

Combined direct and indirect electrooxidation of urea containing water

Carlos Carlesi Jara · Simona Di Giulio ·
Debora Fino · Paolo Spinelli

Received: 15 September 2007 / Revised: 18 January 2008 / Accepted: 22 January 2008 / Published online: 5 February 2008
© Springer Science+Business Media B.V. 2008

Abstract The direct oxidation of urea at high electrode potentials over platinized titanium electrodes in sulphate media generates a high amount of nitrates, representing an environmental problem. Coupling direct and indirect oxidation (using chloride salt), the total amount of generated nitrates can be lowered due to competition between anodic generation of chlorine and nitrates. A qualitative description of the influence of applied current density (ranging from 0.5 to 30 A m⁻²) and the nitrogen-to-chlorine ratio N/Cl (ranging from 0.5 to 3 by weight) on the distribution of urea electrooxidation by-products was obtained. In a highly acidic environment, a decrease in nitrate concentration was observed when operating at relatively high current densities, which suggests the occurrence of a complex heterogeneous reaction involving nitrates and yielding mainly molecular nitrogen.

Keywords Electrooxidation · Urea · Nitrates · Platinized titanium electrode · Active chlorine

1 Introduction

The electro-oxidative treatment of waste waters can serve either specifically as a process of disinfection or as part of a more complex waste water treatment route. Direct

(heterogeneous) electrolytic oxidation processes can be carried out by coupling with an indirect electrochemical process in the presence of an electrolyte capable of generating powerful oxidants. Moreover, in the electrochemical treatment the concentration of disinfectant and the formation of electrolysis by-products can be better controlled than with the mere addition of chemicals.

As demonstrated previously [1], direct electrooxidation of nitrogen-containing molecules enables, on the one hand, a reduction of total carbon content, but, on the other hand, the production of high amounts of inorganic pollutants like ammonia and nitrate ions. The presence of high concentrations of nitrates and ammonia in water has a detrimental effect on the environment and is thus a problem for use in industrial applications, as it necessitates a further specific abatement process. Nowadays, ion exchange represents the most widespread method for the treatment of nitrate-containing drinking water [2].

The inhibition of nitrate formation in a highly oxidizing environment and the removal of nitrates are difficult processes during direct electrochemical treatment in a single divided cell. Consequently, the combination of a direct electrooxidation process within the indirect one was tested by adding sodium chloride to the treated solution in the anodic chamber of a divided cell, thereby enabling combined direct-indirect electrooxidation coupled with electrodialysis. This pathway was devised under the assumption that chlorine and nitrate generation might be competing processes.

In general, it has been found that direct anodic oxidation of urea depends on anode potential, type and composition of electrolyte, urea concentration, pH and solution temperature. Different treatment conditions result in different products of urea decomposition [1]; in an acidic environment at high potentials (over 1.7V versus SCE), oxidation leads primarily to CO₂ and N₂, while, at lower potentials,

C. Carlesi Jara
Department of Chemical Engineering, Pontificia Universidad Católica de Valparaíso, Avda. Brasil 2147, Valparaíso, Chile

S. Di Giulio · D. Fino (✉) · P. Spinelli
Department of Materials Science and Chemical Engineering,
Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129
Turin, Italy
e-mail: debora.fino@polito.it

urea reacts with an $\text{OH}\cdot$ radical and the decomposition products remain in the solution [3]. By adding chloride salt (NaCl) to a sulphate-based electrolytic system working at high enough electrode potentials, a new set of reactions arises, where, in nearly isothermal conditions, the amount of electro-generated active chlorine species depends strongly on the chloride concentration and the current density, both parameters being easily adjustable [4].

The optimum environmental acidity for electrolysis of N-containing pollutants is still a controversial point. On the one hand, some authors [5, and references therein] recognize that nitrate formation in alkaline media is restricted and the electro-chlorination paths lead primarily to molecular nitrogen formation. However, other authors [6 and references therein] have found that, in an alkaline environment, the ammonium nitrogen is removed and oxidized to form a nitrate, while in acidic conditions it is transformed mainly to nitrogen gas.

These differences can be explained by the differing experimental conditions of each study, mainly chloride salt concentration and current density, and by taking into account that the results also depend on the effective ratio between the active chlorine and the nitrogen contained in the solution. This behaviour is analogous to the case of chemical chlorination, where an ultimate correlation between the ratio of produced nitrate to ammonia and the pH value has not yet been established [7].

