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Design and operation of a solid polymer electrolyte reactor for electrochemical hydrodehalogenation

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Abstract

A solid polymer electrolyte reactor is designed for the electrochemical hydrodehalogenation (HDH) of halogenated organic compounds in oil and/or aqueous solutions. The reactor has been evaluated at 0.05, 0.1, 0.2, 1 and 2 dm^3 scales under various conditions and its effectiveness has been demonstrated experimentally using the HDH of 2,4-dichlorophenol (DCP) and 2,4-dibromophenol (DBP) as model reactions of environmental interest. The HDH of low concentration DCP and DBP in oil solutions in the reactor achieved conversions up to 35% within 3–4 h with current efficiencies up to 26%, space–time yields up to 0.70 (kg DCP or DBP) $m^{-3}\,h^{-1}$ and energy consumptions of 4.7 kW h (kg DBP or DCP)$^{-1}$. With the concentrated DCP or DBP–oil solutions, the performances were significantly improved, i.e. current efficiencies of 60–85%, space–time yields of 1.5–5.6 (kg DCP or DBP) $m^{-3}\,h^{-1}$ and energy consumptions of 1.5–2.4 kW h (kg DCP or DBP)$^{-1}$.

The HDH of DCP and DBP in the aqueous solutions was compared to the paraffin oil media and the reactor stability was evaluated for operating times of up to 170 h.

Keywords: Solid polymer electrolyte reactors; Electrochemical hydrodehalogenation (HDH); 2,4-Dichlorophenol (DCP); 2,4-Dibromophenol (DBP); Paraffin oil

1. Introduction

Halogenated organic compounds are toxic and widely distribute at many existing and former industrial sites and contaminate environment. Disposal of such compounds to landfill is now virtually precluded by environmental legislation. Incineration is an energy intensive process due to high operation temperature; it also produces harmful substances, e.g. dioxins and causes adverse public reaction. Therefore, bioremediation [1], chemical and electrochemical dehalogenation [1–3] have been investigated as alternatives.

Bioremediation has been applied to dehalogenate a wide variety of halogenated compounds using the metabolism of microorganisms [1]. 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 [3]. 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 [4].

Hydrodehalogenation (HDH) is a low-waste technology for detoxifying organic halogenated waste and regeneration of the initial raw materials [1]. Chemical hydrodehalogenation has been investigated for many years and one approach is using relatively expensive chemicals, such as $LiAlH_4$ or $NaBH_4$. However, these reagents are too expensive for treatment of wastes and considered only for preparative synthesis [5]. Chemical HDH using zero-valent metals, such as iron, zinc and tin, has been employed to remove chlorinated organic compounds from contaminated groundwater [1,2,6]. This approach faced two major problems, i.e. slow reaction kinetics and ineffectiveness for HDH of aromatic halogenated compounds under ambient conditions [4]. Catalytic HDH provides high reaction rates but it requires harsh conditions, e.g. high temperature (above 400 °C in most cases) high pressure and often experiences a rapid deactivation of the catalyst. Low temperature catalytic HDH of bromobenzene was performed using hydrogen, e.g. at 40 °C, but the results and other reaction conditions are unacceptable for industry [5]. Using hydrogen in large quantities causes safety concerns in industry.

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Recently, electrochemical HDH has been explored to destroy halogenated organic wastes [7–10]. A typical example is the HDH of 1,2,3,5-tetrachlorobenzene (TCB) and chlorobenzene (CB) in methanol or dimethylsulphoxide and acetonitrile (with 0.25 M tetraethyl ammonium bromide) at a cathode potential of—3.3 V versus Ag/AgCl [8]. 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 majority of work in electrochemical hydrodehalogenation concentrated on mechanistic analysis rather than practical applications. Some work used environmentally unacceptable materials, such as Hg and Pb, as cathode materials [8]. Therefore, it is highly required to develop an environmentally-benign hydrodehalogenation technology to attract industry. As a promising method, hydrodehalogenation by electrochemical reduction has been studied and its effectiveness has been demonstrated in this laboratory using chlorophenols [11–14]. The core of the HDH technology was to use a solid polymer electrolyte reactor (SPER), which has long been used in organic electrosynthesis where electrochemical reactions take place in non-conductive media by using ion exchange membranes as solid electrolytes [15–17]. The SPER has not been used for HDH of wastes containing halogenated organics before. As a continuation of our work to improve the electrochemical hydrodehalogenation (HDH), the solid polymer electrolyte reactor design has been improved in order to scale-up the electrochemical HDH process to a potential commercial stage.

There are many factors should be addressed to design a suitable reactor for an electrochemical hydrodehalogenation (HDH) process. The reactor should have a good current density distribution, in order to achieve a high selectivity together with a reasonable production rate. It is necessary to keep a high and uniform rate of mass transport. These targets should be achieved in a popular HDH environment, i.e. treating low or non-conductive media with low reactant concentrations at moderate current densities. A simple design will greatly benefit low capital and running costs, a safe and convenient operation and an easy maintenance at long intervals.

The above requirements can be realised by using a solid polymer electrolyte reactor, particularly using three-dimensional catalysed mesh electrodes, which guarantee a high ratio of the electrode surface area to the electrolyte volume and meanwhile maintain modular arrangement. This paper will detail the related efforts.

2. Design details

2.1. Basic considerations

Based on principles of electrochemical engineering [19,20], the general target of this work is to achieve high reaction rates, high process efficiency and low energy consumption. Since many industrial wastes contain a noticeable content of halogenated organic compounds such as PCB and phenolic compounds, which consist of low- or non-conductive media, it is crucial to achieve a reasonably low reactor ionic resistance for a practical HDH process. The previous work [11–14] proved the feasibility of applying a solid polymer electrolyte technology to treat halogenated organic wastes in aqueous solutions. However, conventional electrolysis, including the reactor used in [11–14], cannot be directly used to treat non-conductive systems, e.g. oil solutions, due to their very high media resistance. For example, our initial experiments demonstrated that HDH in oil media could not be carried out in a solid polymer electrolyte reactor under reported conditions, although it showed effective performance in aqueous solutions [11–14]. Therefore, special attention was paid to reduce cell resistance during HDH in oil solutions. The resistance was significantly reduced using dilute acid anolytes. In addition, electrode materials with high catalytic activity, high conductivity and open structure was used in a solid polymer electrolyte reactor to deliver most of the requirements as a prototype HDH reactor.

