

Product and by-product formation in electrolysis of dilute chloride solutions

A. M. Polcaro · A. Vacca · M. Mascia · F. Ferrara

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Abstract The results of an experimental study on electrochemical disinfection of water are presented. Attention was paid to the behaviour of chlorine compounds during electrolysis of water containing chlorides, with particular regard to the selectivity of the process towards the production of oxidising agents. Two reactor configurations were tested: a stirred tank cell and a filter press cell inserted in a hydraulic circuit. Both cells were equipped with boron doped diamond (BDD) anodes. Experiments were performed in batch and continuous mode. The effect of such operating parameters, current density, stirring rate or recirculating flow rate, on the behaviour of the process was investigated. The results at BDD anodes show that low current densities and perfect mixing of the system should be adopted in order to obtain high values of the concentration of oxidising agents avoiding the formation of such undesired by-products as chlorite, chlorate and perchlorate ions. Runs were also performed in which BDD was substituted by a commercial (Ti/RuO₂) DSA anode and the results obtained with the two materials are compared.

Keywords Active chlorine · BDD electrode · Disinfection by-products · Reactive oxygen species

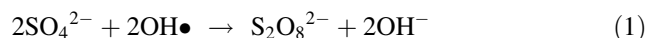
1 Introduction

Research into new and effective methods for water disinfection has provoked interest towards the direct

electrochemical treatment of natural waters. The aim of electrochemical treatment is to generate oxidising species with high bactericidal effect; these species are generally obtained by the oxidation of chloride ions which are usually present, even at low concentrations, in natural waters.

The use of boron doped diamond (BDD) electrodes for electrochemical disinfection, has been recently proposed [1]. In the last decade this anode material has attracted interest for environmental applications because of its chemical stability and the wide potential range of water stability. In the region of anodic polarisation the electrode potential reaches very high values allowing the electro-generation of hydroxyl radicals from which such reactive oxygenated species, as O₃ and H₂O₂, may be generated [2, 3].

It has also been reported that, in the presence of sulphate, peroxodisulphate is produced using this anode material [4]



BDD anodes were recently proposed to mineralise such organic compounds as phenols [5–8], dyes [9] and pesticides [10], and their effectiveness is well documented [11]: high reaction rates are observed and the process is often controlled by mass transfer of the reactant to the anode surface [12]. This anode material has also been verified in a free chlorine disinfection process [13, 14]; in this case the inactivation of bacteria was achieved by means of the reactive oxygenated species generated during water oxidation at BDD.

Although electrochemical cells equipped with BDD anodes for water treatment are commercially available, there is a lack of information about the formation of undesired inorganic by-products during the treatment of water with low chloride ion content. Recently Bergmann

A. M. Polcaro (✉) · A. Vacca · M. Mascia · F. Ferrara
Dipartimento di Ingegneria Chimica e Materiali, Università
di Cagliari, P.zza d'Armi, Cagliari, Italy
e-mail: polcaro@dicm.unica.it

and coworkers [15] highlighted the risk of formation of chlorate and perchlorate ions during electrolysis by using BDD anodes. Although, the effect of these compounds on human health is still under study, they are suspected to have health risks so that the WHO recommends very low concentrations of ClO_3^- and ClO_4^- in drinking water [16].

The aim of this work is to study the formation of products and by-products during the electrolysis of water with low concentration of chloride ions at BDD anodes in order to individuate the operating conditions which minimise the formation of undesired products: this issue is a crucial point when application of BDD anodes is extended to environmentally oriented purposes.