It is generally accepted that more chlorinated intermediates are produced in the pH range 1–7, while at neutral and alkaline conditions (pH 7–12) more oxidation intermediates are formed. The intermediates may indeed react with one another leading to the formation of further intermediates that, in turn, modify the degradation process. Therefore, it may be inferred that, in acidic solutions with high chloride content, the ratio between NO_3^- formed and NH_4^+ removed is lower than in basic media. This results from the fact that ammonia removal should take place mostly via the chloramine homogeneous reaction path, even though the chemical mechanism may indicate that the nitrate concentration was significantly higher in the electrolysis performed in acidic media (pH \sim 6), than in alkaline media (pH \sim 12), under otherwise identical reaction conditions [7].

The aim of this paper is the identification of the optimal relationship between the initial chloride salt content (for indirect electrooxidation) and the imposed current density resulting in minimal nitrates formation and the simultaneous elimination of the chloramine compounds (break-point chlorination) during the batch treatment of urea solutions. This aim was carried out via the oxidation of urea as a model compound, using an electrolytic device with a platinized titanium anode. Urea is of specific interest for regenerative treatment as an application for the re-use of waste waters from aerospace missions [8].

2 Materials and methods

A series of electrolysis runs were carried out by monitoring the behaviour of the oxidation by-products which remained in the solution, specifically: nitrite, nitrate and chloramine species in the anodic chamber, and recovered ammonia in the cathodic one. This recovered ammonia likely came from the anodic compartment through the cationic membrane in the form of ammonium ions and became concentrated in the cathodic compartment, where the possibility of the further reduction of nitrogen did not exist.

The electrochemical oxidation of urea was carried out in a divided cell [9, 10] using a cationic membrane (Neosepta AFN by Tokuyama Soda Co., Japan) that enables the transfer of NH_4^+ cations formed at the anode into the cathodic chamber. The surface area of the electrodes was $2 \times 10^{-2} \text{ m}^2$. The operating temperature was controlled at $30 \pm 2 \text{ }^\circ\text{C}$ by means of a water cooling system placed within the mixing tank. A stainless steel plate was employed for the cathode and platinized titanium for the anode, on which an oxide layer was generated during the electrolysis runs, at high electrode potentials ($>2 \text{ V vs. NHE}$).

In this case, integration of the electrooxidative processes with electrodialysis meant that the oxidative treatment was carried out in acidic conditions (in the anodic compartment). Figure 1 shows the details of the electrochemical cell consisting of a steel plate, plastic compartment electrodes, rubber jackets, membrane and a plastic turbulence promoter placed in the anodic compartment. A synthetic solution (4 L for each run) was prepared using pure grade chemical components (Aldrich): 2 g L^{-1} of urea and three different supporting electrolytes consisting of 0.01 M sodium sulphate plus sodium chloride in the concentrations shown in Table 1, in which the ratio of the nitrogen contained in the urea to the chlorine in the salt is also shown.

Chemical analysis was carried out by periodically sampling 10 mL of the anodic and cathodic solutions and using standard methods for the determination of the nitrogen distribution in the oxidation products. The nitrate concentrations were analyzed by means of reduction and diazotization, whilst the nitrite concentrations were analyzed by means of the iodometric method. The Nessler method was employed for the determination of the ammonia concentration. Finally, combined, free and total chlorine were all measured using the *N,N'*-diethyl-*p*-phenylenediamine (DPD) standard method by spectroscopic detection. All the final concentrations were established using colorimetric determination by means of the Orbeco-Hellige water analysis system (model 975-MP).

Voltammetric analysis of urea absorption was accomplished using a single compartment, three electrode configuration connected to an AUTOLAB PGSTAT 30

Fig. 1 Details of the electrochemical cell structure: (a) anode chamber, (b) anode, (c) turbulence promoter, (d) gaskets, (e) cationic membrane, (f) cathode, (g) cathode chamber