The choice of materials for the reactor was governed by stability, machinability of the surface to a flexible channel fabrication and corrosion resistance to possible aggressive conditions, which may be particularly severe when the reactor is fed with streams of oil catholyte and acid anolyte.

2.2. Solid polymer electrolyte reactor

Fig. 1(a) shows the working principle of a solid polymer electrolyte reactor where anolyte and catholyte chambers are separated by an ion exchange membrane. Porous electrodes are attached to each face of the membrane, forming a membrane–electrode assembly (MEA). Electrochemical reactions occur at the interfaces between the ion exchange membrane and electrochemically active layers of the electrodes. For example, if a cation exchange membrane such as Nafion® is selected, electrogenerated protons (H^+ ions) migrate through the membrane under the influence of the applied electric field. These protons are involved in the hydrogenation reaction or reduced to atomic and molecular hydrogen at the cathode. The membrane is used as a reactor separator and as a conductive electrolyte, so sufficient conductivity of the reactor is realised without other supporting electrolytes. In this way, the model reactions, HDH of DCP and DBP, can effectively occur at cathode in an electrolyte solution, in pure water and in a non-conductive medium, e.g. paraffin oil:

$$\mathrm{Cl_2C_6H_3OH(DCP)} + 2e^- + H^+ \rightarrow \mathrm{ClC_6H_4OH(CP)} + Cl^- \tag{1a}$$

$$\mathrm{ClC_6H_4OH(CP)} + 2e^- + H^+ \rightarrow \mathrm{C_6H_5OH(phenol)} + Cl^- \tag{1b}$$

