

Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes

Simonetta Palmas · Anna Maria Polcaro ·
Annalisa Vacca · Michele Mascia · Francesca Ferrara

Received: 14 March 2007 / Revised: 4 July 2007 / Accepted: 4 July 2007 / Published online: 28 July 2007
© Springer Science+Business Media B.V. 2007

Abstract Results are reported of an investigation of the oxidation products formed during electrolyses of aqueous solutions of NaCl, in which the initial concentration of chloride ions was maintained at levels normally present in natural waters. The Design of Experiments (DOE) technique has been used effectively to plan a framework of experiments, in which the main operative parameters: current density, electrolyte stirring rate, and cell geometry, were varied at two levels. Their effects, as well as their possible interactions have been evaluated on the yield of chloride oxidation and on the selectivity of the reaction towards the formation of hypochlorite.

Keywords BDD · Chloride oxidation products · DOE · Electrochemical disinfection · Water treatment

Nomenclature

A_a	Anode area (m^2)
A_c	Cathode area (m^2)
C_i	Concentration of species i ($mol\ m^{-3}$)
C_i^0	Initial concentration of species i ($mol\ m^{-3}$)
F	Faraday constant ($C\ mol^{-1}$)
I	Current intensity (A)
j_a	Anodic current density ($A\ m^{-2}$)
n_i	Moles of species i (mol)
S	Selectivity (–)
S_0	Selectivity evaluated when $30\ C\ dm^{-3}$ passed through the cell (–)
t	Time (s)

v	Electrolyte flow rate ($m^3\ s^{-1}$)
V	Volume of the electrolyte (m^3)
α	Ratio between cathode and anode areas (–)
Φ_{Cl^-}	Yield of Cl^- removal (–)
$\Phi_{Cl^-}^0$	Yield of Cl^- removal evaluated when $30\ C\ dm^{-3}$ passed through the cell (–)
ν	Electrolyte stirring rate (rpm)

1 Introduction

The catalytic activity of boron doped diamond (BDD) electrodes in electrochemical oxidation processes has been demonstrated widely under different experimental conditions and for different water compositions [1–8]. The high overpotential for oxygen evolution and the low adsorption density of OH radicals onto the BDD surface, allow favourable conditions for effective oxidation: a very high concentration of OH radicals can be reached in a thin liquid film near the electrode surface where the organic compounds are mineralised with high faradaic yield.

Depending on the inorganic salts contained in the water long lived oxidising agents may be electrogenerated at BDD surfaces and diffuse towards the bulk solution, increasing the overall oxidation rate. In particular chlorides are worth considering, since chloride salts are usually found in the waters, as in the case of wastewater from leather or dyes industries, and in ground waters, although at lower concentration levels.

Previous work carried out in our laboratory demonstrated the possibility of using BDD electrodes also for disinfection processes: pathogens such as *Escherichia coli* ATCC 25922, *Enterococcus faecalis* AN39, and a mixture of *coliforms*,

S. Palmas (✉) · A. M. Polcaro · A. Vacca ·
M. Mascia · F. Ferrara
Dipartimento di Ingegneria Chimica e Materiali, Università degli
Studi di Cagliari Piazza d'Armi, 09123 Cagliari, Italy
e-mail: sipalmas@dicm.unica.it

typically selected as indicators of water contamination, were removed rapidly from synthetic solutions, also in the absence of chlorides [9]. However, when a practical application of this process is concerned the presence of chlorides should be considered. In this case oxidation must be performed under controlled conditions in order to avoid the formation of toxic by-products. In the presence of such organic micropollutants as humic and fulvic acids, which are commonly found in ground waters, trihalomethanes and halo-acetic acids may be produced that can represent a chemical risk for public health. Under uncontrolled conditions, chlorite and chlorate and perchlorate may also be produced, affecting the hypochlorite yield from chloride oxidation, which is the only effective disinfecting agent; moreover, due to their toxicity, their concentration levels in drinking water are regulated by legislation [10].

The literature reports different situations that give rise to different distributions of oxidation products: in some cases, the formation of ClO_3^- and ClO_4^- has been reported [1, 11, 12], whereas other authors indicate hypochlorite as the main oxidation product of chloride [13–15]. However, the problem is still open because a very large number of factors may influence the nature and distribution of the different oxidation products of chlorides. Current density, electrolyte flow rate, initial concentration of chlorides, material and dimensions of the electrodes, have been reported as determining parameters [15].

In order to evaluate the effects of the several parameters on the process a very large number of experiments is required if a classic approach is adopted in which the value of one separate factor at a time is changed until no further improvement is accomplished.

In such complicated systems the analysis of the effects can be done more conveniently by means of the Design of Experiments (DOE) technique. A detailed description of this technique is beyond the scope of this work (more details can be found [16]); it is worth underlining that it provides an organised approach in which the experiments are mutually connected and linked in a logical manner so that the joint influence of all the factors is assessed. A map of the system can be derived from this analysis, which can give useful indications to decide what the next experimental step ought to be.

