

A novel perforated electrode flow through cell design for chlorine generation

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Abstract Chlorination remains a predominant method for disinfecting drinking water. Electrogeneration of chlorine has the potential to become the favoured method of chlorine production if costs can be lowered and chlorine generation efficiencies can be improved. A novel perforated electrode flow through (PEFT) cell design has been developed to address these problems. The electrodes were made from low-cost graphite sheets and stainless steel mesh and separated by a non-conducting fabric membrane. This electrode configuration allows reduction of electrode separation to 0.1 mm or less, minimizing cell resistance and increasing electrical efficiency. The new PEFT configuration generates hypochlorite from a 0.5 mol L⁻¹ brine at a current efficiency of better than 60%. As an inline in situ device, it produces chlorine concentrations known to be sufficient to disinfect water, from chloride concentrations as low as 0.004 mol L⁻¹ (available in most natural waters) by a single pass of the water through the cell operating at 11 V. The possibility of a portable device operated by a 12-V battery is indicated.

Keywords Graphite · Perforated electrodes · Fabric membrane · Chlorine generation

1 Introduction

The electrolytic generation of chlorine species has many advantages in the disinfection of drinking water, the principal one being that onsite generation of the chlorine eliminates the transport, handling, and the storage of dangerous chlorine gas or the hazardous concentrated hypochlorite [1, 2]. The electrogeneration of chlorine process is safe, environmentally friendly, easily operated, and known to inactivate a wide range of micro-organisms ranging from bacteria to viruses and algae, the primary function of a disinfectant [2, 3]. Chlorine remains a predominant method for disinfecting drinking water as it provides both the primary and secondary functions despite the disadvantages of unfavorable taste and odor and the generation of potentially toxic chlorinated organic chlorination by-products [4–6]. Alternative processes developed to overcome these disadvantages generally do not meet the secondary function of providing a residual protection in the distribution system [3]. Active chlorine is traditionally introduced to water in the form of hypochlorite or chlorine gas. More recently, electrochemical generation of hypochlorite has been advocated [7].

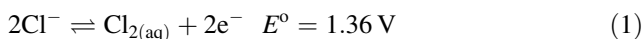
Chlorine electrogenerators are two types: undivided cell and divided cell. Undivided chlorine electrogenerators produce hypochlorite solutions (along with a gaseous mixture of oxygen and hydrogen) whereas divided cell electrogenerators produce separate chlorine and hydrogen gas streams. Undivided cells can be used in two ways: as producers of bulk hypochlorite which is dosed into water, and inline generators which produce a mixture of oxidizing species, such as free chlorine and hypochlorite, formed from the chloride dosed into a parallel side stream of the main flow. The flow through electrode configuration of the cell described in this study can be applied in both

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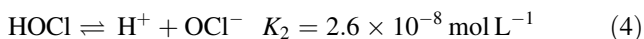
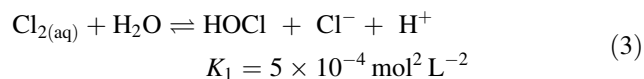
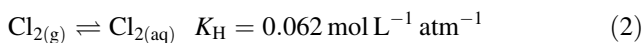
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categories and, because of its low cell constant, may allow electro-chlorination using only the chloride present in natural water.

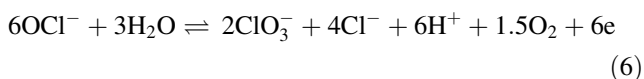
The active chlorine species are generated at the anode by reaction:



The chlorine formed, depending upon the pH, then reacts with water to form HOCl, OCl⁻, and Cl⁻ according to the equilibria (at 298 K) [8]:



Competing anode reactions are the electrolysis of water to produce oxygen, reactive oxidation products, and oxidation of the electrode. Cost effectiveness of undivided cell electro-chlorinators is limited by cell resistance which results in low-current and low-power efficiencies and the high capital costs associated with the expensive electrode materials designed to minimize oxygen production and anode oxidation [9]. The most commonly used anode materials in commercial hypochlorite production are dimensionally stabilized anodes (DSAs) of titanium coated with either oxides of ruthenium and iridium or platinum metal [1, 2, 10–12]. In addition to chlorine production, these electrodes have been reported to produce higher oxides of chlorine by chemical and electrochemical reactions (Eqs. 5–6) at increasing hypochlorite concentrations [13].