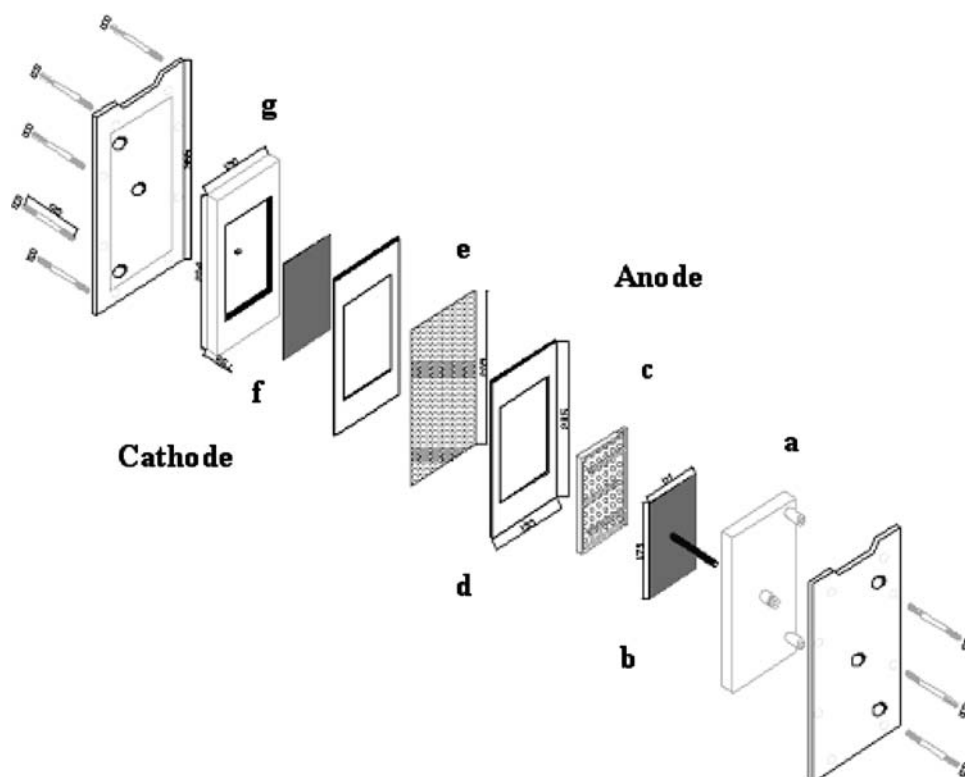


Table 1 Starting ratios between Nitrogen to Chloride in the used electrolytes

NaCl molarity	N/Cl molar ratio	N/Cl weight ratio
0.0125	1.33	0.53
0.0250	2.67	1.05
0.0500	5.33	2.10

(GPES software), with pure platinum for the working electrode and saturated calomel electrode (SCE) for the reference electrode.

3 Results and discussions

3.1 Divided electrochemical cells runs

When operating in a divided configuration, a continuous acidification of anolyte is directly related to the applied current density. In the reactor direct and indirect (chlorine mediated) oxidation of urea occurs.

3.1.1 Low current density runs

Figure 2 shows that, at a very low current density (0.5 A m^{-2}), it is possible to identify a nearly linear behaviour of the recovered ammonia in the cathode.

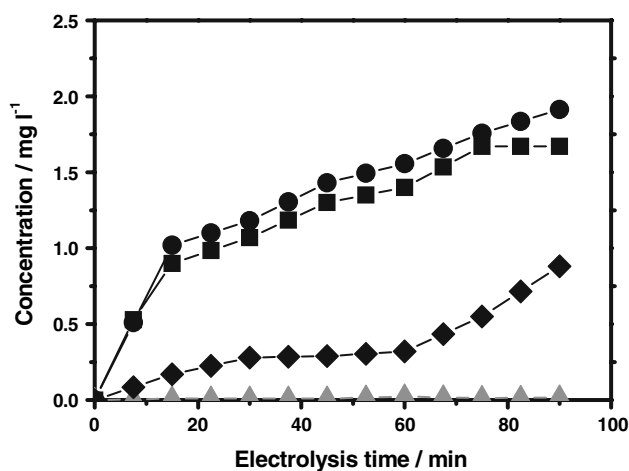


Fig. 2 Generation of the by-products during the electro-oxidation of urea (2 g L^{-1}) over a Ti/Pt anode. Electrolyte = Na_2SO_4 0.01 M + NaCl 0.05 M . Current density (A m^{-2}): 0.5 . Symbols: ◆ NH_3 concentration in the cathodic chamber, anodic chamber concentration of ● dichloroamine; ▲ mono-chloroamine; ■ NO_3^-

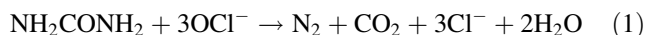
Dichloramine generation is linear with respect to the electric charge passed and mono-chloro amine is quickly transformed to di-chloro amine.