2 Experimental section

2.1 Experimental set up

Two cell configurations were adopted for the experiments: a tank-cell and a filter-press cell. Both the cells worked in batch mode, but different electrode geometries were used, as well as different hydrodynamics achieved, in the two

systems. In both the cases, anodic and cathodic compartments were not separated. The anode material was BDD (supplied by ADAMANT; B concentration in the range 3,500–5,000 ppm) prepared by hot filament chemical vapour deposition (HFCVD) on a low resistivity silicon wafer. Graphite or nickel were used as cathode materials.

Figure 1a shows a schematic view of the tank cell, a three-electrode cell equipped with four sheets of BDD ($A_a = 4 \times 8 \text{ cm}^2$) arranged around a central cathode ($A_c = 5$ or 20 cm^2) and with a saturated calomel reference electrode (SCE). Different stirring rates (v) were achieved in the reactor up to 600 rpm by means of a magnetic stirrer. The solution ($V = 0.25 \text{ dm}^3$) was initially fed to the tank and sampled at regular intervals of time for the concentration of the ionic species.

A different cell geometry was obtained with the filter-press cell in which anode and cathode were parallel plates with an inter-electrode gap of 3 mm. The anode and cathode areas were 80 and 50 cm^2 respectively. Also, in this case the system worked in a batch mode, but in order to achieve a better mixing level in the system, the electrolyte was pumped by a centrifugal pump from the reservoir to the cell and back in a closed loop (Fig. 1b) with flow rates (v) between 1.5 and $0.1 \text{ dm}^3 \text{ min}^{-1}$. The overall volume of the electrolyte was 0.5 dm^3 . Samples for the analyses were withdrawn from the reservoir.

2.2 Solution composition

Aqueous solutions of 200 ppm Na_2SO_4 constituted the base electrolyte, to which NaCl was added up to a nominal chloride concentration of 100 ppm. No correction of the solution pH was performed: a pH value near to the neutrality or slightly alkaline (7.2–8) was always measured during the runs.

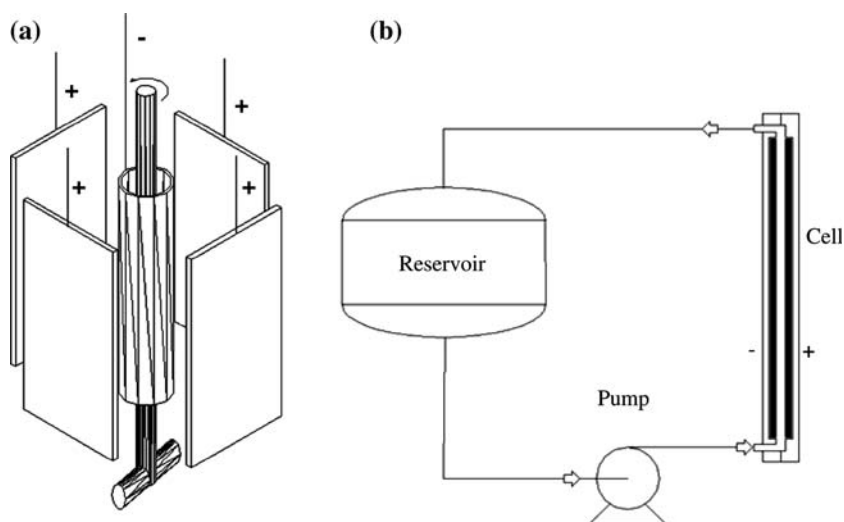
2.3 Experiments

Galvanostatic electrolyses were carried out by using a galvanostat (AMEL-2049). For both tank and filter-press cells, current density values of 31 and 62 A m^{-2} were imposed at the anode: anodic potential values of 2.9 and 3.2 V vs. SCE were measured at the two current levels.

2.4 Analyses

During the experiments, the concentrations of chloride and its oxidation products were monitored with time. Quantification of chlorine products is rather complex [11, 12, 17]: different analytical techniques must be used and their results combined in order to obtain the actual concentrations of the different compounds. DPD method (*N,N*-diethyl-1,4-phenylene diamine), ionic chromatography,

Fig. 1 Electrode arrangements in the tank cell (a) and in the filter-press cell (b)



(Metrohm compact ion chromatograph 761 equipped with a conductivity detector and 6.1006.430 Metrosep Anion supp. 4 column; mobile phase 2 mM NaHCO₃/1.3 mM Na₂CO₃, flow rate 1.5 cm³ min⁻¹) and UV spectroscopy [Varian, Cary 50] were used.

