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Hydrodehalogenation of 2,4-dibromophenol by electrochemical reduction☆

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Abstract

The electrochemical hydrodehalogenation (HDH) of 2,4-dibromophenol (DBP) has been carried out by electrochemical reduction in H-cells and solid polymer electrolyte (SPE) cells using catalysed cathodes. The electrochemical process gave high conversions of up to 95%, high selectivities of up to 98%, high current efficiencies of up to 98.5% and energy consumption as low as 2.2 kW h (kg DBP)$^{-1}$. The type of the catalyst plays a decisive role in the efficiency of the HDH of DBP, with palladium being an attractive material. The effect of current density, DBP concentration, supporting electrolyte and temperature, on the HDH is reported.

1. Introduction

New technologies for remediation of halogenated organic compounds are highly desirable to clean-up and protect the environment. Disposal of such compounds to landfill is now virtually precluded by environmental legislation. Incineration involves high costs, produces harmful substances (e.g., dioxins) and causes adverse public reaction. Hence, bioremediation [1], chemical and electrochemical dehalogenation [1–3] have been investigated as alternatives.

Bioremediation involves the treatment of halogenated compounds using the metabolism of microorganisms [1]. The effectiveness of bioremediation greatly depends on the ability of microorganisms to survive in the environment containing halogenated compounds. An issue with bioremediation is that the products are often toxic and, in some cases, may be more harmful to human health than the parent compounds [3]. Microorganisms can evolve relatively quickly to develop biochemical traits but in some cases, long-term operation is necessary, for example, several months for the bioremediation of PCBs [4].

Hydrodehalogenation (HDH) is a technology for detoxifying organic halogenated waste and regeneration of the initial raw materials [5]. Chemical hydrodehalogenation has been investigated for many years and one approach uses relatively expensive chemicals, such as $LiAlH_4$ or $NaBH_4$. However, these reagents are considered too expensive for treatment of wastes and are used only for preparative synthesis [6]. Chemical HDH using zero-valent metals, such as iron, zinc and tin, is employed to remove chlorinated organic compounds from contaminated groundwater [1, 2, 7, 8]. This approach faces two major problems, that is, slow reaction kinetics and poor effectiveness for HDH of aromatic halogenated compounds under ambient conditions [4]. Catalytic HDH can provide high reaction rates but it typically requires conditions of high temperature (above 400 °C in most cases) and high pressure. Catalytic HDH also suffers from a rapid deactivation of the catalyst [9]. Catalytic HDH of bromobenzene at low temperature (e.g., at 40 °C) has been considered using hydrogen, but the performance data were unacceptable for industrial application [6]. Using hydrogen in large quantities also raises safety issues in industrial operation.

Recently, electrochemical HDH has been used for treatment of halogenated organic wastes [10–14]. 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 tetraethyl ammonium bromide) at a cathode potential of −3.3 V vs Ag/AgCl [11]. With this approach, a conversion of CB greater than 95%, at an initial concentration of 12 mM was achieved, with a current efficiency of 15–20% using carbon cloth or Pb cathodes. On the other hand, Pt, Ti, and Ni cathodes gave low current efficiencies of about 5% at lower conversions.

The majority of studies of electrochemical hydrodehalogenation have concentrated on mechanistic analysis

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rather than practical applications. Some research also used environmentally unacceptable cathodes, such as Hg and Pb [11, 13]. For industrial application of HDH, an environmentally-benign hydrodehalogenation technology is required. As a promising method, hydrodehalogenation by electrochemical reduction has been studied in this laboratory and its effectiveness has been demonstrated using chlorophenols [15–17]. For its future development it is important to apply the technique to treat other halogenated organic compounds and 2,4-dibromophenol was selected as a model compound in this work.

The cathode reactions in the hydrodehalogenation of DBP may be represented as follows:

Cathode (HDH)

$$\mathrm{Br_2C_6H_3OH(DBP)} + 4e^- + 2\mathrm{H}^+ \rightarrow \mathrm{C_6H_5OH} + 2\mathrm{Br}^- \tag{1}$$

Protons for HDH are supplied from the oxidation of water:

Anode

$$3\mathrm{H_2O} \rightarrow \frac{3}{2}\mathrm{O_2} + 6\mathrm{H}^+ + 6e^- \tag{2}$$

A side reaction at the cathode, which introduces a low efficiency, is proton reduction:

Cathode (side reaction)

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H_2} \tag{3}$$

Previously, hydrodehalogenation of bromophenols (3-bromophenol, 4-bromophenol, 2,4-dibromophenol, 2,6-dibromophenol and 2,4,6-tribromophenol) has been carried out at controlled potentials using Ag/Pt wire cathodes in acetonitrile and in acetonitrile–water solutions [18,19]. In acetonitrile solutions, current efficiencies of up to 100% were achieved with phenol yields of 32% $\sim$ 51%. In acetonitrile-water media, current efficiencies were lower, for example, 52% for the hydrodehalogenation of 2,4,6-tribromophenol, and no phenol was detected.