The generation of nitrates NO_3^- is exponentially proportional to the electrolysis time. Nitrite ions NO_2^- can be viewed as a reactive intermediate since their conversion to nitrate is very fast under these conditions. Under these conditions, a large quantity of nitrates is generated and

limited ammonia recovery is attained in the urea oxidation process. In this case it is not possible to identify an interaction between the generated species. The process is mainly due to direct electrooxidation, a heterogeneous process which depends mainly on urea absorption. Bezerra et al. [11] studied the anodic absorption of urea by in situ Fourier transformed infrared spectroscopy in different pH supporting electrolytes. The authors verified the strong influence of both pH and potential on the coordination of electro-absorption of urea carried out using nitrogen, oxygen or carbon atoms. In particular, in acidic solutions adsorbed CO is formed as a result of the hydrolysis of the urea molecule close to the platinum electrode, where nitrite and nitrate ions are also observed as products of oxidation at high electrode potentials.

When the current density is increased up to 20 A m^{-2} , the ratio between the generated nitrogen-containing ions varies significantly compared to the previous case. This ratio is a function of the initial concentration of sodium chloride. As shown in Fig. 3a and b, nitrate generation is the predominant reaction and the recuperation of ammonia by electro-dialysis is not proportional to the increase in the current density (within the explored operating range). This demonstrates a non-proportional generation of NH_4^+ . In this case the amount of chloramines remains relatively low.

As the chloride salt concentration rises, chloramine formation starts to compete with nitrate generation, reducing the maximum amount of nitrates obtained after two hours electrolysis (compare Fig. 3a, b) and the amount of recovered ammonia rises, as a consequence of enhanced urea degradation (via the homogeneous path). In this case the indirect electrooxidation starts to be predominant. Urea reacts with free chlorine in a homogeneous multi-step process that results in the formation of N_2 and CO_2 in accordance with the following reaction:



The intermediate steps of this process involve the formation of chloramines and other forms of combined chlorine. The general scheme of reactions and intermediates can be considered to be analogous to those of chemical chlorination in the presence of urea, with the promoting effect of the electric field on the rate of urea hydrolysis.

The mechanisms and the reaction scheme proposed in [7] and reported in Fig. 4 reveal that nitrate and by-products formation might be restricted whilst promoting, at the same time, the formation of molecular nitrogen through the selection and proper adjustment of certain reaction parameters, primarily pH.

Further increase in NaCl concentration (Fig. 3c) causes the amount of chloramines to surpass the amount of generated nitrates and the maximum amount of nitrates again