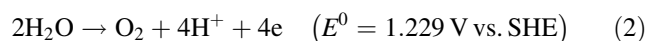
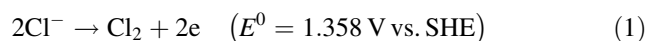
In particular, ion chromatography was used to measure the concentration of Cl⁻, ClO₃⁻ and ClO₄⁻, as well as possible variations in the SO₄⁻ concentration. Analyte identification was accomplished on the basis of the retention times, and the quantification was performed by external calibration. As far as the concentration of hypochlorite is concerned, some problems arose, since chloride and hypochlorite have overlapping peaks. As suggested by Bergmann [12], the analysis was carried out twice with and without hypochlorite elimination and the corresponding concentration values calculated by solving a mathematical set of equations. Indication on the actual concentration of hypochlorite was also derived from the UV spectrum measurements (ClO⁻ absorption peak at 292 nm) at least when its concentration was greater than 4–5 ppm.

DPD method gave a measure of the active chlorine, as global concentration of oxidising species contained in the sample: ClO⁻/HClO, ClO₂, but also H₂O₂, O₃ and peroxodisulphate can be evaluated with this measure. In our case, most of the oxidant seemed to be constituted by ClO⁻/HClO as demonstrated by the analogous concentrations of oxidant obtained from DPD method and UV spectrum.

3 Results and discussion

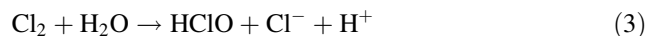
Several reaction paths and different ionic species have to be accounted for in considering the behaviour of chlorine during electrolysis. Among the possible anodic reactions

which occur during the electrolysis of an aqueous solution of sodium chloride, the discharge of Cl⁻ with consequent formation of Cl₂ (reaction 1), and the discharge of water to give O₂ (reaction 2) can be considered, the occurrence of them being dependent on the electrolysis conditions.

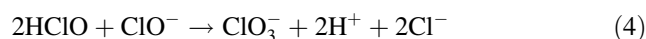


In an alkaline medium there is a predominant discharge of hydroxyl ions favouring the formation of free oxygen; in an acid medium, conditions are favourable for the evolution of gaseous chlorine; in a medium close to neutral, there is a simultaneous, approximately equivalent discharge of OH⁻ and Cl⁻ ions, favouring the subsequent chemical steps for the formation of chlorine products at higher oxidation state [18].

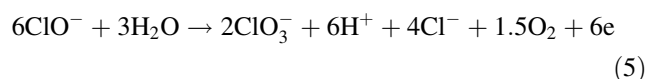
In the bulk, chlorine formed at the anode may react rapidly with water to form hypochlorous acid:



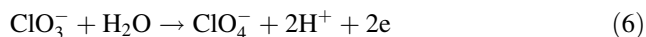
Also the formation of chlorate by a chemical reaction of the hypochlorite ion with hypochlorous acid may occur in the bulk solution when the pH is 6.0–6.5:



Moreover, when the pH is slightly alkaline, the formation of chlorate by electrochemical oxidation of the hypochlorite at the anode is also possible [18]:



Finally, when high concentrations of chlorate are achieved formation of perchlorate must also be accounted for.



The reactions reported above constitute possible routes to obtain the different oxidised chlorine products, the distribution of them being strictly connected to the operating oxidation conditions.

In the present case, during oxidation of chloride solutions, the pH always remained about neutral. In such conditions, hypochlorite and chlorate were initially detected as only reaction products, whereas perchlorate was identified at longer reaction times.

Figure 2 depicts a typical example of the trend in time of concentration of chloride and of its oxidation products measured in the tank cell used in the present work during electrolysis performed at high current density and in solution not stirred other than by H_2 evolution.

As can be seen a continuous decrease of chloride concentration down to very low value is obtained; typical trends of intermediate products are correspondingly measured for hypochlorite and chlorate formation (the maximum of their concentrations being measured at $t = 30$ and 40 min for ClO^- and ClO_3^- , respectively). After a lag time the concentration of perchlorate also started to increase and it represents the main product at the end of the process.

Different trends of reactant and products are obtained in the filter-press cell, when the same initial solution is submitted to electrolysis at low current density and high electrolyte flow rate.

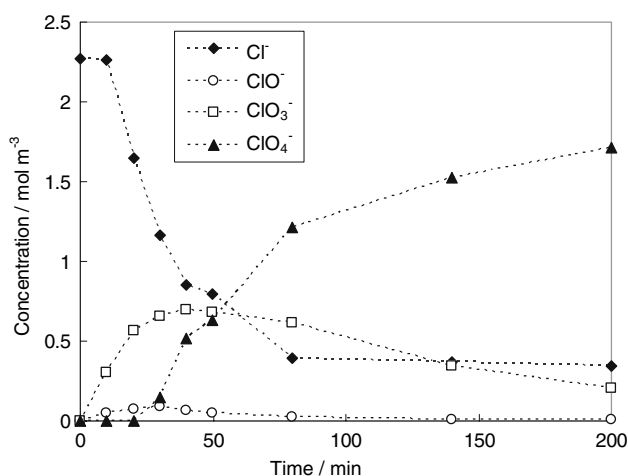


Fig. 2 Time dependence of concentrations of chloride and of its oxidation products, measured in the tank cell during electrolysis at 62 A m^{-2} in not mechanically stirred solution

In this case (Fig. 3), the concentration of chlorides tended to a value that is higher than that in the tank cell, and the formation of perchlorate was not observed even at high reaction times. On the bases of these preliminary results, a reaction mechanism can be sketched as in Fig. 4.