Polcaro et al. [14] report that hydroxyl radicals generated by water oxidation also produce compounds such as hydrogen peroxide, ozone, and eventually chlorites and chlorates at DSAs. Recently, interest has been shown in the use of boron-doped diamond (BDD) anodes to improve chlorine production, but this material increases the formation of the undesired oxidized chlorine products [15, 16].

Graphite, although suffering from low chlorine production current efficiencies, offers the advantages of low cost, drinking water compatibility and a lesser likelihood of the formation of more toxic highly oxidized chlorine products. Perhaps improved cell design can compensate for lower current efficiency.

A cell based on the Zappi cell [17] using porous electrodes separated by a fine non-conducting mesh offers a

way of reducing cell resistance and improving current efficiency. A key feature of the Zappi cell is the open configuration, where the treated electrolyte flows around and through the electrodes to an open chamber. Mathieson et al. [18, 19] also used a fine non-conducting mesh to reduce the distance between a corroding anode and an inert cathode in electro-flotation and electro-flocculation of waste water. Both of these systems have open configurations which do not allow inline operation.

The principal objective of this investigation was to develop an electrochemical system within a closed housing incorporating the ideas of flow through configuration and minimization of electrode separation by incorporation of a fine nylon mesh electrode spacer. The cell differs from the Zappi cell in that flow is contained within a closed configuration and from the Mathieson cell in that both electrodes allow flow through the cell perpendicular to the electrode surfaces. The cell was tested as a bulk chlorine generator (with added NaCl), and as an electro-chlorinator (with environmental concentrations of chloride) to assess feasibility for chlorine generation and electro-chlorination.

2 Materials and methods

2.1 Design of the novel perforated electrode flow through (PEFT) cell

A schematic diagram of the components of the novel flow through cell (internal diameter 90 mm) is given in Fig. 1. The cathode used was a stainless steel mesh (0.25-mm sieve size, and wire diameter 0.10 mm) cut into a disk. The anode was constructed from 2.5-mm-thick graphite sheet (Graphite Australia, No. 11, 161-163 Gympie Terrace, Noosaville, 4566, Queensland, Australia). This material was chosen because of its good electrical and robust mechanical properties, resistance to oxidation, and compatibility with drinking water supplies. The anode was perforated by drilling 1-mm holes at a hole density of 10 holes per square centimeter leaving an exposed planar anode area of 48.3 cm². Titanium wires were used as the electrical connecting leads. The membrane or electrode separator was a nylon mesh (1.0-mm sieve size, and fiber diameter 0.12 mm) giving a cell constant calculated from the cell geometry of approximately $2.5 \times 10^{-4} \text{ cm}^{-1}$. The measured cell constant was somewhat higher because of the obstruction caused by the nylon mesh and the perforated nature of the two electrodes.

The water enters into the cathodic end of the PVC outer casing and moves into the inner casing where the influent distributes evenly and moves perpendicularly through electrodes and out of the cell. The electrodes, separated by the nylon mesh, were sandwiched using the cathodic and