Overall, the electrochemical hydrodehalogenation of bromophenols is at an early stage of development and more research is required for industrial application to be realised. This work was performed to develop a technical process for the dehalogenation of aqueous solutions containing bromophenols.

2. Experimental details

2.1. *Chemicals*

The following chemicals were used as received: 2,4-dibromophenol (DBP, 99%, Aldrich), 4-bromophenol (99%, Aldrich), phenol (99.9%, Aldrich), $PdCl_2$ (99%, Aldrich), Na_2SO_4, (97%, Aldrich), NaOH (AnalaR, BDH), H_2SO_4 (98%, AnalaR, BDH), NaBr (99%, Aldrich).

All solutions were prepared using water with a resistance of 18.2 MΩ cm obtained from a Millipore-Q system.

2.2. *Cells and apparatus*

Two cells were used: an H-cell and a solid polymer electrolyte flow cell. The H-cell was used for voltammetric measurements and for batch electrochemical HDH of DBP. The cell consisted of two compartments, each with a volume of 80 cm^3 separated by a Nafion® 117 membrane (DuPont). Nitrogen was bubbled through the catholyte of the H-cell to deaerate the solution before measurements were taken.

The solid polymer electrolyte cell consisted of an electrode membrane (Nafion® 117) assembly placed between stainless steel blocks with machined flow channels. The cell is shown schematically in Figure 1(a) and the electrochemical reactions take place at the interfaces between the mesh electrodes and the Nafion® membrane. The cell was operated in a batch recirculation mode and the flow circuit, as shown in Figure 1(b), consisted of two pumps (H. R. Flow Inducer, England) and reservoirs for anolyte and catholyte. In operation, catholyte and anolyte, each with a volume of 100 cm^3,

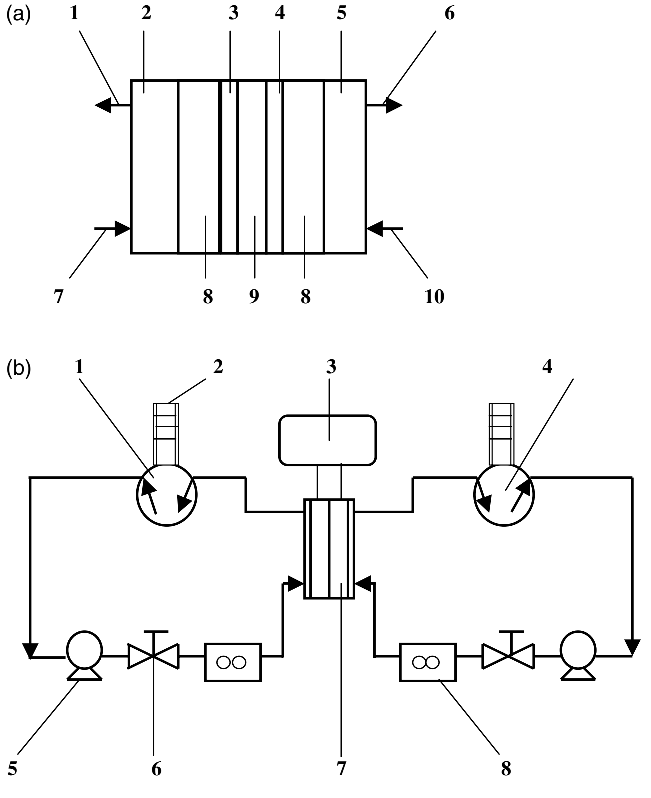

Fig. 1. (a) Solid polymer electrolyte cell. Key: (1) anolyte outlet, (2) anode compartment, (3) anode, (4) cathode, (5) cathode compartment, (6) catholyte outlet, (7) anolyte inlet, (8) stainless steel mesh, (9) Nafion® 117 membrane and (10) catholyte inlet. Cell dimension 22 cm × 14 cm × 3 cm. (b) Flow circuit for the electrochemical HDH of DBP using a solid polymer electrolyte cell. Key: (1) anolyte reservoir, (2) condenser, (3) power supply, (4) catholyte reservoir, (5) pump, (6) valve, (7) solid polymer electrolyte cell and (8) flow meter.

were pumped through the cell and then returned to the reservoirs. The pumps were calibrated before use. Flow rate, electrolyte temperature and applied current were controlled during the electrolyses.