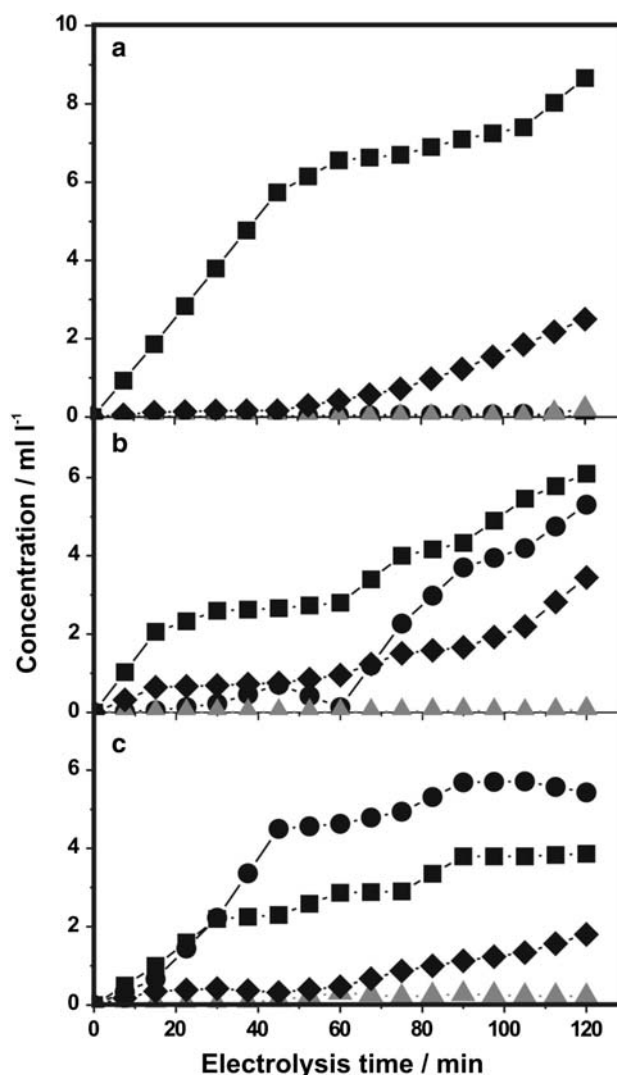


Fig. 3 Generation of the by-products during the electro-oxidation of urea (2 g L^{-1}) over a Ti/Pt anode. Electrolyte = Na_2SO_4 0.01 M + NaCl. Current density (A m^{-2}): 20. (a) 0.0125 M NaCl, (b) 0.025 M NaCl, (c) 0.05 M NaCl. Symbols: \blacklozenge NH_3 concentration in the cathodic chamber, anodic chamber concentration of \bullet dichloroamine; \blacktriangle monochloroamine; \blacksquare NO_3^-

is lowered. Conversely, the amount of recovered ammonia is practically unchanged, likely being limited by the membrane exchange capacity at the corresponding electric field intensity.

Oscillation in the curve corresponding to dichloroamine is attributed to the elimination cycles of chloramines (breakpoint) that are repeated due to the continuous generation of both ammonia and “active chlorine”.

From the increase in current density (Fig. 5), at equal salt concentrations as in Fig. 3c, the behaviour of the generation of ions remains the same but the kinetics are faster. Additionally, dichloramines reach a maximum and

Fig. 4 Reaction schemes proposed. Products include N₂, H₂O, Cl⁻, H⁺, NO₃⁻, and other reactions products (I = intermediates)

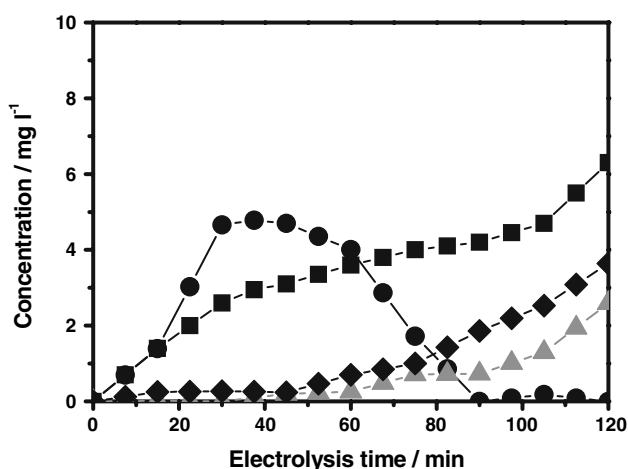
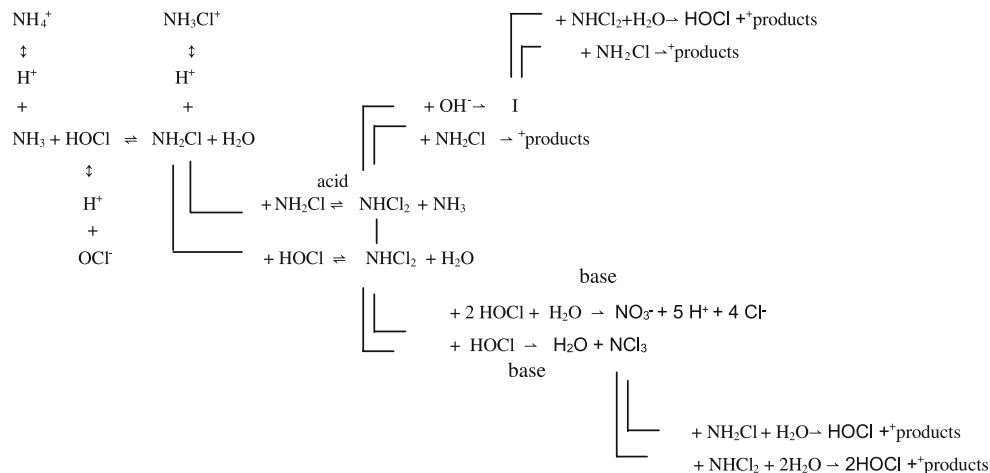


Fig. 5 Generation of the by-products during the electro-oxidation of urea (2 g L⁻¹) over a Ti/Pt anode. Electrolyte = Na₂SO₄ 0.01 M + NaCl 0.05 M. Current density (A m⁻²): 30. Symbols: ♦ NH₃ concentration in the cathodic chamber, anodic chamber concentration of ● dichloroamine; ▲ monochloroamine; ■ NO₃⁻

then decrease due to the increased amount of electro-generated “active chlorine”.