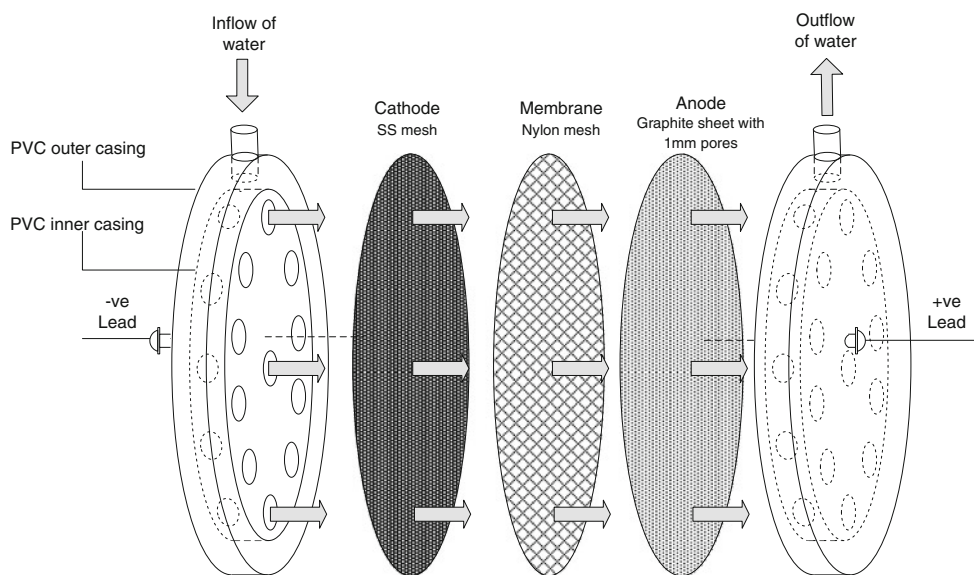


Fig. 1 Schematic diagram of an expanded view of the perforated electrode flow through electrolytic cell assembly

anodic PVC compartments held together by eight sets of stainless steel nuts and bolts. The experimental arrangement is shown in Fig. 2. The flow through cell was connected to a direct current source (Dick-Smith Electronics, 0–30 V, 5 A regulated DC power with variable current limit, input 230–240 V ac 50 Hz) through an ammeter (Fluke 73 III Multimeter) and a voltmeter (Fluke 77 Series II Multimeter) to measure the current and voltage. A variable flow peristaltic pump (Watson Marlow 504S, with regulated DC power supply) fed water to the cell, and the out flow was collected in a measuring cylinder. The pH was measured using a Mettler Toledo (Seven Easy) pH meter, and the conductivity was measured using a CyberScan100 Con. Eutech Instrument.

2.2 Chemicals and analyses

All the sodium chloride solutions were prepared by dissolving NaCl (BDH Analar reagent) in de-ionized water (conductivity $2 \mu\text{S cm}^{-1}$). Chlorine was determined by an iodometric titration [20]. Sodium iodide 10% solution (BDH Analar Reagent), sodium thiosulfate (BDH Analar Reagent) made up to concentrations of 0.1, 0.25, and 0.5 mol L⁻¹, glacial acetic acid (BDH Laboratory Reagent), and starch indicator (BDH Analar Reagent) were used as required. To avoid the escape of chlorine, the electrolyzed solution was collected into a known volume of 10% sodium iodide. The samples were immediately titrated against the standardized thiosulfate. During the electrolyte

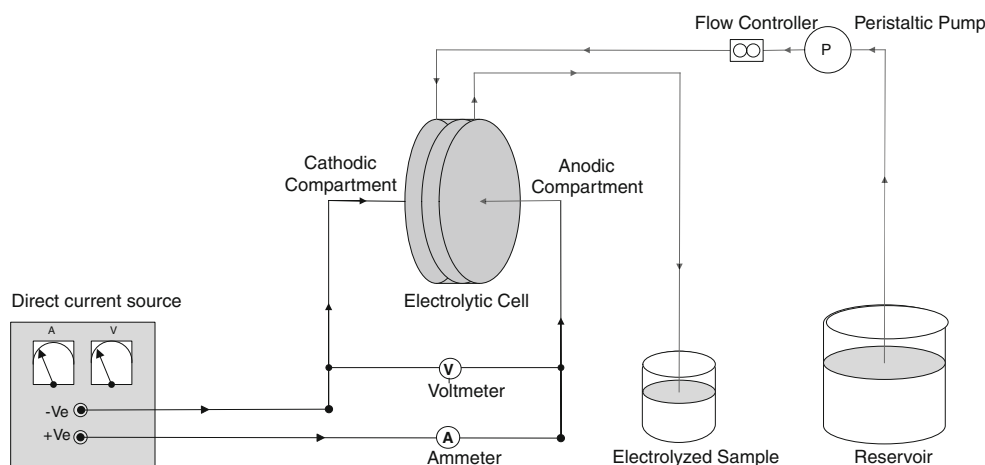


Fig. 2 Line diagram of the chlorine electrogenerator

recycling experiment, the samples were collected after successive cycles through the cell.

