pd-Ni/stainless steel mesh, with geometric areas between 2 and 10 cm², were tested as cathodes. The anode was a platinum mesh (about 10 cm²). Commercial saturated calomel electrode (Russell) or Ag/AgCl electrode (Radiometer model K801) was used as the reference, although all electrode potentials are reported on the reversible hydrogen electrode (RHE) scale. For the measurements using three electrodes, a Luggin probe was used to measure the electrode potential.

Electrode preparation.—Several catalyzed electrodes, *i.e.*, Fe/Ti mesh, Ni/Ti mesh, Pd/Ti mesh, Pd/Ti mesh, Pd/Stainless steel mesh, Pd-Ni/Stainless steel mesh, Pd/Fe gauze, and Pd/carbon cloth, with geometric areas between 2 and 10 cm², were prepared by electrodeposition.^{17,22}

Deposition of Pd onto iron (gauze, wire, or foil) and mild steel from K_2PdCl_6 was carried out spontaneously via the reaction⁵

$$2Fe + PdCl_6^{2-} = 2Fe^{2+} + 6Cl^{-} + Pd$$
 [3]

by exposing to 20 mL of a 2.5 mM solution of K_2PdCl_6 (20 mg K_2PdCl_6 in 20 mL water) for 5 to 15 min. The amount of palladium deposited on the iron surface was assumed to be the result of a 100% completion of Reaction 3, which was determined by comparing the substrate weights before and after deposition and was between 2 and 5 mg/cm² geometric area.

Preparation of metal/membrane cathodes used the ion exchange method.²³ The sandwiched membrane electrode assemblies were prepared by the hot press method from Nafion-bonded iron powder or Pd/carbon powders.²²

A number of electrodes were deposited under identical conditions to check reproducibility.

Voltammetric measurements.—All voltammetric measurements were performed in an H-cell using a Ministat precision potentiostat (Thompson Electrochemical, Ltd.) with a PCI-100 MK3 computer interface (Sycopel Scientific, Limited) controlled by Sycopel Scientific electrochemistry software (Sycopel Scientific, Limited). All of the solutions studied were thoroughly degassed using oxygen-free nitrogen (BOC, Ltd). To obtain stable and reproducible voltammograms, it was necessary to treat the cathode electrochemically before collecting data, *e.g.*, three scans between 0.4 and -1.2 V vs. RHE at a scan rate of 50 mV/s.

Batch electrochemical HDH.—Batch electrolyses were performed in the H-cell and the solid polymer electrolyte cell to determine the HDH efficiency. Galvanostatic electrolysis was generally used, and the constant currents were provided by a Farnell LS60-5 power supply. Potentiostatic electrolyses were also performed, and the total charges passed in the experiments were monitored. The catholytes in the H-cells were magnetically stirred.

Product analysis.—Chloride concentrations were determined using a pH/ion meter (Corning model 135, Corning Glass Works or Orion model 920A, Orion Research, Inc.) and a combination chloride electrode (model 96-17B, Orion Research, Inc.). Calibration curves were obtained from standard solutions, 5×10^{-6} to 0.1 M NaCl in pure water or in 0.05 M aqueous Na₂SO₄ solution, before and after each experiment.

High-performance liquid chromatography (HPLC) was used to determine concentrations of starting material, intermediates, and



Figure 2. Linear sweep voltammograms for electrochemical HDH of PCP and DCP on palladized cathodes. Cell: H-cell divided by a Nafion 117 membrane. Cathode: as shown in the figure (2 mg Pd/cm², 4 cm²). Anode: Pt mesh (10 cm²). Catholyte: 0.05 M Na₂SO₄ (pH 3) solution without (blank) or with saturated (0.071 mM) PCP and saturated (20 mM) DCP. Anolyte: 0.05 M Na₂SO₄ (pH 3) solution. Scan rate: 5 mV s⁻¹. Temperature: 21.5 \pm 0.5°C.