Several series/parallel steps of oxidation are involved which lead to increasing oxidation states of chlorine up to perchlorate. Also, the possible step of reduction of hypochlorite at the cathode was considered along with diffusion steps of the ionic species from the electrode surfaces to the bulk solution or vice versa and electromigrational transport of Cl^- towards the anode surface.

In such a complex system, the DOE technique is used to evaluate the effects of the several parameters on the process. As far as the effect of the cathode material is concerned, preliminary runs performed at Ni and graphite cathodes showed not significant differences in the trends of reactant and product concentrations measured during electrolyses carried out in the same conditions, as expected if hypochlorite reduction were transport controlled (Fig. 5). So, the following investigation focuses on the effects of anodic current density (j_a), stirring rate (v), and ratio between cathode and anode areas (α), assumed as influent parameters which are varied on two levels in a full factorial design.

Firstly the results obtained in the tank cell are considered.

Table 1 indicates the values of the different parameters at the minimum (−1) and maximum (+1) levels.

In order to have suitable system responses, the yield of Cl^- removal (Φ_{Cl^-}) and the selectivity (S) of the reaction towards the production of hypochlorite were considered:

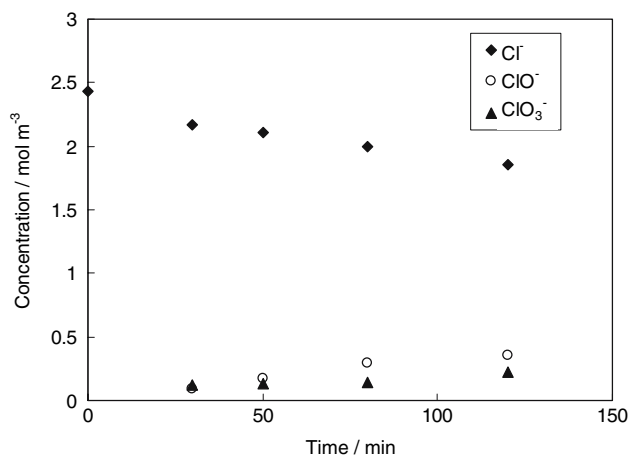


Fig. 3 Time dependence of concentrations of chloride and of its oxidation products, measured in the filter-press cell during electrolysis carried out at 31 A m^{-2} and $v = 1.5 \text{ dm}^3 \text{ min}^{-1}$

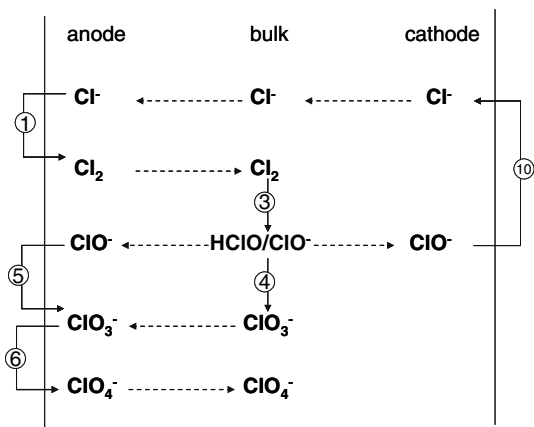


Fig. 4 Reaction path: chemical/electrochemical steps (—); diffusion/migration steps (- - -). Numbers inside circles refer to reaction numbers in the text

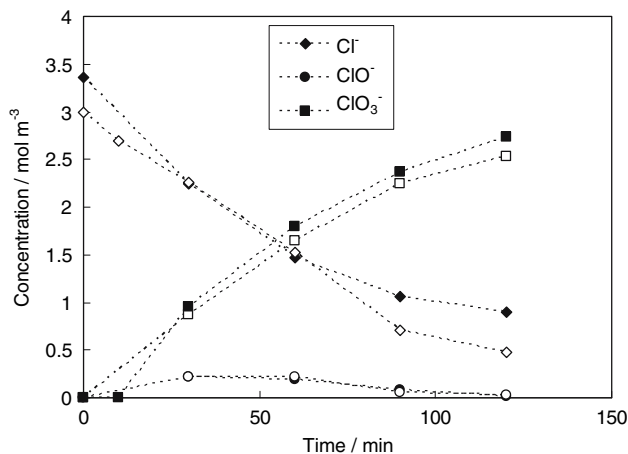


Fig. 5 Time dependence of reactant and product concentrations measured during electrolyses carried out at 31 A m⁻² in not mechanically stirred solution at Ni (empty symbols) and graphite (full symbols) cathodes

$$\Phi_{Cl^-}(t) = 2FV \frac{C_{Cl^-}^0 - C_{Cl^-}^t}{It} \times 100 \tag{7}$$

$$S(t) = \frac{n_{ClO^-}^t}{n_{Cl^-}^0 - n_{Cl^-}^t} \times 100 \tag{8}$$

Figure 6 shows a typical example of the trend with time of the two responses (Φ_{Cl^-} and S) for a run performed at

Table 1 Coded parameters for the DOE analysis

Parameter	Symbol units	Level (-1)	Level (+1)
Anodic current density	$j_a/A\ m^{-2}$	31	62
Cathode area/anode area	α	0.16	0.63
Electrolyte stirring rate	v/rpm	0	600

$j_a = 62\ A\ m^{-2}$ in not mechanically stirred solution and, as expected, they are a function of time.