2.3 Characterization of cell performance

Cell performance was characterized by calculating chlorine current efficiency and power efficiency. The chlorine current efficiency was calculated using [21]:

$$CE = \frac{Q_P}{\Sigma Q} \times 100\% \quad (7)$$

where CE is the current efficiency, Q_P is the charge used forming the product, and ΣQ is the total charge consumed = It (where I is current, and t is time).

The charge used for forming the product was calculated using Faraday Equation [22]:

$$Q = NnF \quad (8)$$

where N is the number of product moles formed in time t , n is the number of electrons transferred per mole, and F is the Faraday constant.

Power efficiency or power consumption (PC) for chlorine production (specific electrical energy consumption) is the electrical energy in kilowatt hours (kWh) required to produce 1 kg of chlorine [23] and was calculated using the equation:

$$PC = \frac{EI}{qc_{Cl_2}M_{Cl_2}} \quad (9)$$

where E is the voltage, q is the volumetric flow rate, and c_{Cl_2} is the concentration of chlorine produced, and M_{Cl_2} is the molecular weight of Cl_2 .

2.4 Experimental variables

The effects of electrolyte concentration, current density, flow rate, and repeated cycling through the cell were investigated to determine optimum operating conditions and assess electrochemical efficiency.

The effect of electrolyte concentration on chlorine generation efficiency was determined by electrolyzing solutions of different NaCl concentrations at constant current density and flow rate.

The variation in current efficiency with current density was determined to assess the performance of the PEFT cell system relative to other undivided chlorine electrogenerators.

Electrolyte volumetric flow rate and flow velocity are important variables because they determine chlorine concentrations achieved. Volumetric flow rates up to 804 mL min^{-1} (effective flow velocity of 16 cm min^{-1}) were achieved using the peristaltic pump.

Recycling the electrolyzed solution provides a possible means of increasing effective chlorine concentrations. This

was investigated using NaCl concentrations of 0.5 mol L^{-1} and 250 mg L^{-1} (optimum for chlorine generation and representative of environmental levels, respectively) where the effluent from the cell was collected and then recycled.

3 Results and discussion

3.1 Effect of electrolyte concentration

The effect of electrolyte concentration on chlorine production, current efficiency, and power consumption at constant current is shown in Fig. 3. The cell performed well as a chlorine generator. At a sodium chloride concentration of 0.5 mol L^{-1} (approximating the concentration used in commercial chlorine generators [24, 25]), a current efficiency greater than the 60% considered effective in an industrial process [21] and comparable to that achieved in purpose designed cells with anodes of titanium coated with precious metals [1] was obtained.

The chlorine generation and current efficiency responses are linear with concentration at low concentration but flatten off at concentrations above about 0.5 mol L^{-1} . This behavior is consistent with transport control at the lower concentrations and electrode kinetic control at the higher concentrations. While we did not investigate their presence, oxides of chlorine higher than hypochlorite may also have been formed.

An advantage of the PEFT cell is that by operating the cell with flow from cathode to anode, the possibility of cathodic reduction of hypochlorite according to Eq. 10 [13] should be avoided.