products of the dechlorination during the course of the electrolysis. The HPLC apparatus consisted of a PU 4010 pump (Pye Unicam, Ltd., England), a Discovery™ C18 column (5 µm particle size and 25×0.46 cm, Supelco), PU 4020 UV detector (Pye Unicam, Ltd., England), and a LY 16100-11 X-Y recorder. The wavelengths used in HPLC measurements were determined using UV-vis spectroscopy (UV-160A UV-visible recording spectrophotometer, Shimadzu, Japan). Normally, the PU 4020 UV detector was set to 270 nm for phenol, 280 nm for DCP and CP, and 300 nm for PCP. The mobile phase was a 0.1 M acetic acid aqueous solution/methanol mixture (60/40 by volume) with flow rate of 1.0 mL/min. The peaks for phenol (retention time $t_r = 10.0 \text{ min}$), CP (retention time, $t_r = 23.9 \text{ min}$), DCP (retention time, $t_r = 32.0 \text{ min}$), and PCP (retention time, $t_r = 42.3 \text{ min}$) were characterized by using standard solutions. Quantification of phenol production and distributions of the chlorophenols was accomplished by the use of calibration curves with standards. A sample volume of 20 µL was generally employed. The detection limit of this method was 0.1 ppm for phenol, CP, and DCP and 0.5 ppm for PCP.

Parameter definitions.—Energy consumption was calculated according to the following equation 24,25

Energy consumption
$$(ECN) = nFE_{Cell}/\varphi M$$
 [4]

where *n* is the number of electrons passed during the reaction, *F* is the Faraday constant, E_{Cell} is the cell voltage, φ is the current efficiency, and *M* is the molar mass.

The current efficiency of the HDH reaction was calculated as the part of current (or charge) passed that was used to convert the starting PCP or DCP to the products according to Eq. 1 and 2.

Results and Discussion

Voltammetric data.—Voltammetric data were collected on a range of cathodes. Typical linear sweep voltammograms (LSV) (Fig. 2) using Pd/Fe gauze as the working electrode showed that the addition of PCP and DCP to the electrolyte caused an increase in cathodic current densities, although all curves showed flat profiles at potentials less negative than -1.0 V vs. RHE. The rapid increase in current density with potential more negative than -1.25 V was ac-



Figure 3. Comparison between the chemical and electrochemical HDH of DCP and PCP in terms of chloride ion release. Cathode: Pd/Fe gauze (2 mg Pd/cm², 4 cm²). Reaction conditions: "Chemical HDH" at the open circuit; "Electrochemical HDH" at a potential of -1.20 V vs. RHE. Electrolyte volume: 60 mL. Other conditions: see Fig. 2.

companied by rapid evolution of gas (hydrogen) bubbles at the cathode. The striking feature of the voltammetric responses using Pd/Ti mesh is that higher cathodic current densities were observed from more positive potentials than those at the Pd/Fe gauze in both PCP and DCP solutions (Fig. 2). Under conditions used in this work, both HDH and hydrogen evolution reactions occurred simultaneously even at less negative potentials, so it was impossible to distinguish the characteristics of these processes from the voltammetric measurements only. Moreover, the voltammetric data could not completely show the effectiveness of cathode materials for releasing chloride ion. This was demonstrated by the electrolysis data shown later. For example, stainless steel mesh and plate cathodes showed different cyclic and linear sweep voltammograms in the blank or in the PCP and DCP solutions. But when these cathodes were used to attempt HDH of PCP and DCP by preparative electrolysis, no chloride ions were detected. Regardless of this, the preliminary voltammetric data suggested that the Fe, Pd/Fe, Pd/carbon cloth, and Pd/Ti mesh were potential cathodes for the HDH process. The program of research thus focused on quantitative preparative electrolysis.

Comparison of chemical and electrochemical dechlorination.—The rates of HDH of DCP and PCP using Fe or Pd/Fe electrodes at open circuit were very small, and significantly less than those observed during electrolysis, see Fig. 3. For example, after 60 min, 16.6 and 5.9 ppm chloride ions were detected from the electrochemical HDH of 1 mM DCP and PCP, respectively. Only 2.4 and 0.97 ppm chloride ions were released from the chemical dechlorination of 1 mM DCP and PCP, respectively (Fig. 3).