3.1.2 High current density runs

A current density ten times higher than that one employed in the previously described runs was employed here. Under these conditions, neither the increases in generated nitrate nor the amount of recovered ammonia were found to be proportional to the enhancement of the applied current density.

In the case shown in Fig. 6a, the kinetics are faster than that observed in Fig. 5. In particular, after the elimination of the chloramine compounds (60 min) the nitrate concentration rises. This non linear behaviour is due to the reaction between the “active chlorine” and ammonia along the chloramines route towards molecular nitrogen. Nitrates

are thus generated from two routes: (i) the direct-homogeneous electrooxidation of ammonia, and a parallel homogeneous reaction between the electro-generated “active chlorine” and the nitrogen-containing molecules, according to a reaction which is not fully understood [6].

The increase in chloride concentration (Fig. 6b) causes the amount of recovered ammonia to slowly increase and the level of dichloramine to be greater than in the previous runs. Using more sodium chloride, there is simply more production of “active chlorine” (Fig. 6c), and the recovered ammonia rises slowly, due mainly to the increase of the homogeneous reaction between active chlorine and ammonia or urea.

When a further increase in current density was applied (Fig. 7), the initial levels of nitrate were also found to rise, but the subsequent drop in concentration was seen sooner in this electrolysis run than in the previous runs. The maximum level of dichloramine remains almost the same but the recovered ammonia rises significantly, mainly as a consequence of the increase in cell potential (electric field) and the enhancement in urea oxidation rate.

In general, it was observed that the total amount of nitrates fell with increasing sodium chloride concentration (more chloride and more anodic generation of chlorine), which implies inhibition of the direct oxidation of urea responsible for nitrate generation.

This reduction in nitrate concentration is an unexpected result, leading to the conclusion that nitrates become consumed under certain conditions when applying relatively high levels of current density.

By comparing Figs. 6c and 7, this reduction in the time of the start of the fall in nitrate concentration can be related to the increase of the applied current through more rapid acidification near the anode surface (derived from the release of protons in the oxygen evolution reaction). In addition, homogeneous reactions of nitrates with HOCl or NH₄⁺ are not favoured from a thermodynamic point of

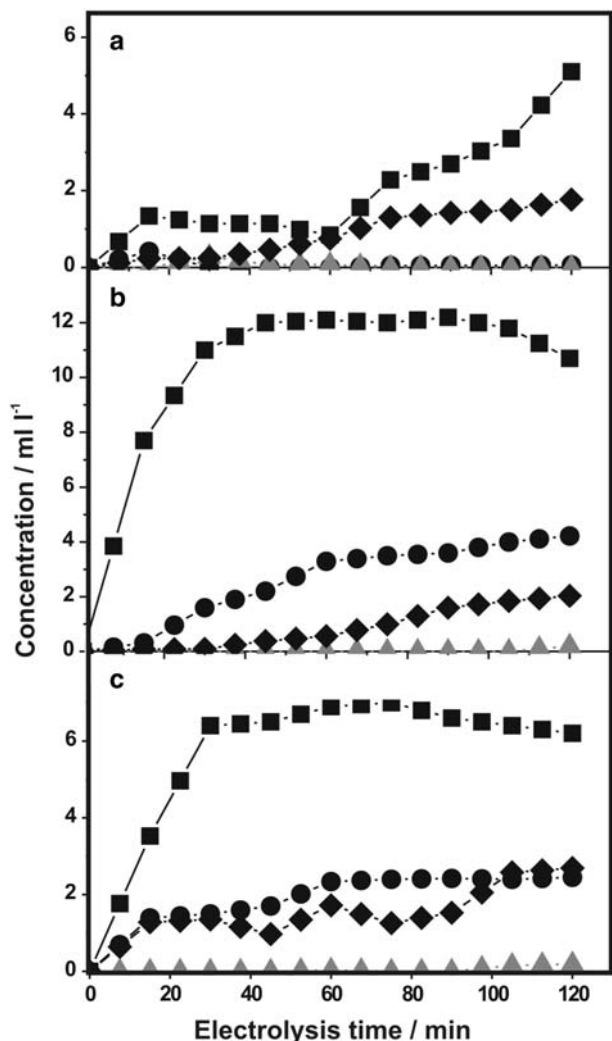
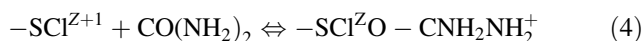