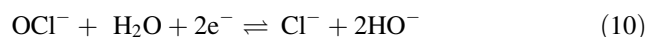


Figure 3 also gives the power consumption curve as a function of concentration. At the optimum concentration

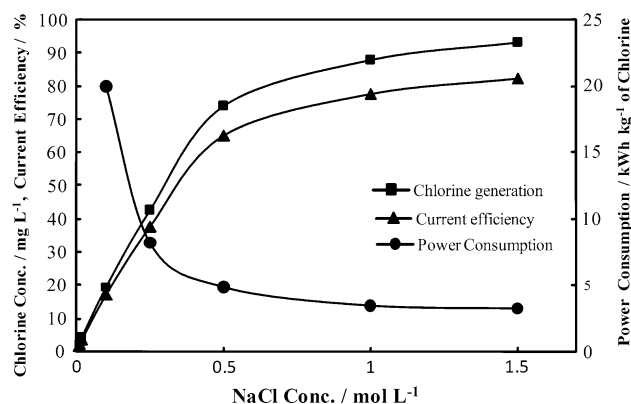


Fig. 3 Effect of NaCl concentration on chlorine production, current efficiency, and power consumption at a current density of 20 mA cm^{-2} and a flow rate of 195 mL min^{-1} in a single pass experiment

for chlorine production in the vicinity of 0.5 mol L^{-1} , bulk producers of active chlorine consume $4.8\text{--}5.5 \text{ kWh kg}^{-1}$ of chlorine [24, 25]. The power consumption results obtained at 0.5 mol L^{-1} NaCl in this study was 4.83 kWh kg^{-1} indicating that the PEFT cell, if scaled up, is capable of cost-effective commercial production of active chlorine.

3.1.1 Operation at low electrolyte concentrations

The initial linear response with NaCl concentration and the slopes of the current efficiency and chlorine production curves at concentrations below 0.5 mol L^{-1} indicate that useful chlorine production might be achieved at concentrations typical of drinking waters. The range of NaCl concentrations was thus extended down to 250 mg L^{-1} . Data for the concentration range from 0.5 to 0.004 mol L^{-1} ($29,000\text{--}250 \text{ mg L}^{-1}$) are included on Fig. 3. Linearity is maintained down to the lowest concentration, and the data appear to extrapolate through the origin. Even at the very lowest chloride concentrations used, finite chlorine production was observed. Furthermore, the chlorine concentration increased linearly with voltage from approximately 2 mg L^{-1} at 11 V to 4 mg L^{-1} at 22 V .

3.2 Effect of current density

Data for the effect of current density on production of chlorine at a flow rate of 195 mL min^{-1} and NaCl concentrations of 0.1 , 0.5 , and 1.0 mol L^{-1} are summarized in Fig. 4.

The curves for chlorine production indicate that, for current densities below 40 mA cm^{-2} , increasing NaCl concentration above 0.5 mol L^{-1} NaCl had little effect on chlorine production. However, above 60 mA cm^{-2} , the chlorine production curves at 0.5 and 1.0 mol L^{-1} diverged, possibly indicating transport limitation at the lower concentration.

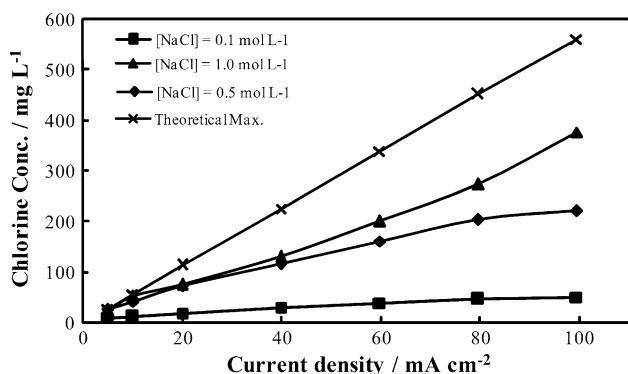


Fig. 4 Effect of current density and NaCl concentration on electro-generation of active chlorine at a flow rate 195 mL min^{-1} in a single pass experiment