Chloride ion release.—The principal analytical method used to measure performance was chloride ion release as this provided a reliable and instantaneous measurement of the HDH process.

Several cathode substrates and catalysts were evaluated in terms of chloride ion release from the HDH of DCP and PCP, and the latter was found to have the most significant effect upon the efficiency of the HDH process. Figure 4 shows chloride ion release data obtained during the electrolysis of 1 mM DCP in the H-cell using a Nafion membrane as the separator and three catalyzed cathodes. In terms of the release of chloride ions, the Ni/Ti mesh gave virtually the same result as the Ti mesh substrate, whereas the Pt/Ti mesh showed an almost fourfold increase in chloride ion release compared to the both



Figure 4. Effect of catalyst on chloride ion release during electrochemical HDH of 1 mM DCP. Cathode: shown in the figure (5 mg catalyst cm⁻², 6 cm²). Controlled cathode potential: -1.0 V *vs.* RHE. Other conditions: see Fig. 2.

Ni/Ti mesh and Ti mesh alone. The best performance was obtained using the Pd/Ti mesh, which dehalogenated 1 mM DCP completely within 75 min. No improvement in HDH efficiency was observed with a Fe/Ti mesh (not shown in the figure for clarity), due to the rapid corrosion of the Fe deposit. The inactivity of Ni with respect to the HDH process was something of a surprise given the increased activity of Fe metal with Ni, and Ni itself towards chemical HDH reported in the literature for liquid phase^{14,15} and gas phase²⁶ processes, respectively. Moreover, the deposition of Ni onto Pd/Ti mesh cathode produced the same HDH characteristics as for the Pd/Ti mesh cathode (not shown in the figures for clarity).

It was found that hydrogen plays a key role in the HDH and that both platinum and palladium are excellent materials for electrochemical evolution of hydrogen. More important, palladium has the ability to absorb hydrogen into its lattice and to maintain a high surface concentration of hydrogen, and platinum lacks this ability. Consequently, palladium gave higher HDH rates than platinum.^{18,27} Our data can be explained on these observations, although further research is necessary to understand the data thoroughly.

The effectiveness of HDH greatly depends on the cathode substrate, as shown in Fig. 5 as a comparison of different cathodes during the electrochemical HDH of 1 mM DCP in an H-cell with a Nafion membrane. As expected, uncatalyzed substrates, e.g., Ti, released very few chloride ions, e.g., below 7 ppm within 2 h electrolysis (Fig. 5). Fe gauze gave a slightly greater chloride ion release, but still less than 10 ppm. The Pd/Fe gauze cathode (5 mg Pd/cm²) gave more than a twofold increase in chloride ion release. Higher activities were obtained using the Pd/carbon cloth cathode (5 mg Pd/cm²), e.g., about 50 ppm at 120 min. This value was even better than that achieved at a 30% Pd/activated carbon powder cathode, although the latter had higher Pd loading (15 mg Pd/cm²). The use of stainless steel as an alternative metal support for Pd produced a performance similar to that of Pd/Ti mesh, although the time for complete HDH was increased by some 25%. Both the metal mesh supported cathodes gave significantly better performances than those of the carbon cloth electrodes, as shown in Fig. 5.