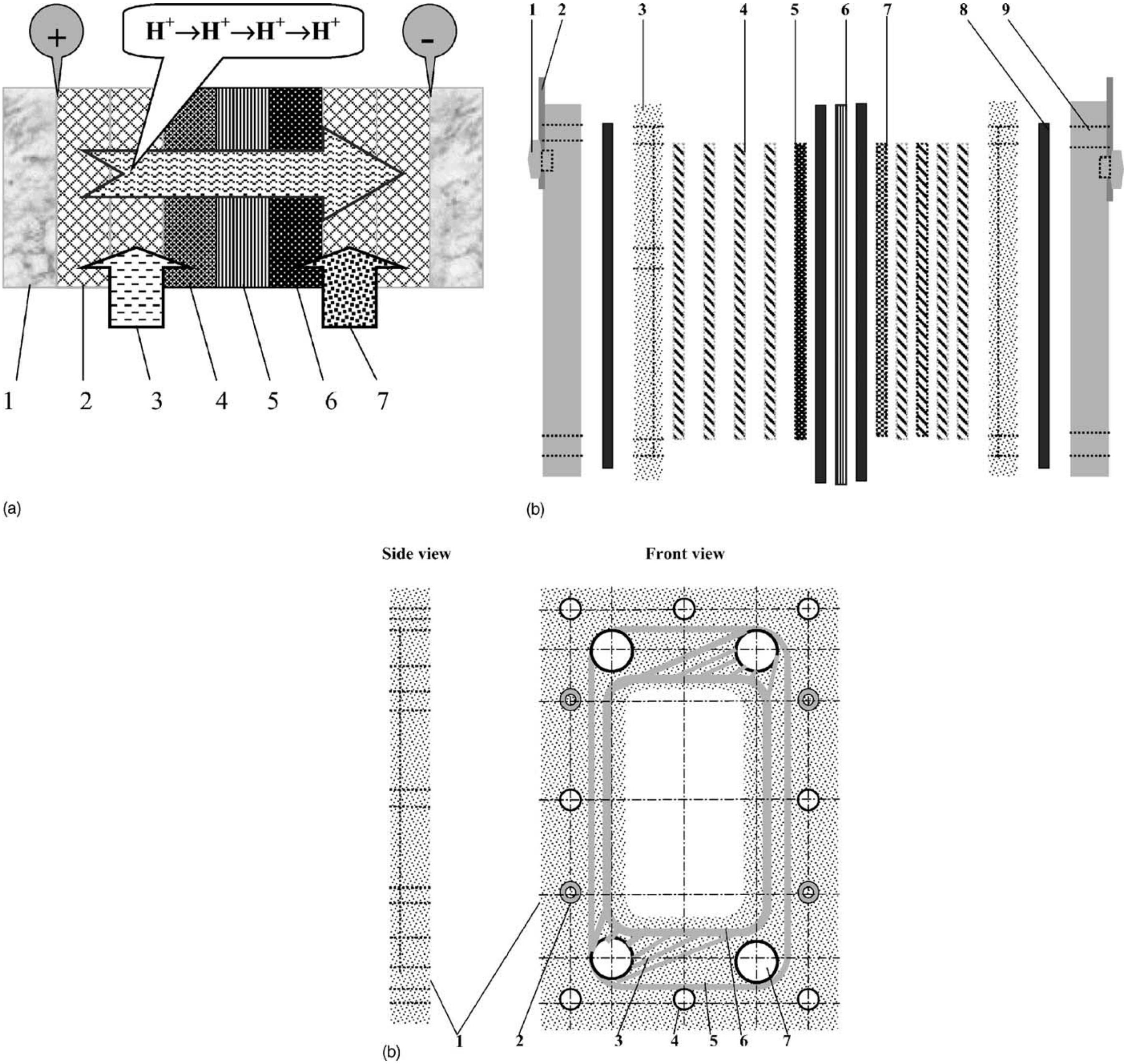

Fig. 1. (a) Principle of the solid polymer electrolyte HDH technology. (1) Stainless steel plate; (2) conductive mesh; (3) anolyte; (4) anode; (5) membrane (solid polymer electrolyte); (6) cathode; (7) catholyte (halogenated organic compounds–oil). (b) Side view of the elements in the solid polymer electrolyte HDH reactor. Screw for the current collector. (2) Electrode terminal; (3) PTFE gasket; (4) stainless steel mesh; (5) cathode; (6) membrane; (7) anode; (8) rubber soft gasket or sealing ring; (9) electrolyte inlet and outlet. (c) Front and side views of PTFE hard gasket of the solid polymer electrolyte reactor for the electrochemical HDH process. (1) PTFE hard gasket; (2) holes for spacers (PTFE tube); (3) corrugated channels; (4) holes for screws (stainless steel); (5) channel for the sealing ring; (6) channel for stainless steel foil of the MEA; (7) electrolyte inlet and outlet.

$$\begin{aligned}&Br_2C_6H_3OH(DBP) + 2e^- + H^+ \\ &\quad \rightarrow BrC_6H_4OH(BP) + Br^-\end{aligned} \tag{2a}$$

$$\begin{aligned}&BrC_6H_4OH(BP) + 2e^- + H^+ \\ &\quad \rightarrow C_6H_5OH(\text{phenol}) + Br^-\end{aligned} \tag{2b}$$

The other reactions involved in the hydrodehalogenation reactor are:

$$\text{Cathode (side reaction)}: \quad 2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

$$\text{Anode}: \quad 3H_2O \rightarrow \tfrac{3}{2}O_2 + 6H^+ + 6e^- \tag{4}$$

The overall reaction may present as:

$$\begin{aligned}\text{Overall}: \quad &X_2C_6H_3OH + 3H_2O \\ &\rightarrow C_6H_5OH + 2X^- + 2H^+ + H_2 + \tfrac{3}{2}O_2\end{aligned} \tag{5}$$

where X represents Cl or Br.

Since no separation and recycling of a supporting electrolyte is necessary in such an HDH technology, process costs can be greatly reduced.

A side view of the reactor components is shown in Fig. 1(b). Two stainless steel plates (15 cm × 10 cm × 2 cm) were used as back-plates, which provided both mechanical support and electrical contact for the MEA. One of the stainless steel plates included a probe to measure local electrode potentials. The stainless steel plates contacted two PTFE plates (with the same dimensions as those of the stainless steel plates), onto which several channels (2 mm in width, 1 mm in depth and 25 mm in length) were machined to provide the transport spaces for liquids and for gases, as shown in Fig. 1(c). The electrolyte inlets and outlets on the stainless steel plates and the PTFE plates are designed to give the required flow characteristics and the distribution patterns, and are able to accommodate most types of materials such as high surface area fibre, wool or mesh or particulate materials. In general, four layers of Ti mini mesh are fixed into the channels of the PTFE plates and contact the electrodes, which serve as both current collectors and turbulence promoters. These meshes provided the electrodes simultaneously with a homogeneous distribution of the both electric current and reactants. The spaces for these current collectors are also used as the electrode spaces when multiple layers of electrodes are used. The active area of the reactor was defined by the space on the PTFE plates. There are four holes for PTFE spacers.

The sandwiched membrane electrode assembly (MEA) of the solid polymer electrolyte reactor was obtained by hot pressing the anode and the cathodes on either side of the pre-treated membranes at 50 kg cm^{-2} and 100 °C for 3 min. The MEA had an approximate thickness of 0.6 mm and an active area of 20 cm^2. After allowing at least 24 h to condition a new MEA in the reactor at ambient temperature and atmospheric pressure with continuous feed of 0.5 M H_2SO_4 solution, the MEA was used at various operating conditions. As mentioned previously, both anode and cathode used in this work were made of Ti mini mesh. The mesh provided the electrodes at the same time with a homogeneous distribution of both electric current and reactants and a complete contact with the membrane. The MEA was positioned across the electrolyte flow paths and all edges of the MEA were sealed by the PTFE gaskets and two Tiron plastic o-rings (Cole-Parmer). In this way, the electrolytes passed through the active portions of the MEA, thereby preventing the electrolytes from channelling around or bypassing the MEA.

The end plates, the PTFE plates, the Viton gaskets and the MEA were clamped into a rigid reactor assembly (22 cm × 14 cm × 3 cm) using four PTFE spacers and eight stainless steel bolts and nuts. The clamping bolts were insulated using thin layers of Tiron rubber and a layer of silicon gel. The electrolytes passed from the reactor to reservoirs using Tiron tubing (Cole-Parmer).

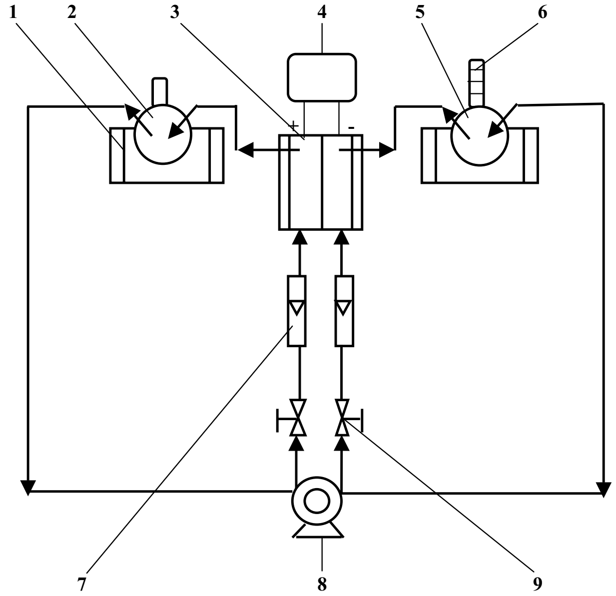

Fig. 2. Flow circuit of the solid polymer electrolyte reactor rig. (1) Heating mantle; (2) anolyte reservoir (dilute aqueous H_2SO_4 solution); (3) the solid polymer electrolyte reactor; (4) power supply; (5) catholyte reservoir (halogenated organic compounds + paraffin oil); (6) condenser; (7) flow meter; (8) two head pump; (9) valve.