2.3. *Electrode preparation*

Ni-coated, platinised and palladised electrodes (10 cm^2) were prepared by electrodeposition using Ti mini mesh (99.6%, open area 37, wire diameter 0.2 mm) substrates. During the deposition, the Ti mini mesh was first abraded with emery paper and rinsed thoroughly with water. After drying, the Ti mini mesh was rinsed in acetone. Following etching with 20% HCl solution at 90 °C for 1 min, the mesh was put into the deposition cell in which a N_2-saturated deposition solution was filled and stirred magnetically. The catalyst was electrodeposited onto the substrate at a controlled potential, which was chosen according to the linear sweep voltammograms. The amount of charge required to deposit the catalyst was monitored through a computer-controlled potentiostat [20]. A number of electrodes were produced and tested under identical conditions to check reproducibility.

2.4. *Voltammetric measurements*

Voltammetric techniques were used to examine the electrochemical response of electrodes and to assess the performance of the various cathodes. All voltammetric measurements were performed in the three electrode H-cell using a Ministat Precision Potentiostat (Sycopel Scientific Ltd) with a PCI-100 generator (Sycopel Scientific Limited) controlled by Sycopel Scientific Electrochemistry Software. The solutions studied were thoroughly degassed using oxygen free nitrogen (BOC Ltd). To obtain stable and reproducible voltammograms, it was necessary to pretreat the cathode electrochemically before collecting data, for example, by cycling at a scan rate of 50 mV s^{-1} between 0.4 and −1.2 V vs RHE at least three times.

2.5. *Batch electrochemical HDH*

Batch electrolyses were performed galvanistatically, in the solid polymer electrolyte cell, using a FARNELL LS60-5 power supply. All electrolyses in the solid polymer electrolyte cell were carried out at constant current density, ranging from 5 to 100 mA cm^{-2}, for periods between 30 min and 5 h. The concentrations of bromide, DBP, intermediates and phenol were monitored during the electrolysis.

2.6. *Product analysis*

Bromide ions were determined using the ion analyser (Corning model 135, Corning Glass Works or Orion model 920A, Orion Research, Inc.) fitted with a combination bromide electrode (model 96-17B, Orion Research). Calibration curves were obtained using standard solutions of 5×10^{-5} to 0.025 mol dm^{-3} NaBr in pure water or in the supporting electrolyte used in the electrolysis and at the operational temperature. The calibrations were carried out before and after each experiment.

High-performance liquid chromatography (HPLC) was used to determine concentrations of DBP, monobromophenols and phenol during the electrolysis. The HPLC consisted of a P 580 Pump and a Softron 2000 UVD 170S/340S UV–Vis detector with an Econosphere C8 column (5 μm particle size and 25 cm × 0.46 cm, Alltech Associates). The wavelengths used in the HPLC measurements were determined using UV–Vis. spectroscopy (UV-160A UV–Visible recording spectrophotometer, Shimadzu, Japan). Normally, the UV detector was set to 270 nm for phenol and 290 nm for DBP and BP. The mobile phase was an acetonitrile/water mixture (52/48 by volume) with a flow rate of 1.0 mL min^{-1}. The peaks for phenol (Retention time, $t_r = 2.75$ min), BP ($t_r = 3.15$ min) and DBP ($t_r = 3.65$ min) were characterized by using standard solutions. Quantification of phenol production and distributions of the bromophenols 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, BP and DBP.

2.7. *Current efficiency and energy consumption*

The current efficiency was calculated as that part of current (or charge) passed used to convert the starting DBP to the products, that is, the bromide ions and the organic product distribution, according to Equation 1.

Energy consumption was calculated according to the following equation:

$$\text{Energy consumption (ECN)} = \frac{nFE_{\text{Cell}}}{M\varphi} \tag{4}$$

where n is the number of electrons in the reaction, F the faradaic constant (96 500 C mol^{-1}), E_{Cell} the cell voltage, M the molar mass, and φ the current efficiency of the HDH reaction.