A similar cathode effect was observed for the HDH of 0.071 mM PCP, as shown in Fig. 6. The poor performance at the iron cathodes mainly resulted from material instability. It was observed that the Fe gauze and the Pd/Fe gauze cathodes formed surface oxides (rusted) after 15 min electrolysis and rusting was severe after 2 h. In con-



Figure 5. Effect of cathode substrate on chloride ion release during electrochemical HDH of 1 mM DCP. Cathode: shown in the figure (5 mg catalyst cm^{-2} , 6 cm², except for the "Pd/C powder" with 15 mg Pd cm⁻²). Controlled current density: 10 mA cm⁻². Other conditions: see Fig. 2.

trast, the Pd/carbon cloth, Pd/stainless steel mesh, and Pd/Ti mesh cathodes showed great stability under the HDH conditions. Particularly, there was no visual damage of the Pd/Ti mesh cathode after more than 50 h of use. The palladized mesh cathodes have much more open areas, which led to better mass transport between PCP and the catalysts and thus higher HDH rates, compared to the palladized carbon cloth. In the case of the stainless steel-supported cathodes, loss of Pd from the surface was observed after use. Thus the stainless steel supported cathode would not seem to be a viable cathode for long term HDH, at least not with the particular preparation procedure used.

In this work, the Pd/carbon cloth was formed by electrochemically depositing palladium onto the carbon cloth substrate and the



Figure 6. Effect of cathode material on chloride ion release during electrochemical HDH of 0.071 mM PCP. Cathode: shown in the figure (5 mg catalyst cm⁻², 6 cm²). Controlled cathode potential: -1.0 V *vs.* RHE. Other conditions: see Fig. 2.



Figure 7. Effect of cell and separator on chloride ion release during electrochemical HDH of 1 mM DCP. Cell and separator: shown in the figure. Cathode: Pd/carbon cloth (5 mg Pd/cm², 9 cm²). Anode: Pt mesh (10 cm²). Controlled current: 200 mA. Catholyte solvent and anolyte: 100 ml 0.05 M Na₂SO₄ (initial pH 3) solution. Flow rate for the solid polymer electrolyte cell: 150 mL/min. Temperature: $20.5 \pm 0.5^{\circ}$ C.

Pd/carbon powder was made using bonded palladized carbon powder. For the Pd/carbon powder, quite severe mass-transport limitations could occur in the carbon cloth substrate and the bonded catalyst region, especially when a large amount of hydrogen gas was generated. The system also relied on good ionic contact between the Pd and Nafion membrane. As a consequence of these factors, the Pd/carbon powder cathode showed poorer HDH efficiency than the Pd/carbon cloth cathode.

In this work, an objective was to explore for possible cell configurations for electrochemical HDH. Two types of cells were compared, an H-cell and solid polymer electrolyte zero-gap flow cell (solid polymer electrolyte cell). Figure 7 shows data obtained from galvanostatic HDH (22 mA/cm^2) of 1 mM DCP solutions in these cells with Pd/carbon cloth cathodes (5 mg Pd/cm²). The solid polymer electrolyte cell gave good performance for the HDH of 1 mM DCP solution, although the best result was obtained using the H-cell, *e.g.*, in terms of total amount of released chloride ions, after 3 h of electrolysis, *ca*. 0.174 and 0.14 mmol of chloride ions were released using the H-cell and the solid polymer electrolyte cell, respectively.

One aspect of the work was a preliminary evaluation of two solid polymer membranes, a cation exchange, and an anion exchange. A comparison of chloride ion in the cathode chamber of the H-cell, with three types of separator, using the Pd/carbon cloth cathodes (5 mg Pd/cm²) under identical conditions for HDH of 1 mM DCP, is shown in Fig. 7. After 3 h of electrolysis at 200 mA, the total released chloride ions were 0.093, 0.132, and 0.174 mmol in the cells with the glass frit, the FuMATech membrane and Nafion 117 membrane, respectively. The Nafion proton conductor effectively excludes chloride ion transport and thus exhibits the highest chloride content. The anion exchange (FuMATech) membrane, however, allows a significant amount of chloride ion transport into the anode chamber, *i.e.*, lower chloride ion content. Thus with the anion exchange membrane the simultaneous dechlorination and separation of phenol from chloride ion is possible. The use of a simple porous glass frit enables a greater chloride ion transfer into the anode chamber, but this is at the expense of some chlorophenol transfer.