2 Materials and methods

2.1 Experimental apparatus and procedures

Electrochemical treatments were performed in two single compartment cells (Fig. 1):

Cell 1—Stirred batch tank electrolyser

Cell 2—Filter press electrolyser

Cell 1 was a tank ($\Phi = 6$ cm, $h = 10$ cm) equipped with four anodes (anode area $A_a = 4 \times 7.5$ cm²) and a central cathode (cathode area $A_c = 20$ cm²). Different stirring levels in the reactor were realised by means of a mechanical stirrer (impeller rotational speed from 10 to 300 rpm). The cell temperature was controlled by a thermostatic bath at 25 ± 2 °C. The volume of the electrolyte was $V = 250$ cm³. A reference saturated calomel electrode (SCE) in an outer beaker connected with a salt bridge containing 0.25 M Na_2SO_4 was used to measure the anode potential.

Cell 2 was a commercial reactor (EC Electro MP-Cell) with two parallel electrodes (anode area $A_a = 80$ cm², interelectrode gap = 0.3 cm). The cell was inserted into a hydraulic circuit in which the electrolyte was pumped by a centrifugal pump from the reservoir to the cell and back in

a closed loop. The volume of the electrolyte was 500 cm³ so that the value of the ratio between area of electrode and volume of solution was the same as that of Cell 1. Flow rate (N_R) ranged from 0.7 to 7.0 dm³ min⁻¹. Runs were carried out at constant temperature (25 °C) controlled by a heat exchanger also inserted in the hydraulic circuit.

Batch electrolyses were performed in both cells by imposing current density values ranging from 1.25 to 10.0 mA cm⁻² by means of a galvanostat (AMEL-2049). The anodic potential ranged from 2.8 to 3.1 V versus SCE when the BDD anode was used.

Continuous galvanostatic electrolyses were performed using cell 2: the solution flowed into and out of the reservoir at fixed flow rate ranging from 0.1 to 0.5 dm³ min⁻¹ by means of a peristaltic pump. The residence times in the electrochemical system ranged from 1 to 5 min. The range of imposed current densities and recycle flow rates was equal to that used in the batch experiments.

The electrolyses were carried out with solutions initially containing 100 mg dm⁻³ of Cl^- and 200 mg dm⁻³ of SO_4^{2-} in order to simulate the composition of natural waters.

2.2 Electrode materials

The anodes comprised p-type semiconducting boron-doped diamond (B concentration in the range 3,500–5,000 ppm), supplied by ADAMANT. Some experiments were also performed with cell 1 equipped with DSA anode (Ti activated with IrO_2 and RuO_2) supplied by DeNora. Stainless steel (AISI 304) was used as cathode.

2.3 Analytical methods

The concentration of total oxidising species was determined by the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method. DPD is oxidised to form a red-violet product, the concentration of which is determined reflectometrically (ASTM 4500 G). Hypochlorite concentration was determined by spectrophotometric analysis at 294 nm (Spectrophotometer VARIAN—Cary 50). Ion concentrations were measured by a Metrohm compact ion chromatograph 761 equipped with a conductivity detector and 6.1006.430 Metrosep Anion supp. 4 column, (mobile phase 2 mM NaHCO_3 /1.3 mM Na_2CO_3 , flow rate 1.5 cm³ min⁻¹). Because chloride and hypochlorite have overlapping peaks ion chromatography analyses were carried out twice: the sample was analysed first and then treated with sodium sulphite in order to reduce hypochlorite to chloride and re-analysed. The concentration of chloride was then obtained by solving the algebraic equations in which the

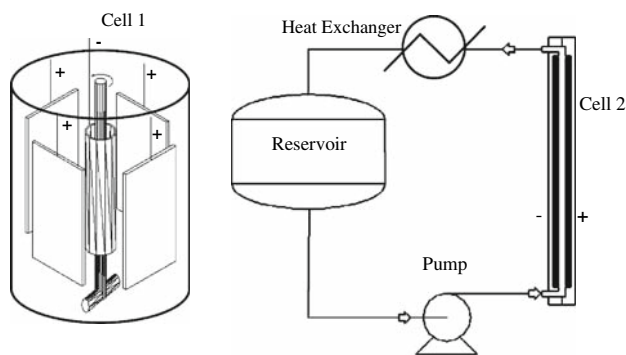


Fig. 1 Schematic view of the experimental set-up

unknown are the chloride concentration and the scale factor from peak area to hypochlorite concentration (β).