3. Results and discussion

3.1. *Voltammetry*

Figure 2 shows typical linear sweep voltammograms (LSV) obtained using a palladised cathode in 0.05 M sulfuric acid solutions with or without DBP at the saturation concentration (10 mM). The addition of DBP to the catholyte caused an increase in cathodic current densities from −0.05 V vs SCE, compared to that observed in the blank solution. The increase in current was due to the HDH reaction and to hydrogen evolution. In particular, the rapid increase in current density at potentials more negative than −0.30 V vs SCE

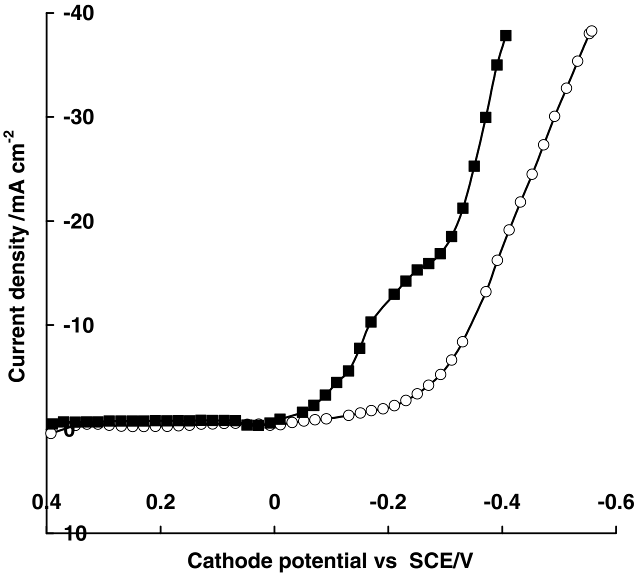

Fig. 2. Linear sweep voltammograms for hydrodehalogenation of DBP. Cell: an H-cell divided by a Nafion® 117 membrane. Cathode: Pd/Ti minimesh (2 mg Pd cm^{-2}, 4 cm^2). Anode: Pt mesh (10 cm^2). Anolyte: 0.05 M H_2SO_4 solution. Scan rate 5 mV s^{-1}. Temperature 19.5 ± 0.5 °C. Key for catholyte: (○) 0.05 M sulfuric acid, and (■) 10 mM DBP + 0.5 M sulfuric acid.

was accompanied by rapid evolution of hydrogen bubbles at the cathode. These data show that using voltammetric measurements can provide information on the HDH of DBP but cannot investigate the HDH reaction and the hydrogen evolution separately. More data to guide reactor design and process development can only be obtained from quantitative electrolysis.

3.2. *Process characteristics*

Figure 3 presents typical product distribution data and shows that 85% of the DBP was converted to phenol and bromide ions during the electrochemical HDH of 10 mM DBP after two hours using the solid polymer electrolyte cell and a palladised cathode. Such a high conversion and high selectivity demonstrates the feasibility of HDH using electrochemical reduction. It can be seen in this data that there was good correspondence between bromide ion and phenol released.

Figure 4 shows current efficiency and energy consumption data, obtained from the electrochemical HDH of 10 mM DBP using the Pd/Ti mesh cathode. As can be seen, a current efficiency of up to 98.5% was achieved. The high current efficiency, combined with the low cell voltages of the solid polymer electrolyte cell, which ranged between 1.6 and 2.5 V under the experimental conditions, led to low energy consumptions (i.e., 2.1–2.6 kW h (kg DBP^{-1}).

The above characteristics suggest that the HDH of DBP by electrochemical reduction was successful at a small scale. To achieve scale-up, the effect of operation parameters (current density, DBP concentration, supporting electrolyte and temperature, and catalyst material) have been evaluated.

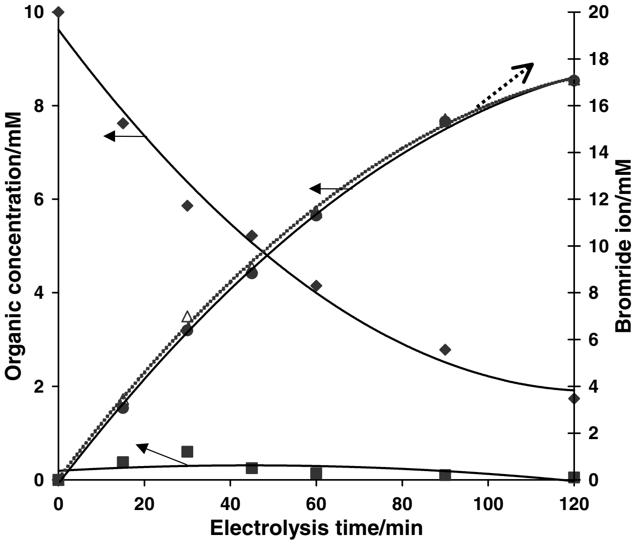

Fig. 3. Changes in bromide ion release and organic product distribution with electrolysis time for electrochemical hydrodehalogenation of DBP. Cell: solid polymer electrolyte cell divided by the Nafion® 117 membrane. Cathode: Pd/Ti minimesh (2 mg Pd cm^{-2}, 16 cm^2). Anode: Pt/Ti mesh (16 cm^2). Controlled current density: 10 mA cm^{-2}. Catholyte: 100 ml 10 mM DBP in 0.05 M H_2SO_4 aqueous solution. Anolyte: 0.05 M H_2SO_4 aqueous solution. Electrolyte flow rate: 100 ml min^{-1}. Temperature 19.5 ± 0.5 °C. Key: (◆) DBP, (●) phOH, (■) BP and (△) bromide ion.