Product distribution.—In order to confirm the effectiveness of the electrochemical HDH approach as demonstrated by chloride ion



Figure 8. HPLC concentration profiles of reactant and product during electrochemical HDH of 1 mM DCP. Conditions: same as those in Fig. 7 for the H-cell.

analysis, product distributions were determined by HPLC with UV detection at 270 nm for phenol, 280 nm for CP and DCP, and 300 nm for PCP. Figure 8 shows product distributions, including DCP, the intermediate 4-chlorophenol (CP) and phenol, obtained from HPLC measurements during the electrochemical HDH of 1 mM DCP in aqueous solution. As expected, a rapid decrease in the concentration of DCP and corresponding increase in the concentration of phenol due to the effective dechlorination of DCP can be seen. Small amounts of 4-chlorophenol were also detected. As mentioned previously, the electrochemical HDH of DCP involved the removal of chloride ions and the addition of four or two electron(s) to the phenol ring, depending on the product, phenol or chlorophenol. The above product distribution agreed well with the results obtained from analysis of chloride ion concentrations (see Fig. 7). The mass balances in the above HPLC measurements were close to 100% when DCP, CP, and phenol were considered.

Current efficiency.—The influence of the cathode material on the current efficiency of the HDH process is shown in Fig. 9. For the H-cell, the current efficiency of dechlorination of 1 mM DCP solution varied from 0.75 to 65%, depending on the materials and electrolysis time. The best current efficiencies, 60-65%, were achieved using the Pd/Ti mesh cathode. The high surface area deposits, demonstrated by the SEM measurements (not shown here), and open structure of the Pd/Ti mesh cathode gave very high efficiency. The Pd/carbon cloth and Pd/Fe gauze cathodes gave lower current efficiencies, around 10 and 8%, respectively. With other materials, current efficiencies were very low, *i.e.*, less than 3%. As stated above, the poor performance of the iron cathodes was mainly a result of their instability. The mass-transport limitations of the Pd/carbon powder cathode led to the lower efficiency for the HDH process, although it had three times the Pd loading as those of the Pd/Ti mesh and Pd/carbon cloth cathodes. It must be stated that these electrode structures were not optimized and represent our adapted method of manufacture. For HDH of PCP solutions, lower efficiencies were observed, e.g., below 10%, even using a Pd/Ti mesh cathode (Fig. 10).

Current efficiencies varied greatly in the different cells, as shown in Fig. 10. Current efficiencies obtained in the solid polymer electrolyte cell were lower than those obtained in the H-cell for the HDH of PCP and DCP solutions. The current efficiencies were in a range of 60-65% and 14-28% in the H-cell and 3.1-7.5% and 1.3-



Figure 9. Effect of cathode on current efficiency for the electrochemical HDH of 1 mM DCP in 0.05 M Na_2SO_4 solution. Palladium loading for the palladized cathodes: 5 mg cm⁻². Other conditions: same as those in Fig. 7 for the H-cell.

3.5% in the solid polymer electrolyte cell for the HDH of 1 mM DCP and 1 mM PCP, respectively. However, no supporting electrolyte was used for the operation of the solid polymerelectrolyte cell. This feature should be beneficial for practical applications of this type of cell provided that operating conditions are optimized. The preferred cell for HDH should be an solid polymer electrolyte cell.

Energy consumption.—A key parameter when designing an electrochemical process is energy consumption.^{24,25} Not surprisingly, energy consumption varied with cell types and cathode materials for the electrochemical HDH of DCP and PCP. Figure 11 shows the data for the HDH of 1 mM DCP in the H-cell using the Pd/Ti mesh cathode or in the solid polymer electrolyte cell using different cathodes. The solid polymer electrolyte cell gave lower energy con-



Figure 10. Effect of cell type on the current efficiency of HDH of 1 mM DCP and PCP solutions. Conditions: same as those in Fig. 7.



Figure 11. Effect of cathode on energy consumption for the electrochemical HDH of 1 mM DCP-pure water solution in the solid polymer electrolyte cell with different cathodes. Cathode: shown in the figure (palladium loading: 5 mg/cm²). Other conditions: same as those in Fig. 7.

sumption than the H-cell, e.g., 30 and 59 kWh/kg DCP after 3 h for the solid polymer electrolyte cell and the H-cell, respectively.