For application of this technique to water disinfection only short reaction times are of particular concern: values of specific charge in the range of $10\ C\ dm^{-3}$ were sufficient to effectively kill even the most resistant bacteria [9]. Thus, the values ($\Phi_{Cl^-}^0$ and S_0) of these functions measured when $30\ C\ dm^{-3}$ of charge were passed through the cell are considered as objective functions for the DOE analysis. Table 2 shows the values of objective functions measured under different experimental conditions, as well as the relevant concentrations of the different species measured in solution.

As indicated by the technique the influence of the parameters on these functions is measured, planning the runs in which the parameters are suitably set. For a full factorial design, in which three parameters are considered at two levels, 8 runs ($N = 2^3$) are needed to evaluate the effects.

Table 3 summarises the combination of the different coded parameters and the related responses registered in the planned experiments. Equation 9 has been used to calculate the effects of the i -th parameter.

$$E_i = \bar{y}^{(+)} - \bar{y}^{(-)} = \frac{\sum_i y_i^{(+)} - \sum_i y_i^{(-)}}{4} \tag{9}$$

where $\bar{y}^{(+)}$ and $\bar{y}^{(-)}$ represent the mean of the values of the responses obtained from runs in which the i -th parameter was set at the highest (+1) and lowest (-1) levels, respectively. In order to evaluate the combined effects between two parameters $i\ j$, Eq. 9 can be still used if the related columns (ij) in Table 3 are considered to identify the maximum and the minimum levels of the combination of parameters.

Figures 7 and 8 depict the effects of the parameters and their interactions on the two responses $\Phi_{Cl^-}^0$ and S_0 , respectively, demonstrating in both the cases strong combined effects are evidenced indicating different sensitivity of the functions to the different parameters. As indicated by the technique, the main effect of a parameter should be interpreted individually only if there is no evidence that this parameter interacts with the others, otherwise the interacting parameters should be considered jointly.

Among the single effects, the most significant was the negative effect of α on the chloride oxidation yield, whereas the same parameter has to be considered along with the stirring rate when their effects on selectivity are considered. The single effect of the anodic current density appeared to be important for selectivity, whereas the combined effect of j_a and stirring rate should be considered with respect to the $\Phi_{Cl^-}^0$. Thus, the presence of these

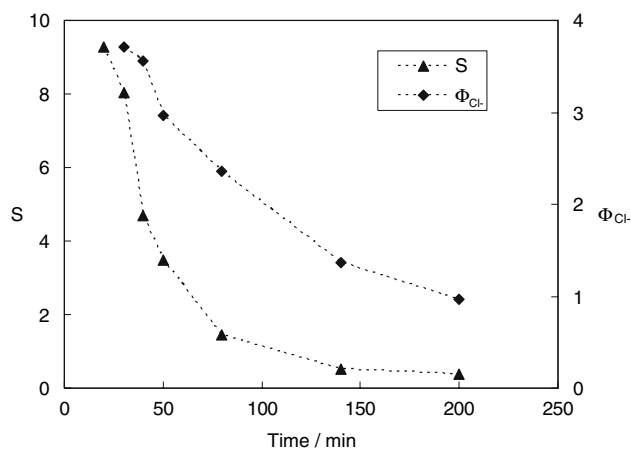


Fig. 6 Typical time dependence of the selectivity of the reaction towards the production of hypochlorite (S) and of the yield of Cl^- removal (Φ_{Cl^-})

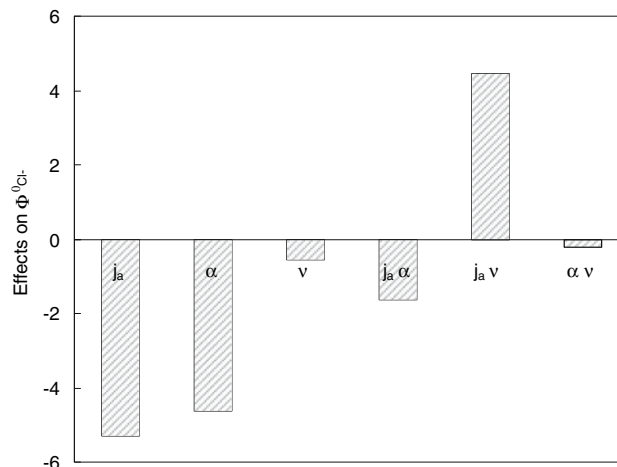


Fig. 7 Effects of the parameters and their interactions on the yield of Cl^- removal ($\Phi_{Cl^-}^0$) for experiments performed in the tank cell