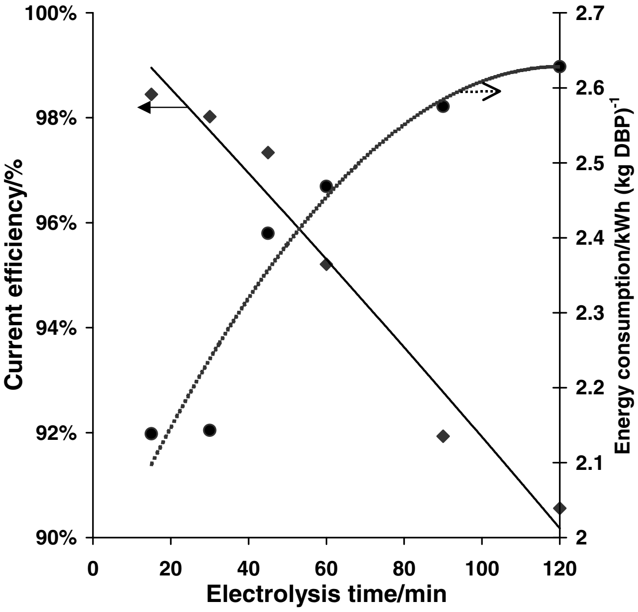

Fig. 4. Characteristics in current efficiency and energy consumption for electrochemical hydrodehalogenation of DBP. Conditions: same as those in Figure 3. Key: (◆) current efficiency and (●) energy consumption.

3.3. *Effect of operation parameters*

3.3.1. *Catalyst*

The catalyst plays a decisive role in the HDH of DBP. Figure 5 shows bromide ion release obtained from three catalysed electrodes during the electrochemical HDH of 10 mM DBP. The platinized Ti mini mesh gave better

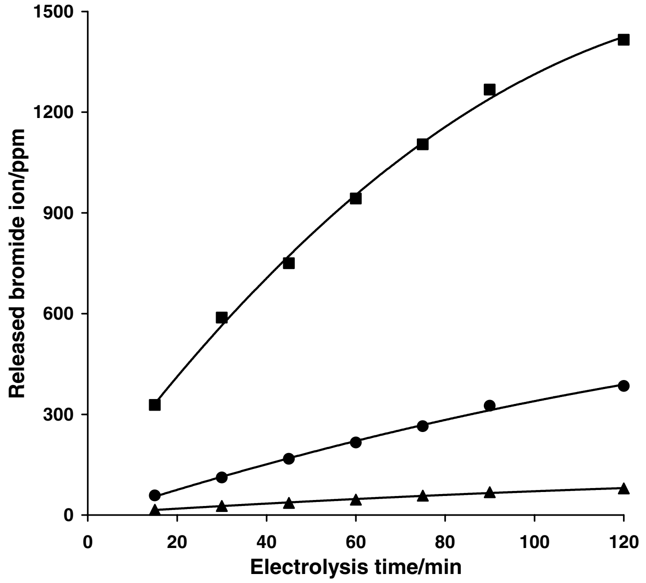

Fig. 5. Relationship between bromide ion release and electrolysis time for electrochemical hydrodehalogenation of DBP at different catalysed electrodes. Other conditions: same as those in Figure 3. Key for catalyst: (■) Pd, (●) Pt and (▲) Ni, (Ti minimesh as substrates).