The reactor system was placed in a flexible trolley, onto which three mild steel bars were welded to support the reactor. The two bars were positioned vertically with a slot on each bar to adjust heights of the third bar, on which the reactor was located.

A characteristic of the design is multi-functions of the reactor components. For instance, the stainless steel meshes served as both fluid distributor and current collector; the stainless steel plates served as end plates and current collector; the PTFE plates served as flow paths and gaskets.

2.3. Reactor rig

A compact auxiliary system was designed to constitute a reactor rig, as shown in Fig. 2. The designed solid polymer electrolyte reactor was inserted into a circulation loop consisting of anolyte and catholyte peristaltic pumps (Cole-Parmer) and reservoirs (0.1, 1 or 2 dm^3) placed in two heating mantles (Electrothermal® Flask/Funnel, Cole-Parmer). The rig was operated in a batch recirculation mode and used in both oil and aqueous media, which can be treated continuously. A glass condenser was mounted on top of each reservoir to condense organic vapour from the gases exiting the reservoir before passing through a concentrated alkaline aqueous solution. Non-condensible gases were vented to the atmosphere. In operation, catholyte and anolyte, each with a volume of 0.05, 0.1, 0.2, 1 or 2 dm^3, were pumped through the cell and then returned to the reservoirs for recycle by the pumps. Flow rate, electrolyte temperature and applied currents were controlled using the control unit.

Table 1
Design parameters of the solid polymer electrolyte reactor rig

Item	Specification
Reactor number	Single or stack (multiple reactors)
Reactor dimensions	25 cm × 15 cm × 2 cm or 15 cm × 10 cm × 2 cm for a single reactor
Active electrode area	20–200 cm^2 for a single reactor
Electrode materials	Foil, mesh, foam and particles, etc.
Solid polymer electrolytes	Nafion® or FumaTech®
Reactor block materials	Stainless steel or PTFE
Piping materials	PTFE
Gasket materials	Tiron® or PTFE
Volume of the batch of solution	0.05–10 dm^2 for a single reactor
Organic concentration	1–1000 mM
Electrolysis media	Electrolyte, water or non-aqueous or mixture
Applied current density	0.5–20 $kA\,m^{-2}$
Fluid flow rate	0.05–5 $dm^3\,min^{-1}$
Temperature	Ambient to 100 °C

2.4. Design parameters

Typical design parameters are listed in Table 1.

3. Experimental

3.1. Materials and chemicals

The following materials and chemicals were used as received: Ti mini mesh (Ti purity 99.6%, mesh size 1.5 mm, open area 37%, wire diameter 0.2 mm, Goodfellow), PTFE plate (Goodfellow), L316 stainless steel plate or foil (Goodfellow), Tiron sheet (Cole-Parmer), 2,4-dichlorophenol (DCP, 99%, Aldrich), 2- or 4-chlorophenol (CP, 99%, Lancaster Synthesis), 2,4-dibromophenol (DBP, 99%, Aldrich), 2- or 4-bromophenol (99%, Aldrich), phenol (99.9%, Aldrich), $PdCl_2$ (99%, Aldrich), H_2PtCl_6 (99%, Johnson Matthey) and H_2SO_4 (98%, AnalaR, BDH).

All oil solutions were prepared using light paraffin oil (Aldrich) and all aqueous solutions were prepared using Millipore-Q water (18.2 MΩ cm).

3.2. Electrodes

Palladised cathodes (2 mg Pd cm^{-2}, 20–100 cm^2 in the geometric area) and platinised anodes (2 mg Pt cm^{-2}, 20–100 cm^2 in the geometric area) were prepared by electrodeposition. The substrate for both electrodes was titanium mini meshes, which was made of woven metal wires having mesh apertures of 2 mm, to ensure a multiplicity of contact points between the electrodes, membrane and also providing a very open structure for delivering reactants and products. 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 boiling 37% HCl solution for 1 min, the mesh was put into the deposition cell in which a N_2-saturated deposition solution (0.02 M $PdCl_2$ or H_2PtCl_6 aqueous 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. A number of electrodes were produced and tested under identical conditions to check reproducibility. The prepared electrodes had high conductivity, open structure, uniform catalyst distribution and high activity for the HDH process, as described later. More details regarding the deposition, including pre-treatment of substrates and after-treatment of electrodes, are given elsewhere [18]. The cathodes were regenerated by thoroughly washing with acetone between two runs, to realise reproducible initial surface conditions. Change in ratio of electrode surface area to the volume of the batch of solution (α) was achieved using varying waste volumes in a reactor with fixed electrode surface area.

3.3. Batch electrochemical HDH

Batch electrolyses were performed in the solid polymer electrolyte reactor using a FARNELL LS60-5 power supply. All electrolyses in the solid polymer electrolyte reactor were carried out at constant current density, ranging from 5 to 100 mA cm^{-2}, for periods between 2 and 170 h. The longer-term testing was performed to investigate the durability of the reactor components. There were several short shutdown periods during the long-term operation to ensure continued operation of the experiments by changing the anolyte feeds. The concentrations of DCP and DBP, intermediates and phenol during the electrolysis were monitored using HPLC.