Table 2 Values of yield of chloride removal ($\Phi_{Cl^-}^0$), selectivity (S_0) and concentrations of the main ionic species originated during electrolyses under different experimental conditions

Experimental conditions				Composition of the solution after 30 C dm ⁻³ are supplied to the system			Objective functions	
I/A	A_c/cm^2	v/rpm	$C_{Cl^-}^0/mol\ m^{-3}$	$C_{ClO^-}^-/mol\ m^{-3}$	$C_{Cl^-}/mol\ m^{-3}$	$C_{ClO_3^-}/mol\ m^{-3}$	$\Phi_{Cl^-}^0$	S_0
0.1	5	0	3.45	1.32×10^{-2}	3.42	1.32×10^{-2}	17	50
0.1	5	600	2.02	9.79×10^{-3}	1.99	1.82×10^{-2}	18	35
0.1	20	0	3.09	1.71×10^{-2}	3.05	1.40×10^{-2}	20	55
0.1	20	600	2.64	8.39×10^{-3}	2.63	5.60×10^{-3}	9	60
0.2	5	0	3.43	5.93×10^{-3}	3.41	1.69×10^{-2}	14.7	26
0.2	5	600	3.45	4.04×10^{-3}	3.43	1.62×10^{-2}	13	20
0.2	20	0	2.43	6.65×10^{-4}	2.43	3.77×10^{-3}	2.9	15
0.2	20	600	3.93	9.95×10^{-3}	3.92	9.19×10^{-3}	12.3	52

All the values are measured when 30 C dm⁻³ were passed in the system

Table 3 Matrix for the calculation of the effects and their interactions for experiments with the tank cell

Trial no.	j_a	α	v	$j_a \alpha$	$j_a v$	αv	$\Phi_{Cl^-}^0$	S_0
1	1	1	1	1	1	1	12.3	52
2	-1	1	1	-1	-1	1	9	60
3	1	-1	1	-1	1	-1	13	20
4	-1	-1	1	1	-1	-1	18	35
5	1	1	-1	1	-1	-1	2.9	15
6	-1	1	-1	-1	1	-1	20	55
7	1	-1	-1	-1	-1	1	14.7	26
8	-1	-1	-1	1	1	1	17	50

combined effects suggests caution in evaluating the single effect of v on both functions, at least under this experimental condition.

In order to explain these effects it must be considered that the concentration of Cl^- , measured in the bulk solution,

results from the balance between chloride consumption at the anode and chloride generation from reduction of ClO^- at the cathode, which is usually a mass transfer controlled process. In this context the negative effect of α on $\Phi_{Cl^-}^0$ could be explained considering that a high α value (i.e. high

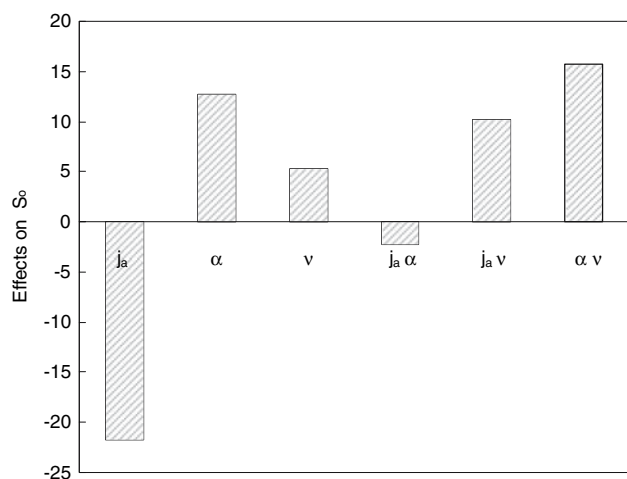
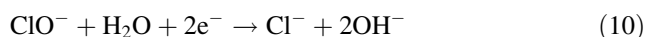


Fig. 8 Effects of the parameters and their interactions on the selectivity of the reaction towards the production of hypochlorite (S_0) for experiments performed in the tank cell

cathode area) may result in an increase of mass transfer rate towards the cathode, which leads to a higher regeneration of Cl^- (reaction 10) and an apparent decrease of $\Phi_{\text{Cl}^-}^0$:



For the same reason, the effects of α and v on S_0 should not be considered separately, as clearly shown in the interaction plots (Fig. 9): while in not mechanically stirred solution changing the cathode area had little effect, the same change led to a strong variation in selectivity when the experiment was performed in stirred solution. Figure 9 also shows the strong interaction between the effects of j_a and v on $\Phi_{\text{Cl}^-}^0$: the negative single effect of j_a on $\Phi_{\text{Cl}^-}^0$ could be explained easily (higher current density favours the reaction of oxygen evolution), but also the presence of a binary effect $j_a v$ on $\Phi_{\text{Cl}^-}^0$ is not surprising: an opposite sensitivity of the function $\Phi_{\text{Cl}^-}^0$ to the stirring rate at the two levels of j_a is evident in this case (Fig. 9b).