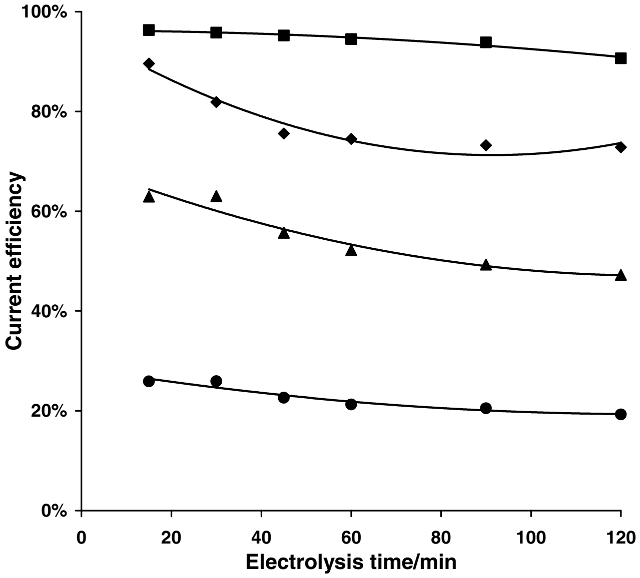

Fig. 6. Effect of current density on current efficiency during the hydrodehalogenation of 10 mM DBP solution. Other conditions: same as those in Figure 3. Key for current density: (◆) 5, (■) 10, (▲) 20 and (●) 50 mA cm^{-2}.

results than the Ni/Ti mini mesh, whereas the palladized Ti mini mesh showed an almost fourfold increase in bromide ion release compared to the platinized Ti mini mesh.

HDH is a combination of dehalogenation and hydrogenation in which hydrogen plays a key role. Both platinum and palladium are excellent materials for electrochemical production of hydrogen. More importantly, palladized cathodes are better than platinised cathodes with respect to the absorption of hydrogen into the metal lattice and maintaining a high surface concentration of hydrogen [12, 21]. Consequently, the palladised cathodes gave higher HDH rates than the platinized cathodes. In the case of Ni, poor performance may be due to Ni loading and $NiBr_2$ formation on the catalyst surface. In other previous work, nickel leaching to the groundwater was observed [22] and the strong poisoning effect during the hydrodehalogenation due to the formation of $NiCl_2$ at the Ni catalyst surface was reported [23]. The instability and the possible poisoning of the Ni catalyst may be responsible for its poorer performance, although further research is needed to understand the data completely.

3.3.2. *Current density*

Current density had a great effect on reaction rate and process efficiency of the electrochemical HDH of DBP. Figure 6 shows current efficiencies obtained during the HDH of 10 mM DBP in the solid polymer electrolyte cell with a Pd/Ti minimesh cathode. A current density of 10 mA cm^{-2} gave the maximum current efficiency, which was between 91% and 98.5%. A current density of 5 mA cm^{-2}, led to lower current efficiencies (i.e., 73% to 90%). Current efficiency decreased rapidly at higher current densities (e.g., 47% to 63% at 20 mA cm^{-2} and 19% to 26% at 50 mA cm^{-2}). The decrease was probably due to higher hydrogen gas generation in the structure of the electrode restricting the access of liquid and thus limiting mass transport of DBP to the surface of the catalyst.

The current densities effectively used for HDH at the three higher overall current densities are approximately the same, that is, $\varphi \times j \approx$ constant.

3.3.3. *DBP concentration*

The rate of HDH and the current efficiency depended strongly on the DBP concentration, as shown in the data of Figure 7, obtained in the solid polymer electrolyte cell with a Pd/Ti mini mesh cathode. The effect of an increase in DBP concentration was to increase the rate of bromide ion release and the current efficiency. From Figure 7, it can be seen that increasing the DBP concentration from 1 to 10 mM increased the bromide ion release by a factor of 4 to 6. Obviously, a higher concentration increased mass transfer of DBP to the electrode and thus increased the reaction rate. A three- to fourfold increase in current efficiency was achieved when the concentration of DBP was increased from 1 to 5 mM. A further increase in DBP concentration to 10 mM gave higher current efficiencies, for example, from 82% to 91% in 5 mM and 10 mM DBP solutions, respectively, after 2 h electrolysis.

The above results show that in the electrochemical HDH of DBP, greater bromide ion release and higher current efficiency can be achieved with the more concentrated solutions.

3.3.4. *Supporting electrolyte*

Figure 8 compares the HDH performance in terms of bromide ion release using different supporting electro-