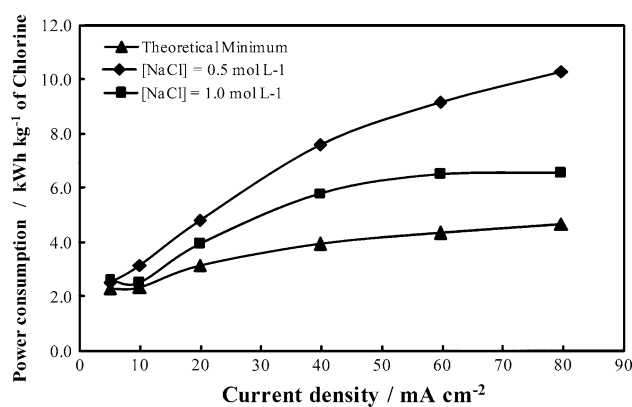


Fig. 5 The effect of current density on power consumption at 0.5 and 1.0 mol L^{-1} and a flow rate of 195 mL min^{-1} in a single pass experiment

The change in power consumption with current density at different concentrations is plotted in Fig. 5. As expected, power consumption approached the theoretical minimum at the higher NaCl concentrations where cell resistance is low, and, hence, power loss through resistive heating was less. The data show that a satisfactory power consumption less than 5.5 kWh kg^{-1} of chlorine can be achieved at current densities of up to 20 and 35 mA cm^{-2} for 0.5 and 1.0 mol L^{-1} , respectively.

3.3 Effect of flow rate

The effect of flow rate on chlorine generation is shown in Fig. 6. The current density was maintained at 20 mA cm^{-2} , and the electrolyte concentration was 0.5 mol L^{-1} NaCl. As expected, active chlorine concentration decreases with

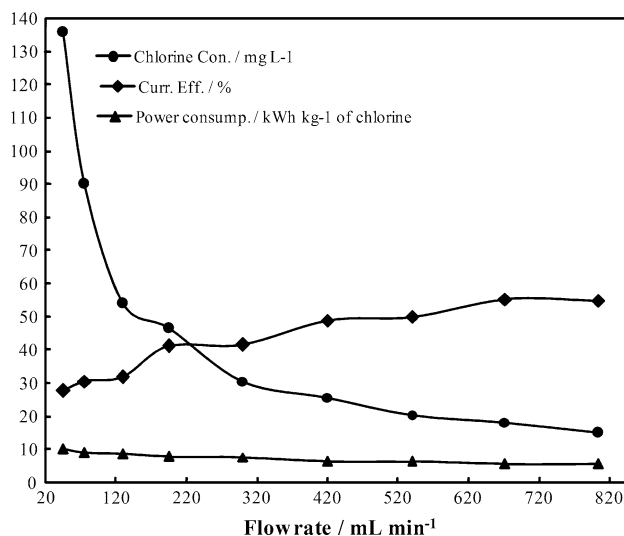


Fig. 6 The effect of flow rate on active chlorine generation at a current density of 20 mA cm^{-2} ; an electrolyte concentration of 0.5 mol L^{-1} NaCl, and with a single pass experiment

increased flow rate because of dilution. Improvement in current efficiency could be due to the improved flushing of gas bubbles from the inter-electrode space at the higher flow rates or the thinning of the diffusion layer at the anode surface.

3.4 Effect of recycling electrolyzed solution

Data for experiments in which the electrolyte was recycled through the cell a number of times are summarized in Fig. 7 and indicate that the active chlorine concentration increases linearly with cycle number. For the 0.5 mol L⁻¹ NaCl solution, a constant increment in chlorine concentration was observed whereas, for the 250 mg L⁻¹, the increment for successive recycles was approximately half the chlorine concentration produced by the initial pass through the cell. This reduced chlorine increment was probably due to chlorine loss during the time taken to recycle the solution. The power consumption for the 0.5 mol L⁻¹ concentration remained below 5.5 kWh kg⁻¹ of chlorine but increased slightly with cycle number possibly resulting from gas build-up at the electrodes.