Finally, the negative single effect of the anodic current density on S_0 could be explained considering that an increase of current density leads to a corresponding increase of anode potential, which in turn favours the formation of species chlorine at higher oxidation state. However, the presence of an appreciable value of the combined effect of $j_a v$, suggests a careful evaluation of the effects of j_a which could be very different, depending on the level of v .

The same analysis was then repeated on the experiments performed in the filter-press cell.

Table 4 shows the matrix of a full factorial design that in this case considered only two parameters, j_a and v : the low and high levels for v were in this case 0.1 and $1.5 \text{ dm}^3 \text{ min}^{-1}$, respectively; the same levels as in the tank cell were maintained for j_a , whereas a value of $\alpha = 0.63$

was maintained for all the experiments in this cell. Moreover, only the yield of chloride oxidation was considered as the objective function because, in the short reaction times considered, a value of near unity was measured for the selectivity: only traces of chlorates were found, that were rather difficult to measure.

The values of $\Phi_{\text{Cl}^-}^0$ measured in these experiments were always lower than those obtained with the tank cell. As already pointed out, these should be considered as apparent yields: in this case, the main reaction product was hypochlorite which can be reduced at the cathode to chloride, thus decreasing the apparent chloride oxidation yield.

As shown in Fig. 10, a strong interaction between anodic current density and electrolyte flow rate was indicated by the results of the DOE analysis.

From a global analysis of the results, the best conditions with which to achieve a high selectivity towards hypochlorite were: low current density and high stirring rate of the solution. These conditions could indicate a global reaction path in which the oxidative steps are in series with each others. For such types of processes, the maximum yield in the intermediate product is obtained when homogeneity of the solution is guaranteed [19], whereas the presence of concentration profiles enhances the formation of the final product.

In this case, the worst condition was obtained in the tank cell with not mechanically stirred solution: dead zones in which the reaction is nearly absent, are faced with zones—near to the electrodes—where the oxidation reaction can proceed up to very high rates. Even leading to high conversion of chlorides, this situation did not realise a favourable condition for a high selectivity towards hypochlorite.

In a well-mixed system, as in the case of the filter-press cell, homogeneity results in an increase of selectivity towards the intermediate product which, at least at low reaction times, becomes about unity.

4 Conclusions

The oxidation of chloride containing solutions has been investigated to identify favourable conditions for a possible application in disinfecting processes. In such cases one of the most important points is to guarantee the presence in the bulk solution of appreciable concentration of hypochlorite, the main disinfecting agent.

The control of by-product formation is also of great concern. Conditions in which the selectivity towards hypochlorite is low, or the formation of ClO_3^- and ClO_4^- leads to levels not allowed by legislation, have to be avoided strongly.

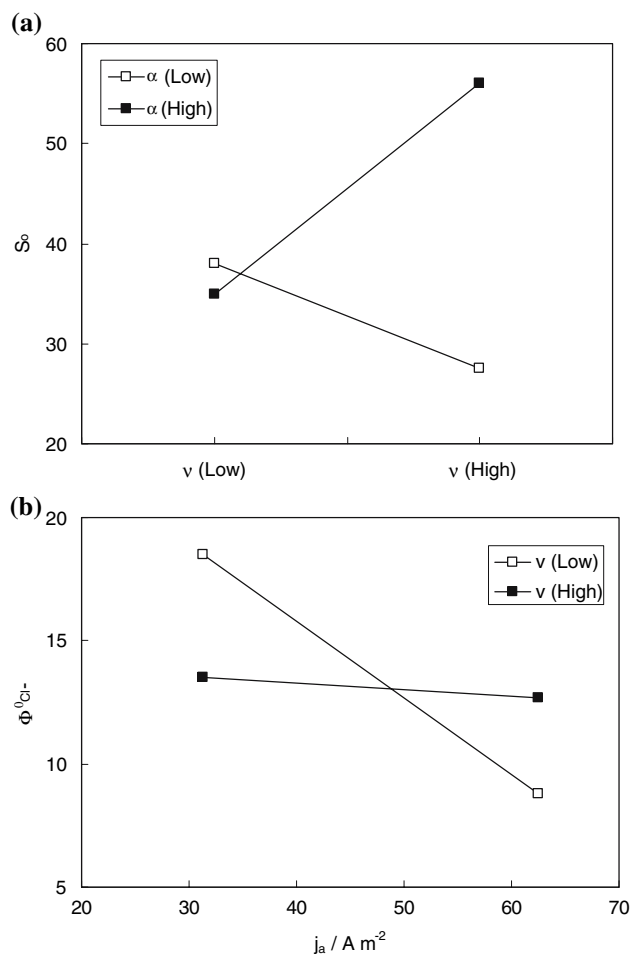


Fig. 9 Interaction plots: effects of α and v on S_0 (a), effects of j_a and v on $\Phi_{Cl^-}^0$ (b)