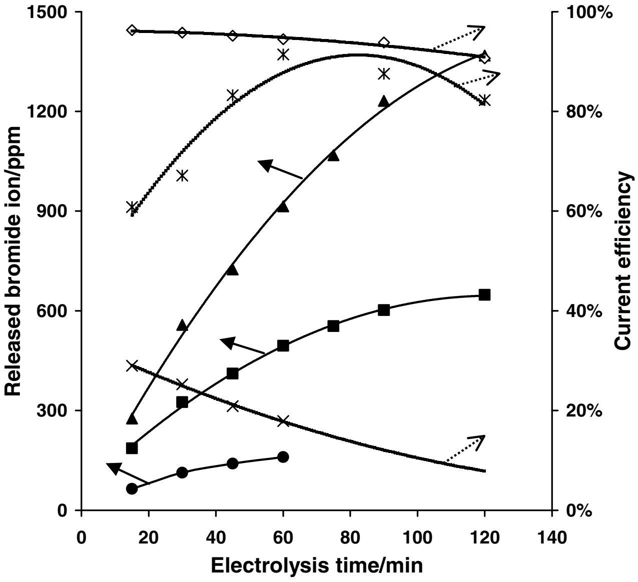

Fig. 7. Effect of DBP concentration on bromide ion release and current efficiency (CE). Other conditions: same as those in Figure 3. DBP concentration: (●) 1 mM, RBI; (■) 5 mM, RBI; (▲) 10 mM, RBI; (X) 1 mM, CE; (✻) 5 mM, CE; (◆) 10 mM, CE.

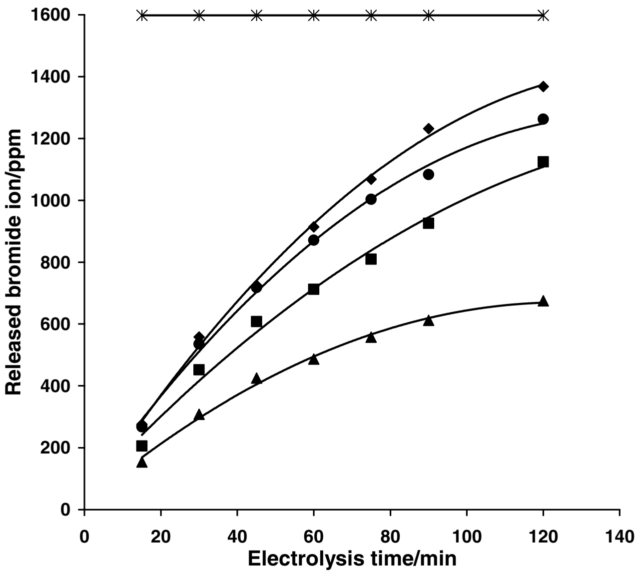

Fig. 8. Bromide ion release in different supporting electrolytes during the hydrodehalogenation of 10 mM DBP solution. Other conditions: same as those in Figure 3. Supporting electrolyte: (◆) 0.05 M sulfuric acid; (●) water, (■) 0.05 M sodium sulfate; (▲) 0.05 M sodium hydroxide; (✻) maximum bromide ions possible.

lytes. The HDH of DBP using the solid polymer electrolyte cell can operate as a 'zero gap' electrolysis in water (no aqueous electrolyte) and, in this work, gave better performance than that in neutral and alkaline solutions. For example, after 2 h electrolysis, 1262, 1124 and 675 ppm of bromide ions were released in water, 0.05 M Na_2SO_4 and 0.05 M NaOH solution, respectively. The highest bromide ion release was achieved in 0.05 M H_2SO_4 solution, for example, 1368 ppm from 2 h electrolysis.

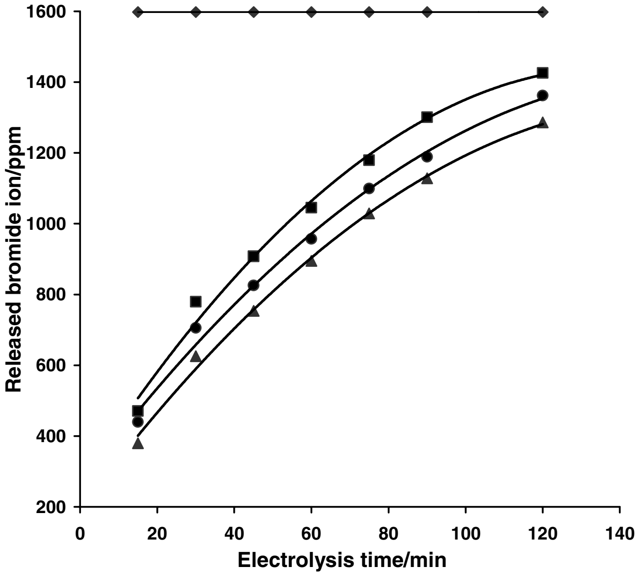

Fig. 9. Effect of temperature on bromide ion release during the hydrodehalogenation of 10 mM DBP solution. Other conditions: same as those in Figure 3. Temperature: (▲) 293.95 K, (●) 323.15 K (■) 343.15 K, (◆) maximum bromide ions possible.

It is reasonable to expect that better HDH performance can be achieved in acidic solutions, compared with other media because the acidic media can provide a better environment for the hydrogenation process.