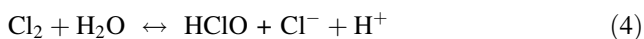
$$A_1 = \alpha[\text{Cl}^-] + \beta[\text{OCl}^-] \tag{2}$$

$$A_2 = \alpha [\text{Cl}^- + \text{OCl}^-] \tag{3}$$

3 Results and discussion

Figure 2 shows the typical trend with time of the concentrations during batch electrolysis in the undivided cell with BDD anode.

The chloride concentration decreases while rapid formation of oxidizing species takes place soon after starting the experiment. The global concentration of these compounds, reported in Fig. 2 as mg dm^{-3} of active chlorine, was obtained by the DPD method, but it was not possible to determine the exact composition of the mixture of these highly oxidative species generated by the anodic process. Among the forms of active chlorine, HClO/ClO^- was analysed by the spectrophotometric method but its concentration represents, at the most, 30% of the global oxidising concentration. The mass distribution between the main active chlorine components depends on the pH of the solution through reactions 4, 5.



At the pH measured during the runs ($\text{pH} = 6.5$) the equilibrium (4) should be shifted toward the HClO formation. However, this condition may only be verified in the bulk solution. In the region near the anode the electrochemical oxygen evolution, which competes with chloride oxidation, may lower the pH of the anodic

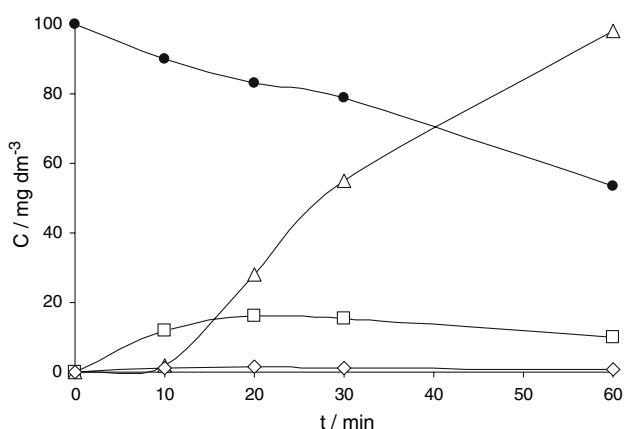


Fig. 2 Trend with time of chloride (●), chlorite (◇), chlorate (Δ) concentrations and oxidising species concentration (□) during electrolysis at BDD anodes with a solution initially containing 100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-} at $j = 5 \text{ mA cm}^{-2}$, $\text{rpm} = 300$

electrolyte layer enhancing the dissolved chlorine concentration. It has also been suggested [17] that at BDD electrodes ClO_2 may be formed, so this compound could be present in the oxidising mixture, although it was not detected in solution during our experiments.

Chromatographic analyses showed the presence of chlorine compounds other than the oxidising species. Chlorite ions were detected only in few experiments and always at low concentration. In the cell 1 only at high current density and low stirring rate were detectable concentrations of perchlorate ions found after long electrolysis times, whereas chlorate ions were found under all the experimental conditions adopted.

Figure 3 shows the trend with time of oxidant concentration during electrolyses carried out with the two reactors under different experimental conditions.

As can be seen the oxidising species show the typical behaviour of reaction intermediates: the curves present an initial increase, reach a maximum and then decrease at longer electrolysis times. We also observe that an increase in current density and stirring rate in cell 1 leads to faster kinetics of the process. A quantitative interpretation of this result is shown in Fig. 4, which shows the values of the initial flux of the oxidising species J_0

$$J_0 = \frac{V}{A_a} \left. \frac{d[\text{OX}]}{dt} \right|_{t=0} \tag{6}$$

as a function of the current density.

J_0 was calculated from the initial slope of the curves in Fig. 3: the trend of J_0 is not linear with current density. Figure 3 also shows that the higher the current density and the lower the stirring rate the faster is the depletion rate of these species.