Table 4 Matrix for the calculation of the effects for experiments with the filter-press cell

Trial no.	j_a	v	$j_a v$	$\Phi_{Cl^-}^0$
1	1	1	1	5.8
2	-1	1	-1	4.5
3	1	-1	-1	4.5
4	-1	-1	1	7.0

The application of the DOE technique allowed comparison of the different effects of anodic current density, hydrodynamics, and geometry of the cell on the selected functions, assumed as responses of the system. The results indicated a complex system in which the two-factors interactions were often very strong. Nevertheless, some final considerations can be done from a global analysis of the results. The configuration of the reactor seems to be particularly influential: great attention has to be paid so that non-homogeneous zones are avoided in the system, which could favour the formation of highly oxidised chlorine

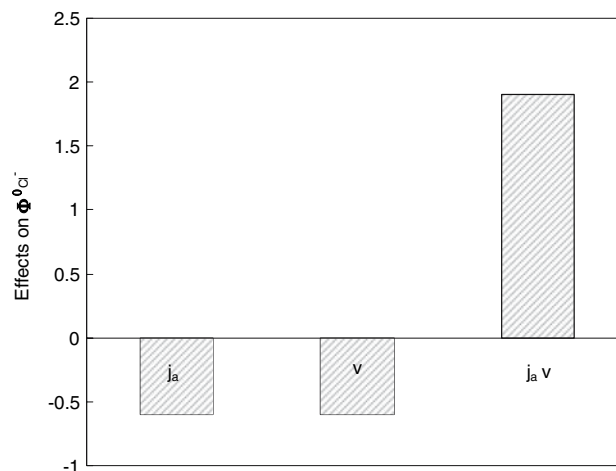


Fig. 10 Effects of the parameters and their interactions on the yield of Cl^- removal ($\Phi_{Cl^-}^0$) for experiments performed in the filter1-press cell

products. For the same reason, the optimal conditions to obtain a highly disinfecting environment have to be searched in the range of lower current densities and with an electrochemical cell, in which good mixing of the electrolyte is achievable.

These considerations will constitute the basis for further work in which the analysis DOE will be focused on experiments performed in the filter-press cell and extended to more investigation levels of the influential parameters. This will allow modelling of the system: the relationship between the different parameters will be evaluated and the optimal operative conditions identified.

References

- Kraft A, Stadelmann M, Blaschke M (2003) J Hazard Mat 103(3):247
- Cañizares P, Gadri A, Lobato J, Nasr B, Paz R, Rodrigo MA, Saez C (2006) Ind Eng Chem Res 45(10):3468
- Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis Ch (2001) J Electrochem Soc 148(5):D60
- Iniesta J, Michaud PA, Panizza M, Cerisola G, Aldaz A, Comninellis Ch (2001) Electrochim Acta 46(23):3573
- Cañizares P, Lobato J, Paz R, Rodrigo MA, Sáez C (2005) Water Res 39(12):2687
- Polcaro AM, Vacca A, Palmas S, Mascia M (2003) J Appl Electrochem 33(10):885
- Michaud PA, Panizza M, Ouattara L, Diaco T, Foti G, Comninellis Ch (2003) J Appl Electrochem 33(2):151
- Brillas E, Boye B, Sirés I, Garrido JA, Rodríguez RM, Arias C, Cabot P-L, Comninellis Ch (2004) Electrochim Acta 49(25):4487
- Polcaro AM, Vacca A, Mascia M, Palmas S, Pompei R, Laconi S (2007) Electrochim Acta 52(7):2595
- World Health Organization (2006) Guidelines for drinking-water quality, vol 1. WHO Press, Geneva
- Bergmann H, Iourtchouk T, Schops K, Bouzek K (2002) Chem Eng J 85(2–3):111

12. Bergmann H, Rollin J (2007) *Catal Today* 124(3–4):198
13. Lissens G, Pieters J, Verhaege M, Pinoy L, Verstraete W (2003) *Electrochim Acta* 48(12):1655
14. Hastie J, Bejan D, Teutli-Leon M, Bunce NJ (2006) *Ind Eng Chem Res* 45(14):4898
15. Khelifa A, Moulay S, Hannane F, Benslimene S, Hecini M (2004) *Desalination* 160:91
16. Box GPE, Hunter WG, Hunter JS (1978) *Statistics for experimenters. An introduction to design, data analysis and model building*. John Wiley & Sons, NY
17. Bergmann H, Koparal AS (2005) *J Appl Electrochem* 35:1321
18. Vasudevan S, Mohan S (2006) *Ind Eng Chem Res* 45(9):2923
19. Levenspiel O (1972) *Chemical reaction engineering*. John Wiley and Sons, NY