3.3.5. *Temperature*

The effect of increasing the solution temperature above ambient on the bromide ion release during the HDH of 10 mM DBP in the solid polymer electrolyte cell using Pd/Ti mini mesh cathode is shown in Figure 9. The effect of increasing the temperature from 293.95 to 343.15 K was relatively small and only led to an increase of 10% in the bromide ion release.

4. Conclusions

(i) Electrochemical HDH is a promising method to treat wastewater containing halogenated organic compounds (such as DBP) and is much more efficient than chemical HDH. Total hydrodehalogenation of DBP can be achieved with high selectivity (up to 98%), high current efficiency (up to 98.5%) and low energy consumption (2.2 kWh kg^{-1} DBP).

(ii) The cathode material, including catalyst and substrate, had a decisive influence on HDH with respect to both reaction rate and efficiency. Palladised cathodes were much more effective for the HDH of DBP than platinized cathodes and nickel coated cathodes.

(iii) The HDH of DBP can be performed with solid polymer electrolyte cells in DBP–water solutions (no additional supporting electrolyte is required) with low cell voltages ($1.6 \sim 2.5$ V).

(iv) The best HDH performance was achieved in acidic solutions, with higher DBP concentration, at moderate current densities (around 10 mA cm^{-2}) and high temperatures. However, the optimal temperature should be selected based on a balance of HDH rate, efficiency and cost for a practical process.

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References

1. M.L. Hitchman, R.A. Spackman, N.C. Ross and C. Agra, *Chem. Soc. Rev.* **423** (1995).
2. S. Zhang and J.F. Rusling, *Environ. Sci. Technol.* **27** (1993) 1375.
3. C.S. Criddle and P.L. McCarty, *Environ. Sci. Technol.* **25** (1991) 937.
4. C. Grittini, M. Macomson, Q. Fernando and N. Korte, *Environ. Sci. Technol.* **29** (1995) 2898.
5. L.N. Zanaveskin, V.A. Averganov and Y.A. Treger, *Russ. Chem. Rev.* **65** (1996) 617.
6. M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, J.M. Marinas and F.J. Urbano, *Appl. Catalysis B: Environmental* **20** (1999) 101.
7. G.W. Reynolds, J.T. Hoff and R.W. Gillham, *Environ. Sci. Technol.* **24** (1990) 135.
8. S.F.O'Hannesin, MSc Dissertation, The University of Waterloo, Ontario (1993).
9. E.S. Creyghton, M.H.W. Burges, J.C. Jansen and H. Van Bekkum, *Appl. Catalysis A* **128** (1995) 275.
10. F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi and A. De Battisti, *J. Electrochem. Soc.* **146** (1999) 2175.
11. S.M. Kulikov, V.P. Plekhanov, A.I. Tsyganov, C. Schlimm and E. Heitz, *Electrochim. Acta* **41** (1996) 527.
12. I.F. Cheng, Q. Fernando and N. Korte, *Environ. Sci. Technol.* **31** (1997) 1074.
13. S. Zhang and J.F. Rusling, *Environ. Sci. Technol.* **29** (1995) 1195.
14. D. Schmal, J. van Erkel and P.J. van Duin, *Ichem. Symp. Ser.* No. **98** (1986) 259.
15. K. Scott, H. Cheng and P.A. Christensen, *in* E.W. Brooman, C.M. Doyle, C. Cominellis and J. Winnick (Eds) 'Energy and Electrochemical Processes for a Cleaner Environment', **PV 2001-23**, San Francisco, CA (Fall 2001), pp. 45–58.
16. H. Cheng, K. Scott and P. Christensen, *J. Electrochem. Soc.* **150** (2003) D17.
17. H. Cheng, K. Scott and P. Christensen, *J. Electrochem. Soc.* **150** (2003) D25.
18. S. Rondinini, P.R. Mussini, M. Specchia and A. Vertoya, *J. Electrochem. Soc.* **148** (2001) D102.
19. S. Rondinini, P.R. Mussini, P. Muttini and G. Sello, *Electrochim. Acta* **46** (2001) 3245.
20. H. Cheng, *PhD thesis*, The University of Newcastle upon Tyne, Newcastle upon Tyne (1999).
21. D.R. Lawson, M.J. Teirney, I.F. Cheng, L.S. Van Dyke, M.W. Espenscheid and C.R. Martin, *Electrochim. Acta* **36** (1991) 1515.
22. E.L. Appleton, *Environ. Sci. Technol.* **30** (1996) 536A.
23. Y. Cesteros, P. Salagre, F. Medina, J.E. Sueiras, D. Tichit and B. Coq, *Appl. Catalysis B* **32** (2001) 25.