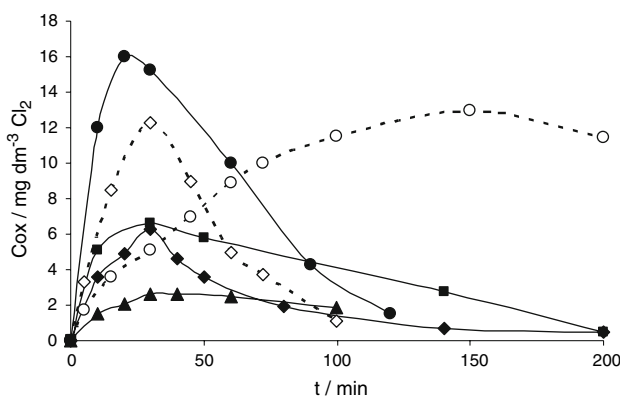


Fig. 3 Trend with time of the concentration of oxidising species during electrolyses at BDD anodes with solutions initially containing 100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-} under different experimental conditions in cell 1 (full symbols) and cell 2 (empty symbols): $j = 1.25 \text{ mA cm}^{-2}$, $\text{rpm} = 300$ (▲); $j = 2.5 \text{ mA cm}^{-2}$, $\text{rpm} = 300$ (■); $j = 5.0 \text{ mA cm}^{-2}$, $\text{rpm} = 300$ (●); $j = 5.0 \text{ mA cm}^{-2}$, $\text{rpm} = 0$ (◆); $j = 5.0 \text{ mA cm}^{-2}$, $N_R = 7.0 \text{ dm}^3 \text{ min}^{-1}$ (○); $j = 10.0 \text{ mA cm}^{-2}$, $N_R = 7.0 \text{ dm}^3 \text{ min}^{-1}$ (◇)

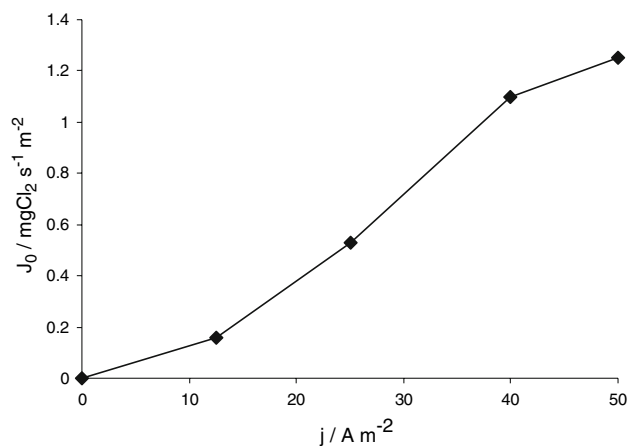


Fig. 4 Values of initial flux of oxidising species as a function of the applied current density for runs performed in cell1 at rpm = 300

Although a direct comparison between the numerical results obtained with the two cell configurations is not significant, we can observe from Fig. 3 a difference in the kinetic behaviour of the process: slower production and removal rates were obtained in the flow cell (cell 2) with respect to the stirred mechanically tank cell (cell 1).

The main product from the removal of active chlorine consisted of chlorate ion, and the highest chlorate concentrations were observed during electrolyses carried out at high current density and low stirring rate (Fig. 5).

Only in non-stirred solutions did perchlorate ions represent the main final product: as can be seen in Fig. 6; under these experimental conditions chlorates behave as intermediates and their concentration reaches a maximum.