3.4. Product analysis

High-performance liquid chromatography (HPLC) was performed in a DIONEX HPLC system, which 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, Inc.). The wavelengths used in 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 DCP, DBP, 2- or 4-CP and 2- or 4-BP. The mobile phase was an acetonitrile–water mixture (52/48 (v/v)) with a flow rate of 1.0 mL min^{-1}. The peaks for phenol (retention time, t_r = 1.92 min), CP (retention time, t_r = 2.05–2.15, it was not possible to discriminate between 2- and 4-CP under the analytical conditions), DCP (retention time, t_r = 2.96 min), 2- or 4-BP (retention time, t_r = 2.20–2.30 min, it was not possible to discriminate between 2- and 4-BP under the analytical conditions) and DBP (retention time, t_r = 3.15 min) were characterised by using standard paraffin oil solutions. Quantification of the product distribution during the electrolysis was accomplished by the use of calibration curves with the authentic samples. A sample volume of 20 μL was generally employed.

3.5. Parameter definitions

Percentage of DCP or DBP removal (χ), space–time yield (γ), current efficiency (ϕ) and energy consumption (ψ) were used to evaluate the process performance and efficiency.

The percentage of DCP or DBP removal (χ) is expressed as:

$$\chi(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{6}$$

where C_0 and C_t are DCP or DBP concentrations at start and at electrolysis time t, respectively.The HDH capacity is expressed, in terms of the space time yield (kg $\mathrm{m^{-3}\,h^{-1}}$), using the following formula [19]:

$$\gamma = \frac{3600 \times \alpha \times j \times \phi \times M_{\mathrm{FW}}}{n \times F} \tag{7}$$

where α is a specific area ($\mathrm{m^{-1}}$), defined as a ratio of the electrode area to the volume of the batch of solution undergoing treatment, j the current density ($\mathrm{A\,m^{-2}}$), ϕ the current efficiency, n the number of electrons in the concerned reaction, F the Faraday constant (96,500 $\mathrm{C\,mol^{-1}}$) and M_{FW} the molar mass ($\mathrm{kg\,mol^{-1}}$).

The current efficiency was calculated as that part of current (or charge) passed to convert the starting DCP or DBP to phenol, 2- or 4-CP and 2- or 4-BP:

$$\phi_i = \frac{m_i \times n_i \times F}{q} \tag{8a}$$

where i represents phenol, 2-CP, 4-CP, 2-BP or 4-BP, m_i is quantity of the formed species i (mol), n_i the number of electrons in forming i and q the total electrical charge C.

Total current efficiency is the sum of the individual current efficiencies of forming phenol, 2- or 4-CP and 2- or 4-BP according to Eqs. (1a) and (2b), i.e.:

$$\phi = \sum \phi_i \tag{8b}$$

Energy consumption for HDH processes was calculated according to the following equation [19,20]:

$$\psi = \frac{n \times F \times E_{\mathrm{cell}}}{\phi \times M_{\mathrm{FW}}} \tag{9}$$

where E_{cell} is the cell voltage. Considering the fact that only small quantities of mono-halogenated phenols were produced during the HDH, i.e. <5%, the energies used for the HDH processes were approximated those for phenol formation, i.e. n_i and ϕ_i were used. The total energy consumption included the energies used for the HDH processes, heaters and pumps, etc.

4. Evaluation of the solid polymer electrolyte reactor

The reactor was evaluated during the electrochemical HDH of DCP and DBP in aqueous solutions and in paraffin oil.

4.1. Process capacity

High process capacity was achieved during the electrochemical HDH of DBP in paraffin oil using the designed solid polymer electrolyte reactor, particularly at a high ratio of the electrode surface area to the volume of the batch of solution undergoing treatment (α). Fig. 3 shows the space–time yield (γ) collected during the HDH of 50–1000 $\mathrm{cm^3}$ 200 mM DBP with different volumes using a Nafion® 117 membrane reactor with fixed electrode surface areas. The γ ranged between 0.3 and 7.6 (kg DBP) $\mathrm{m^{-3}\,h^{-1}}$, depending on the α-values and the electrolysis time. The data suggest that increasing α can greatly enhance the HDH rates. It is not surprising that increasing α enhanced the rate of fall in the concentration of DCP and DBP. Since α can be increased by decreasing the volume of solution (which will not effect the operation of the cell), the rate of change of concentration will naturally increase. Overall, the data demonstrate that an HDH process can be carried out using the solid polymer electrolyte reactor with high HDH rates.

Possible intermediates were identified and mono-halogenated phenols formed were below 1% of the initial DCP and DBP concentration and the amount of mono-halogenated phenols observed were less than one-tenth of the amount of

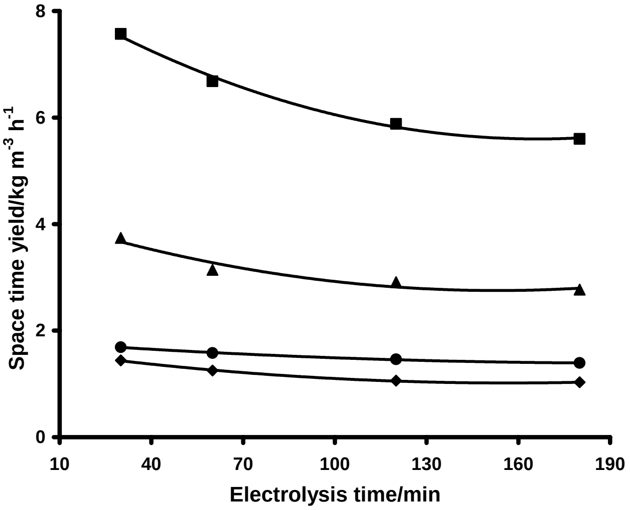

Fig. 3. Change in space–time yield during the electrochemical HDH of 200 mM DBP in paraffin oil media using a Nafion® 117 membrane reactor. Ratio of the cathode surface area to the volume of the batch of solution α ($\mathrm{m^{-1}}$): (■) 40; (▲) 20; (●) 10; (◆) 2. Cathode: three-layer Pd/Ti mini-mesh (20 $\mathrm{cm^2}$, 2 mg Pd $\mathrm{cm^{-2}}$); anode: three-layer Pt/Ti mini-mesh (20 $\mathrm{cm^2}$, 2 mg Pt $\mathrm{cm^{-2}}$); controlled current density: 10 mA $\mathrm{cm^{-2}}$; catholyte: 200 mM DBP in paraffin oil (50–1000 $\mathrm{cm^3}$); anolyte: 0.5 M H_2SO_4 aqueous solution (50–1000 $\mathrm{cm^3}$); flow rate: 100 ml $\mathrm{min^{-1}}$; temperature: 18.5 ± 0.5 °C.