In the solid polymer electrolyte cell, the Pd/Ti mesh and the Pd/carbon cloth cathodes showed much lower energy consumptions than other materials for the HDH process, which can be attributed to their high effectiveness and stability during the HDH process. For example, the energy consumption was 400, 350, 32, and 30 kWh/kg for the Pd/Fe gauze, 30% Pd/activated carbon powder, Pd/carbon cloth and Pd/Ti mesh cathodes, respectively. High energy consumption observed at the Pd/Fe gauze, as mentioned above, mainly resulted from its low current efficiencies. The Pd/activated carbon powder gave lower energy consumption than the Pd/Fe gauze.

Catholyte pH change.--An interesting observation during the HDH of DCP and PCP was that the catholyte pH greatly depended on cell type. Figure 12 shows such a typical change in pH during HDH of 1 mM DCP in 0.05 M Na₂SO₄ with the Pd/Fe gauze cathode (5 mg Pd/cm²). The pH increased due to the accumulation of OH⁻ ions from the electrolysis of water in the H-cell. In the solid polymer electrolyte flow cell, protons formed at the anode crossed the Nafion membrane into the catholyte, which partly cancelled the effect of the hydrogen evolution and led to a small catholyte pH change.

Conclusions

1. The chemical HDH of DCP and PCP was not effective on reducing metals, such as Fe and Pd. However, DCP and PCP were effectively hydrodehalogenated by electrochemical reduction using iron and palladium cathodes, which provides a new technology for treatment of wastewater containing halogenated organic compounds.

2. HDH could be performed with H-cell or/and solid polymer electrolyte cells and cathode material, including catalyst and substrate, had a decisive influence on HDH regarding both reaction rate and efficiency. Palladized cathodes were much more effective for the HDH of DCP and PCP than iron and platinized cathodes. Electrochemical HDH using iron cathodes was effective with almost complete HDH possible at low concentrations of DCP and PCP. The use of palladized iron electrodes in both the solid polymer electrolyte cell and the H-cell markedly improved the HDH efficiency which, with 1.0 mM DCP and PCP solutions, gave current efficiencies up to 14 and 8%, respectively, at 94% chloride removal. How-



Figure 12. Change of catholyte pH values during the electrochemical HDH of 1 mM DCP in 0.05 M Na₂SO₄ solution. Cathode: Pd/Fe gauze (5 mg Pd/cm², 6 cm²). Other conditions: same as those in Fig. 7.

ever, the corrosion of these iron-based materials was severe, particularly during long-term operation. As technically more acceptable electrodes, carbon cloth, and titanium mesh supported Pd electrodes showed high catalytic activity and stability for HDH process. Using these cathodes good HDH performance of DCP and PCP were achieved with dilute solutions. In particular, using a simple batch H-cell with pH 3, 0.05 M sodium sulfate/H₂SO₄ supporting electrolyte, electrolysis resulted in virtually complete HDH of DCP and PCP with current efficiencies up to 70 and 16%, respectively. For the low concentrations of organics treated the current efficiencies were quite respectable and energy consumptions were reasonable, 6 and 21 kWh kg⁻¹ for DCP and PCP, respectively. Pd/stainless steel also hydrodehalogenated PCP and DCP efficiently, although the deposit stability needs to be improved.

Although either cation or anion exchange membranes could be used for HDH, the use of an anion exchange membrane may be particularly useful when the simultaneous removal of chloride ion is desirable.

To scale-up the electrochemical HDH to industrial application, optimization of electrode fabrication, HDH cells, and operation parameters is necessary and is in progress in this laboratory.

Acknowledgments

The authors thank the United Kingdom Engineering and Physical Sciences Research Council (EPSRC) for a postdoctoral award during this work.

Thanks also to FuMATech (Germany) for providing membranes for this work.