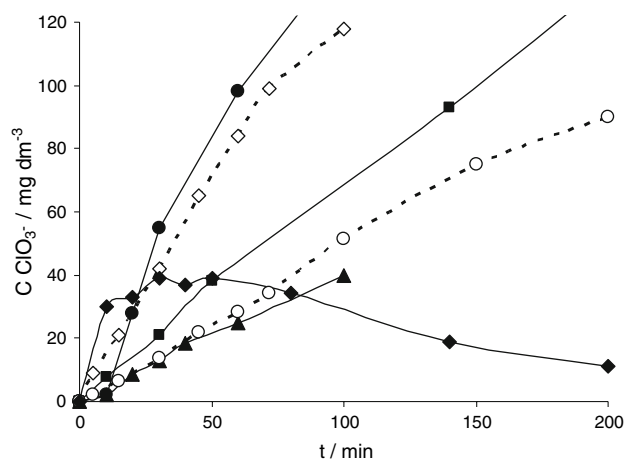


Fig. 5 Trend with time of chlorate ions concentration during electrolyses at BDD anodes with solutions initially containing 100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-} under different experimental conditions in cell 1 (full symbols) and cell 2 (empty symbols): $j = 1.25 \text{ mA cm}^{-2}$, rpm = 300 (\blacktriangle); $j = 2.5 \text{ mA cm}^{-2}$, rpm = 300 (\blacksquare); $j = 5.0 \text{ mA cm}^{-2}$, rpm = 300 (\bullet); $j = 5.0 \text{ mA cm}^{-2}$, rpm = 10 (\blacklozenge); $j = 5.0 \text{ mA cm}^{-2}$, $N_R = 7.0 \text{ dm}^3 \text{ min}^{-1}$ (\circ); $j = 10.0 \text{ mA cm}^{-2}$, $N_R = 7.0 \text{ dm}^3 \text{ min}^{-1}$ (\diamond)

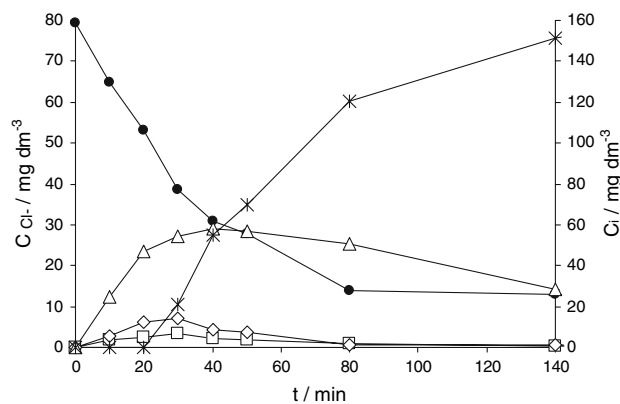


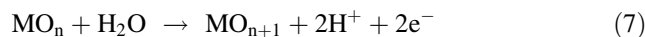
Fig. 6 Trend with time of chloride (\bullet) and products C_i (chlorite (\diamond), chlorate (Δ), perchlorate ($*$) and oxidising species (\square)) concentrations during electrolysis at BDD anodes with a solution initially containing 100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-} in cell 1 at $j = 5.0 \text{ mA cm}^{-2}$, rpm = 0

Under different experimental conditions only traces of perchlorate ions were found at long electrolysis times.

In order to analyse the effect of the anode material on the complex electrochemical kinetics of the process, electrolyses were carried out using the same electrolyte composition and the same cell only replacing the BDD anode with a commercial DSA anode (Ti/RuO_2).

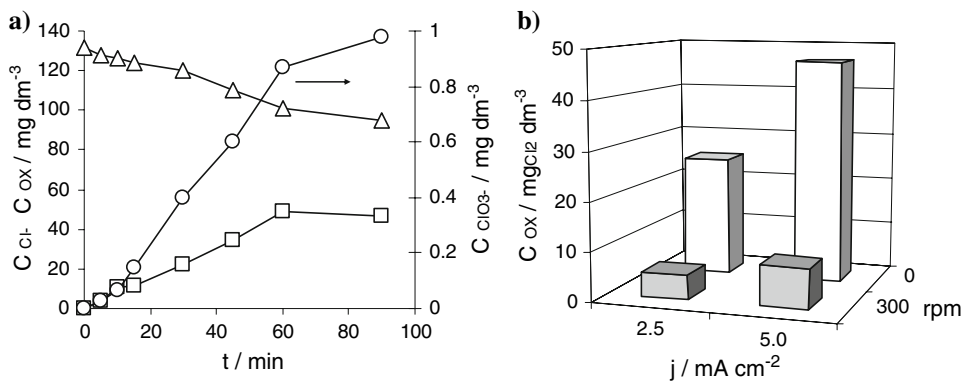
When DSA was used, experimental conditions being the same, a slower decrease in the chloride concentration was observed (Fig. 7) and the active chlorine concentration usually increased continuously until reaching a limiting value.