phenol, suggesting that the experimental conditions favoured formation of phenol rather than mono-halogenated phenols. There was a mass balance between initial DCP or DBP, the formed mono-halogenated phenols and phenols. No other side products were detected in the catholytes or the concentrated alkaline solutions used to collect condensed organic vapour, suggesting that a high DBP concentration does not favour side reactions under the experimental conditions employed. The analysis of the possible volatiles and small molecular weight products should be considered at process scale-up stage, although no such products was detected under our experimental conditions.

4.2. HDH media

HDH process can be performed in both oil and aqueous solutions using the solid polymer electrolyte reactor. Due to the solubility restriction, only concentrations of up to 10 or 20 mM for DBP or DCP, respectively, can be treated in an aqueous solution. The HDH in paraffin oil has higher treatable concentrations, e.g. 0.2 M for DBP and 0.4 M for DCP.

Fig. 4 shows space–time yield data for the HDH of 10 mM DBP and 20 mM DCP in both the paraffin oil and in the aqueous solutions. The space–time yields observed in the aqueous solutions are significantly higher than those achieved in the paraffin oil for the DCP and the DBP, respectively. Hence, the HDH of the dilute halogenated organic compounds in aqueous solutions was faster than in the oil media.

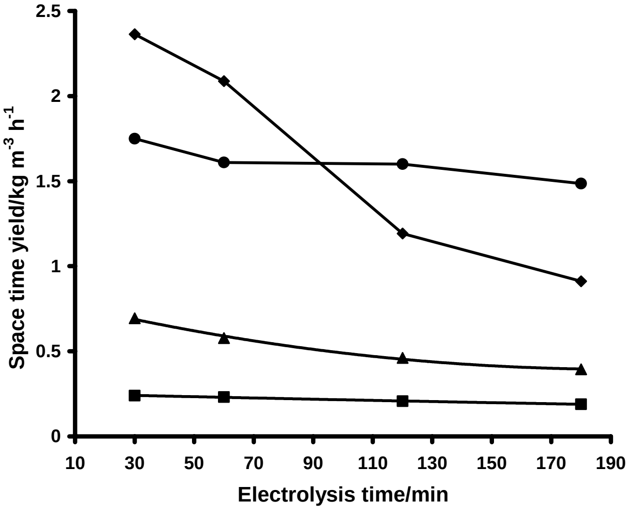

Fig. 4. Comparison of the space–time yields obtained during the electrochemical HDH of DCP and DBP in paraffin oil media and in aqueous solutions using a Nafion® 117 membrane reactor. (■) 10 mM DBP, water; (□) 10 mM DBP, oil; (●) 20 mM DCP, water; (○) 20 mM DCP, oil; cathode: Pd/Ti mini-mesh (20 cm^2, 2 mg Pd cm^{-2}); anode: Pt/Ti mini-mesh (20 cm^2, 2 mg Pt cm^{-2}); catholyte: 20 mM DCP or 10 mM DBP in paraffin oil or in water (100 cm^3); anolyte: 0.5 M H_2SO_4 aqueous solution (100 cm^3); ratio of the cathode surface area to the waste volume α (m^{-1}): 20; current density: 10 mA cm^{-2}; flow rate: 100 ml min^{-1}; temperature: 17.5 ± 0.5 °C.

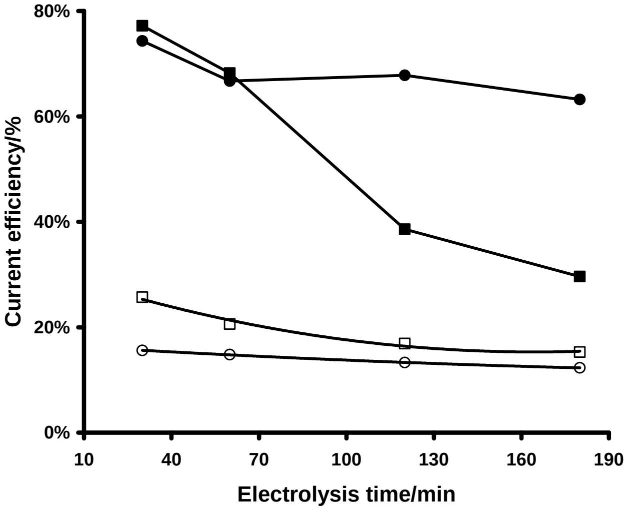

Fig. 5. Comparison of the current efficiency obtained during the electrochemical HDH of DCP and DBP in paraffin oil media and in aqueous solutions using a Nafion® 117 membrane reactor. (■) 10 mM DBP, water; (□) 10 mM DBP, oil; (●) 20 mM DCP, water; (○) 20 mM DCP, oil. Conditions: same as those in Fig. 4.

Moreover, complete HDH of DCP and DBP within 3 h were only achieved in the aqueous solutions. For instance, during the HDH of 20 mM DCP and 10 mM DBP, the percentages of DCP and DBP removal reached 100% after 3 h and 150 min electrolysis in aqueous solutions but only 17.2% for the DCP and 27.5% for the DBP in the oil solutions.