The University of Newcastle upon Tyne assisted in meeting the publication costs of this article.

References

- 1. DOE, The Special Waste Regulations, HMSO, London (1996).
- 2. M. L. Hitchman, R. A. Spackman, N. C. Ross, and C. Agra, Chem. Soc. Rev., 1995, 423.
- S. Zhang and J. F. Rusling, *Environ. Sci. Technol.*, **27**, 1375 (1993).
 C. S. Criddle and P. L. McCarty, *Environ. Sci. Technol.*, **25**, 937 (1991).
- C. Grittini, M. Macomson, Q. Fernando, and N. Korte, Environ. Sci. Technol., 29, 5. 2898 (1995)
- L. N. Zanaveskin, V. A. Averganov, and Y. A. Treger, Russ. Chem. Rev., 65, 617 6 (1996).
- 7. M. A. Aramendia, V. Borau, I. M. Garcia, C. Jimenez, J. M. Marinas, and F. J. Urbano, Appl. Catal., B, 20, 101 (1999).

- 8. S. T. Srinivas, L. T. Lakshmi, N. Lingaiah, P. S. S. Prasad, and P. K. Rao, Appl. Catal., A, 135, L201 (1996).
- 9. E. N. Balko, E. Przybylski, and F. V. Trentini, Appl. Catal., B, 2, 1 (1993).
- 10. E. S. Creyghton, M. H. W. Burges, J. C. Jansen, and H. Van Bekkum, Appl. Catal., A, 128, 275 (1995).
- 11. G. W. Reynolds, J. T. Hoff, and R. W. Gillham, Environ. Sci. Technol., 24, 135 (1990).
- 12. S. F. O'Hannesin, MA Thesis, University of Waterloo, Ontario, Canada (1993). 13. H. K. Yak, B. W. Wenclawiak, I. F. Cheng, J. G. Doyle, and C. M. Wai, Environ. Sci. Technol., 33, 1307 (1999).
- 14. R. Muftikian, Q. Fernando, and N. Korte, Water Res., 29, 2434 (1995).
- 15. E. L. Appleton, Environ. Sci. Technol., 30, 536A (1996).
- 16. F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi, and A. De Battisti, J. Electrochem. Soc., 146, 2175 (1999).
- 17. S. M. Kulikov, V. P. Plekhanov, A. I. Tsyganov, C. Schlimm, and E. Heitz, Electrochim. Acta, 41, 527 (1996).

- 18. I. F. Cheng, Q. Fernando, and N. Korte, Environ. Sci. Technol., 31, 1074 (1997).
- 19. S. Zhang and J. F. Rusling, Environ. Sci. Technol., 27, 1375 (1993); S. Zhang and J. F. Rusling, Environ. Sci. Technol., 29, 1195 (1995).
- 20. D. Schmal, J. van Erkel, and P. J. van Duin, Inst. Chem. Eng., 98, 259 (1986).
- 21. M. Gattrell and B. MacDougall, J. Electrochem. Soc., 146, 3335 (1999).
- 22. H. Cheng, Ph.D. Thesis, University of Newcastle upon Tyne, Newcastle upon Tyne, U.K. (1999).
- 23. S.-A. Sheppard, S. A. Campbell, J. R. Smith, G. W. Lloyd, T. R. Ralph, and F. C. Walsh, Analyst (Cambridge, U.K.), 123, 1923 (1998).
- 24. F. Goodridge and K. Scott, Electrochemical Process Engineering, pp. 15-191, Plenum Press, New York (1995).
- 25. D. Pletcher and F. C. Walsh, Industrial Electrochemistry, 2nd ed., pp. 74-75, Chapman and Hall, New York (1990).
- E.-J. Shin and Mark A. Keane, *Appl. Catal.*, *B*, **18**, 241 (1998).
 D. R. Lawson, M. J. Teirney, I. F. Cheng, L. S. Van Dyke, M. W. Espenscheid, and C. R. Martin, Electrochim. Acta, 36, 1515 (1991).