This limiting value increased as the applied current density increased, while high stirring rates caused a depletion in the oxidising compound concentration. Moreover during the electrolysis only small amounts of chlorate were detected, the other ions arising from chloride oxidation not being detectable. The reaction behaviour was therefore significantly different. The experimental results may be explained by considering the mechanisms of oxygen evolution reaction and chloride oxidation in dilute solution. In the case of the Ti/RuO_2 anode the oxygen evolution reaction takes place by means of the oxidation of active surface sites followed by the decomposition of superior oxide formed [18]:



Chloride ions react in a complex manner at active Ru sites to give chlorine [19] which reacts with water to give hypochlorous acid and hypochlorite, depending on the pH. The further disproportionation reactions from which chlorate and perchlorate ions are produced are very slow at 25°C . Thus, during the electrolysis with this anode, only

Fig. 7 (a) Trend with time of chloride (Δ), active chlorine (\square) and chlorate (\circ) during electrolysis at DSA anode with a solution initially containing 100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-} in cell 1 at $j = 5 \text{ mA cm}^{-2}$, $\text{rpm} = 0$; (b) values of limiting oxidising concentrations as a function of the operative parameters

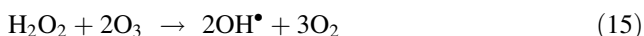


traces of chlorate were found and perchlorate ions were not detected in the solution. The positive effect on the active chlorine production caused by an increase in applied current density (Fig. 7), was observed in a previous paper [20] and was explained by considering the chloride oxidation in dilute solutions as a migration controlled process. Consequently, it can be accelerated by higher current densities. Higher stirring rate may lower active chlorine concentration thus enhancing side effects. In particular, high stirring rate may improve the stripping of dissolved chlorine as well as the rate of cathodic reduction of oxidising species which, in the undivided cell is a fast reaction controlled by mass transfer.

More complex reactions occur using the diamond electrode that weakly adsorbs $\text{OH}\cdot$ radicals generated by water oxidation. Chemical and electrochemical reactions, involving $\text{OH}\cdot$ radicals, may produce highly oxidising compounds which diffuse to the bulk solution [21]:



The reaction of peroxide with ozone may be a source of radicals in the bulk solution:



Moreover, peroxides may also react with chlorine through a fast process which decomposes both reactants.



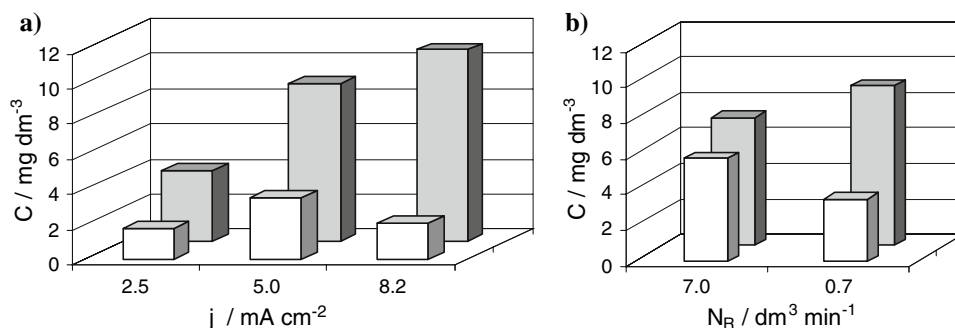
In addition, active chlorine may react with $\text{OH}\cdot$ radicals to form chlorites and chlorates. This process may cause the high chlorate concentrations always observed during experiments carried out with the BDD anode. The low