Higher current efficiencies and lower energy consumptions were observed in the aqueous solutions, compared to those achieved in the paraffin oil (Figs. 5 and 6). The current efficiencies achieved in the aqueous solutions were between 65 and 80% for the DBP and 30 and 80% for the DCP, but below 26% for the DBP and 16% for the DCP in the oil solutions. As a consequence, much higher energy consumptions were required for the HDH of DCP and DBP in the oil compared with the aqueous solutions. Additional factor for the higher energy consumptions in the paraffin oil was the higher cell voltages, about 0.3 V higher, in the oil, compared to those in the aqueous solutions.

These observations were determined by change in reactor conditions, particularly significant changes in the three phase region of the reactor (the electrode, oil and ionic media interfaces). The changes in the three phase region affected solubility and transfer of DCP or DBP, movement of hydrogen through the palladium coating into the oil phase, the electroosmotic drag of water through the membrane and the build-up of HCl product in the aqueous part of the interface, etc. Moreover, the change in DCP or DBP concentration and the accompanied side reactions, etc. affected the HDH rate and efficiency. These effects will be less significant in aqueous solution than in oil.

Although better results were produced in the aqueous solutions than in the oil systems in the dilute DCP and DBP solutions, concentrated solutions of up to 0.4 or 0.2 M for DCP or DBP can only be treated in an oil media. The

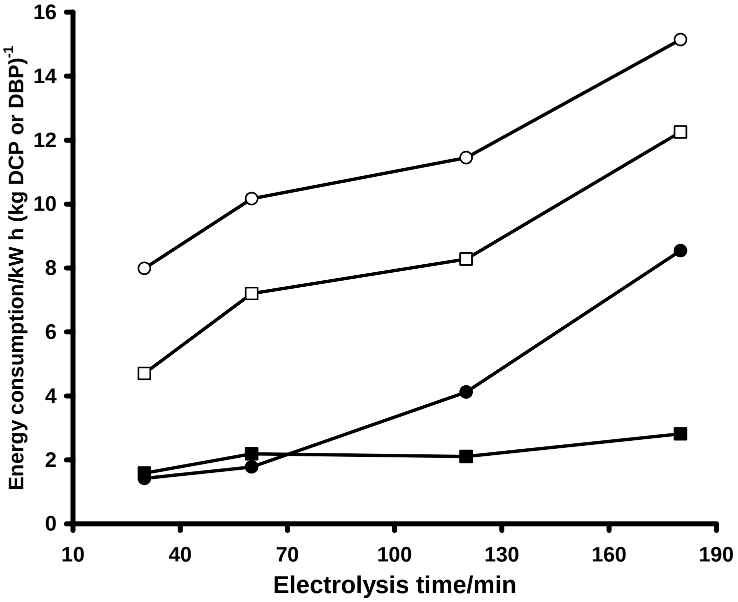

Fig. 6. Comparison of the energy consumption obtained during the electrochemical HDH of DCP and DBP in paraffin oil media and in aqueous solutions using a Nafion® 117 membrane reactor. (■) 10 mM DBP, water; (□) 10 mM DBP, oil; (●) 20 mM DCP, water; (○) 20 mM DCP, oil. Conditions: same as those in Fig. 4.

latter gave much better results than in the aqueous solutions, as shown in the previous section. This means that HDH of halogenated organic compounds in oil systems is more attractive for most industrial applications. It is possible to concentrate the dilute DCP and DBP–oil solutions then treat the concentrated oil solutions in the solid polymer electrolyte reactor. So, greater reaction rates and much higher process efficiency can be maintained in the oil solutions, compared to those realised in the aqueous solutions.

4.3. Long-term evaluation

The solid polymer electrolyte reactor was evaluated for a relatively long period of up to 170 h. In such an operation, the effectiveness and stability of the reactor will be more thoroughly assessed, particularly for the electrodes. The assessment will allow us to consider appropriate means of regeneration of the electrode surfaces if required. The long-term experiments focused on the HDH of 200 mM DCP or 150 mM DBP in the paraffin oil, using one litre of solution at current densities of 10 and 50 mA cm^{-2}.

Fig. 7 shows the data of percentage of DCP or DBP removal obtained during the HDH of 200 mM DCP or 150 mM DBP in paraffin oil. The rate of HDH decreased with time due to the decrease in DCP or DBP concentration during the HDH. In the short-duration HDH in oil solutions, higher percentages of DCP and DBP removal were achieved at 10 mA cm^{-2} than at 50 mA cm^{-2}, e.g. 17.2 and 8.8% at 10 and 50 mA cm^{-2}, respectively, after the 3 h HDH of 100 ml 20 mM DCP–paraffin oil solution. Similarly to those observed in the short-term operations, higher HDH conversions were achieved at 10 mA cm^{-2}, compared to those at 50 mA cm^{-2}, during the long-term HDH.

Tables 2 and 3 show other results from the long-term HDH of DCP and DBP. The data show that higher space–time yields and higher current efficiencies were also observed at 10 mA cm^{-2}, compared to at 50 mA cm^{-2} during the long-term HDH of DCP and DBP in paraffin oil. During the long-term HDH of the DCP or DBP, the cell voltage in-