3.5 Applications of the PEFT cell for electro-chlorination and electrogeneration of chlorine

One useful application of the PEFT cell could be the electro-chlorination of drinking water, particularly if developed as a portable device for water disinfection in times of emergency. A recent study of sodium hypochlorite (NaOCl) dosages required disinfecting household water and for disaster response water treatment revealed that

1.875 mg L⁻¹ NaOCl was 86.6% effective for samples with turbidity < 10 NTU and 3.75 mg L⁻¹ NaOCl was 91.7% effective for unimproved sources with turbidity of 10–100 NTU. The free chlorine residual criteria of <2.0 mg L⁻¹ 1 h after NaOCl addition and >0.2 mg L⁻¹ after 24 h of storage have been recommended [26]. The active chlorine produced by the PEFT cell at a chloride concentration of 250 mg L⁻¹ and a current density of 20 mA cm⁻² after one cycle was 4.88 mg L⁻¹, significantly higher than the results reported for other electro-chlorinators at similar current densities [1–3] and sufficient to provide effective disinfection. Furthermore, control of current density provides a means of ensuring that drinking water standards are not exceeded (USEPA 1980, recommend a chloride limit of 250 mg L⁻¹, and WHO drinking water standards specify a maximum permissible limit of 600 mg L⁻¹ [27]). Sufficient chlorine concentrations to effect disinfection of natural waters containing chloride concentrations 250 mg L⁻¹ and above can be achieved using the PEFT cell electro-chlorinator, without addition of salt, by a single pass of water through the cell operating at 11 V. The possibility of a portable device operated by a 12-V battery is indicated.

It is possible that the PEFT cell could be applied to the commercial production of hypochlorite solutions. Power efficiencies obtained at the bench scale demonstrate that this would be economically viable and feasible. Issues relating to the durability, scaling, and clogging of the perforated electrodes under prolonged operating conditions would need to be investigated. Acid cleaning may necessitate the use of more durable materials such as DSAs currently used commercially. Such electrodes are not incompatible with the PEFT system and could offer the advantage of even further improved efficiencies.

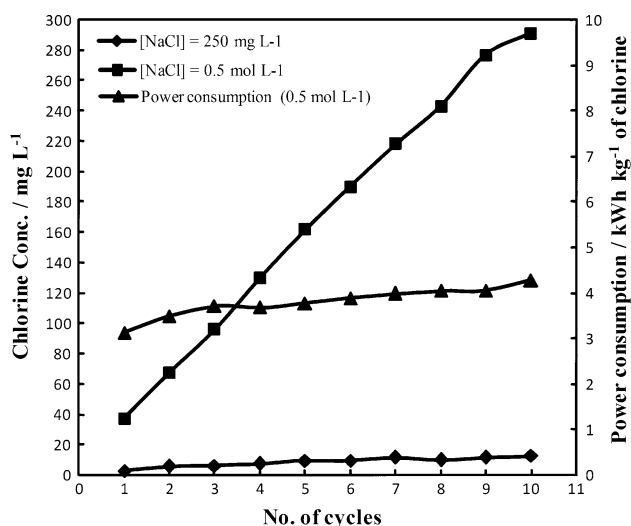


Fig. 7 The effect of electrolyte recycling on chlorine production at 0.5 mol L⁻¹ and 250 mg L⁻¹ NaCl, at a current density 10 mA cm⁻² and at a flow rate 195 mL min⁻¹

4 Conclusions

A novel, inline, perforated electrode flow through (PEFT) cell electro-chlorinator based on perforated electrodes separated by a fine non-conducting nylon mesh has been developed. The reduced resistance of this configuration has allowed low cost electrodes to produce chlorine with improved current efficiency and at lower chloride concentration. When operated with 0.5 mol L⁻¹ NaCl, commercially viable current efficiencies for chlorine production were achieved with graphite and stainless steel electrodes. When operated using water with natural levels of chloride, sufficient chlorine to effect disinfection was achieved at less than 12 V. The active chlorine concentration generated by the cell can be controlled by the current density and the flow rate. Increased flow rates probably improve current efficiency by reducing polarization effects.

The lower chlorine concentrations produced at higher flow rates can be raised by recycling.

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