concentration of chlorite may be due to the high reactivity of this compound, according to the results obtained by Bergmann et al. during electrolysis at a BDD anode of NaClO_2 solutions: ClO_2 and ClO_3^- were found as reaction products. Perchlorate formation was also reported by the authors [15]. The reactions between reactive oxygen species and active chlorine may be the reason for the influence of the applied current density and stirring rate on the system behaviour observed during electrolysis at BDD. Higher current density may cause not only the observed initial faster production of oxidising species, but also their faster decrease since all the subsequent steps are accelerated by the high reactant concentration. Moreover, low stirring rate may lead to poor mixing so giving rise to dead zones in the reactor with local accumulation of reactants enhancing the further oxidation of active chlorine to ClO_3^- and ClO_4^- .

On the basis of these considerations the importance of the reactor configuration is evident in order to realise good mixing conditions. Since in both the reactor configurations adopted in this work the ratio between anode and cathode areas, as well as the ratio between electrode area and solution volume, were not significantly different, the performance of cell 2 may be attributed to the better homogeneity of the solution composition in comparison with the tank cell. Due to the low conversion per pass cell 2 may be considered as a differential reactor, inserted in a loop with a well mixed reservoir.

A set of experiments was also carried out using the flow cell operating in continuous mode with a BDD anode. The composition of the inlet stream (100 mg dm^{-3} of Cl^- and 200 mg dm^{-3} of SO_4^{2-}) was equal to that used in the discontinuous electrolyses. Under the selected operating conditions ($2.5 \text{ mA cm}^{-2} \leq j \leq 8.2 \text{ mA cm}^{-2}$; $0.7 \text{ dm}^3 \text{ min}^{-1} \leq N_R \leq 7.0 \text{ dm}^3 \text{ min}^{-1}$) only oxidising compounds and chlorates were found in the outlet stream at steady state. Using a short residence time ($\tau \leq 2 \text{ min}$) little influence of operating conditions was observed. In all the experiments concentrations of oxidising species close to 1.5 mg dm^{-3} active chlorine and 1.7 mg dm^{-3} of chlorate were measured.

Fig. 8 Effect of current density at $N_R = 0.7 \text{ dm}^3 \text{ min}^{-1}$ (a) and recycle flow rate at $j = 5 \text{ mA cm}^{-2}$ (b) on the steady state concentrations of oxidising species (\square) and chlorates (\blacksquare) in the outlet stream during continuous electrolyses at BDD anode. $\tau = 5 \text{ min}$



Appreciable effects of experimental conditions were observed as the residence time in the cell increased (Fig. 8a, b). As can be seen in Fig. 8a, with a residence time of 5 min and a recycle flow rate of $0.7 \text{ dm}^3 \text{ min}^{-1}$, a concentration of chlorates increasing with the current density was observed, while the concentration of oxidising compounds reached its maximum when an intermediate value of current density ($j = 5.0 \text{ mA cm}^{-2}$) was used. Figure 8b shows that higher recycle flow rates produced an increase in the concentration of oxidising species and a decrease in that of chlorate.

4 Conclusions

The results supply useful information about the dependence on the operating conditions of the formation of inorganic disinfection products and by-products during the direct electrolysis of natural water with low chloride concentration at BDD or DSA anodes. The mechanism of formation of oxidising compounds and the reaction behaviour differs significantly at mixed oxide and diamond electrodes. In particular, a higher formation rate of ClO_3^- and ClO_4^- from active chlorine was observed at BDD compared with DSA anodes. Experimental electrolyses at BDD electrodes indicate that under selected conditions, a sufficient concentration of strongly oxidising compounds may be obtained for water disinfection and, at the same time, low concentration of by-products having high health risk are produced.

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