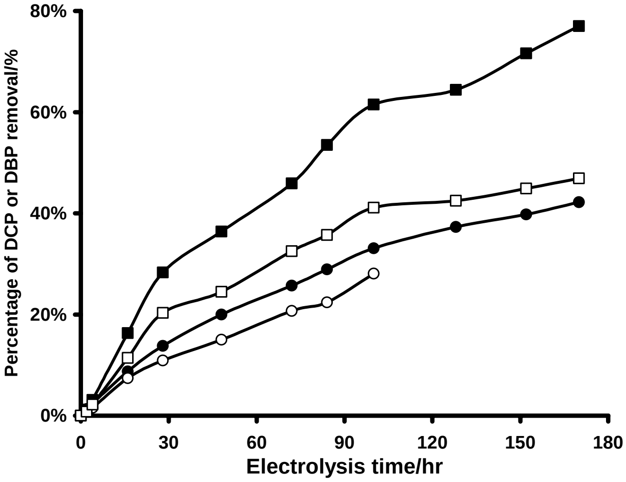

Fig. 7. Long-term evaluation on the percentage of DCP or DBP removal (PR) during the electrochemical HDH of 200 mM DCP and 150 mM DBP in paraffin oil using a Nafion® 117 membrane reactor. (■) DBP, 10 mA cm^{-2}; (□) DBP, 50 mA cm^{-2}; (●) DCP, 10 mA cm^{-2}; (○) DCP, 50 mA cm^{-2}; cathode: Pd/Ti mini-mesh (20 cm^2, 2 mg Pd cm^{-2}); anode: Pt/Ti mini-mesh (20 cm^2, 2 mg Pt cm^{-2}); catholyte: 200 mM DCP in paraffin oil (1000 cm^3); anolyte: 0.5 M H_2SO_4 aqueous solution (1000 cm^3); flow rate: 100 ml min^{-1}; temperature: 16.8–19.5 °C.

Table 2
Data from the long-term HDH of DCP[a]

Time (h)	C (mM)			χ_{DCP}(%)	γ (kg m^{-3} h^{-1})	ϕ (%)	ψ (kW h kg^{-1})	E_{cell} (V)
DCP CP phenol								
0	200	0	0	0	0	0	0	2.68[b] or 4.65[c]
170[b]	115.6	8.5	75.6	42.2	0.081	25.2	8.66	3.02
100[c]	143.8	18.5	29.4	28.1	0.078	4.1	67.1	4.18

[a] The conditions are in Fig. 7.
[b] At a current density of 10 mA cm^{-2}.
[c] At a current density of 50 mA cm^{-2}.

Table 3
Data from the long-term HDH of DBP[a]

Time (h)	C (mM)			χ_{DBP} (%)	γ (kg m^{-3} h^{-1})	ϕ (%)	ψ (kW h kg^{-1})	E_{cell} (V)
DBP BP phenol								
0	150	0	0	0	0	0	0	2.60[b] or 3.28[c]
170[b]	34.5	3.85	111.2	77.0	0.17	35.7	4.09	3.05
170[c]	79.6	7.22	61.8	46.9	0.10	4.1	47.4	4.52

[a] The conditions are in Fig. 7.
[b] At a current density of 10 mA cm^{-2}.
[c] At a current density of 50 mA cm^{-2}.

creased, e.g. from 2.68 to 3.02 V after 170 h HDH of 200 mM DCP in the paraffin oil at 10 mA cm^{-2}. The increase in the cell voltage and the decrease in the current efficiency led to higher energy consumptions during the long-term HDH. The energy consumption increased, e.g. from 2.3 to 8.7 kW h (kg DCP)$^{-1}$ after 170 h HDH of DCP at 10 mA cm^{-2}.

During the HDH process, there are significant changes in the three phase region of the reactor where the electrode, oil and ionic media meet and the HDH reactions take place. The changes in the three phase region can affect solubility and transfer of DCP or DBP, movement of hydrogen through the palladium coating into the oil phase, the electroosmotic drag of water through the membrane and the build-up of HCl product in the aqueous part of the interface. Moreover, the change in DCP or DBP concentration and the accompanied side reactions, etc. can affect the HDH rate and thus explain the above observations.

No obvious damage of the electrodes was observed after the HDH of DCP and DBP for over 400 h, indicating that the cathodes have relatively good stability during HDH operation. To satisfy the requirements of a commercial HDH process, the electrode stability will need to be examined in much longer experiments, e.g. thousands of hours, which may then require researching more effective procedures for preparation of electrodes.

Many industrial halogenated organic compounds exist in oil or as concentrated organic solutions, which are not suitable for conventional remediation, for example, by bioremediation or chemical treatment [21,22]. For such compounds, conventional electrolysis cannot be directly used due to the very high resistance of the media. For example, our initial experiments demonstrated that HDH in oil media could not be carried out in a conventional electrolytic cell. The popular disposal practice for the halogenated wastes is landfill for short chain chlorinated organics, incineration for resistant and intractable compounds such as PCBs and pesticides, which introduced severe pollution. Hence, the SPE HDH showed advantages over other methods in non-aqueous media.

It is useful to compare the solid polymer electrolyte HDH reactor with alternatives, including more conventional electrochemical, chemical and physical techniques, but this requires more data. However, at the moment, there are no literature values for treating DCP or DBP in oil using the above techniques and, thus, it is impossible to compare our data with the mentioned techniques.

5. Conclusions

The solid polymer electrolyte reactor has been successfully used to hydrodehalogenate DCP and DBP in aqueous solutions and in paraffin oil.

Conversions up to 35% were achieved for the HDH of low concentration DCP and DBP in oil solutions within 3–4 h with current efficiencies up to 26%, space–time yields up to 0.70 (kg DCP or DBP) m^{-3} h^{-1} and energy consumptions of 4.7 kW h (kg DBP or DCP)$^{-1}$. The performances were significantly improved in the concentrated DCP or DBP–oil solutions, i.e. current efficiencies of 60–85%, space–time yields of 1.5–5.6 (kg DCP or DBP) m^{-3} h^{-1} and energy consumptions of 1.5–2.4 kW h (kg DCP or DBP)$^{-1}$. No observable organic side reactions were detected in these processes.

The HDH of dilute DCP and DBP in the aqueous solutions provided better results than those achieved in the oil systems. But only solutions with low DCP and DBP concentrations, i.e. up to 20 mM for DCP and up to 10 mM for DBP, can be treated in aqueous solutions.

However, concentrated solutions of up to 0.4 or 0.2 M for DCP and DBP, respectively, can be treated in the oil media and higher HDH rates and process efficiencies were achieved in these solutions, compared with the aqueous solutions.

The long-term HDH of halogenated organic compounds in oil media, up to 170 h, displayed reasonable HDH rates and acceptable efficiency.

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