Fig. 6 Generation of the by-products during the electro-oxidation of urea (2 g L^{-1}) over a Ti/Pt anode. Electrolyte = Na_2SO_4 0.01 M + NaCl 0.0125 M. Current density (A m^{-2}): 200. (a) 0.0125 M NaCl, (b) 0.025 M NaCl, (c) 0.05 M NaCl. Symbols: \blacklozenge NH_3 concentration in the cathodic chamber, anodic chamber concentration of \bullet dichloroamine; \blacktriangle monochloroamine; \blacksquare NO_3^-

view. All these considerations suggest that electrochemical heterogeneous reactions catalysed in highly acidic conditions are the cause of the reduction in nitrate concentration.

As a first hypothesis, one can consider a possible mechanism for the reaction of the nitrates as follows (Equations 2, 3 include the presence of chloride ions absorbed at the anode and Eq. 3 involves absorbed urea):



The absorption of urea on platinum electrodes can block active sites for chlorine evolution. Additionally, Simka

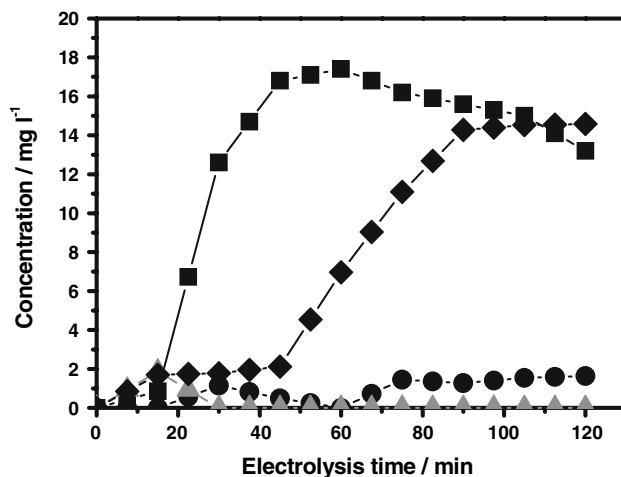
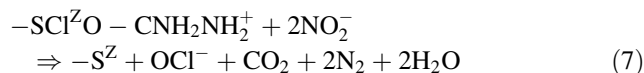
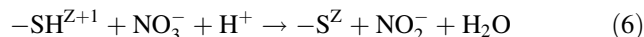


Fig. 7 Generation of the by-products during the electro-oxidation of urea (2 g L^{-1}) over a Ti/Pt anode. Electrolyte = Na_2SO_4 0.01 M, NaCl 0.025 M. Current density (A m^{-2}): 300. Symbols: \blacklozenge NH_3 concentration in the cathodic chamber, anodic chamber concentration of \bullet dichloroamine; \blacktriangle monochloroamine; \blacksquare NO_3^-

et al. [3] showed that urea was decomposed on the surface of the electrode by reacting with absorbed chlorine.

The formation of the absorbed radical cation is promoted by the dipole-type-resonance-stabilized structure which enhances its adsorption on electrode surfaces [12]. At very low pH levels the hydrogen ions compete with chloride ions [13] and the urea can be absorbed at this site instead of the site with chloride, with a subsequent oxidation to nitrite. Therefore oxidation to nitrate can be avoided by reacting with another reactive absorbed species in some form similar or equal to that of Eq. 7. In addition, in Eqs. 5 and 6, an acid catalyzed reaction of nitrate with absorbed protons could be responsible for the nitrate concentration decrease observed in the cell.



3.2 Voltametric analysis

In order to find preliminary evidence of the reaction mechanism for the nitrates and the urea, cyclic voltammetry was carried out with the aim of investigating the influence of urea in the chlorine evolution reaction in the presence of nitrates in an acidic environment.

The voltammetric behaviour of a neutral solution when urea alone is added and when both urea and nitrates are present are shown in Fig. 8. The differences indicate that, as expected, urea absorption is related to the fact that urea

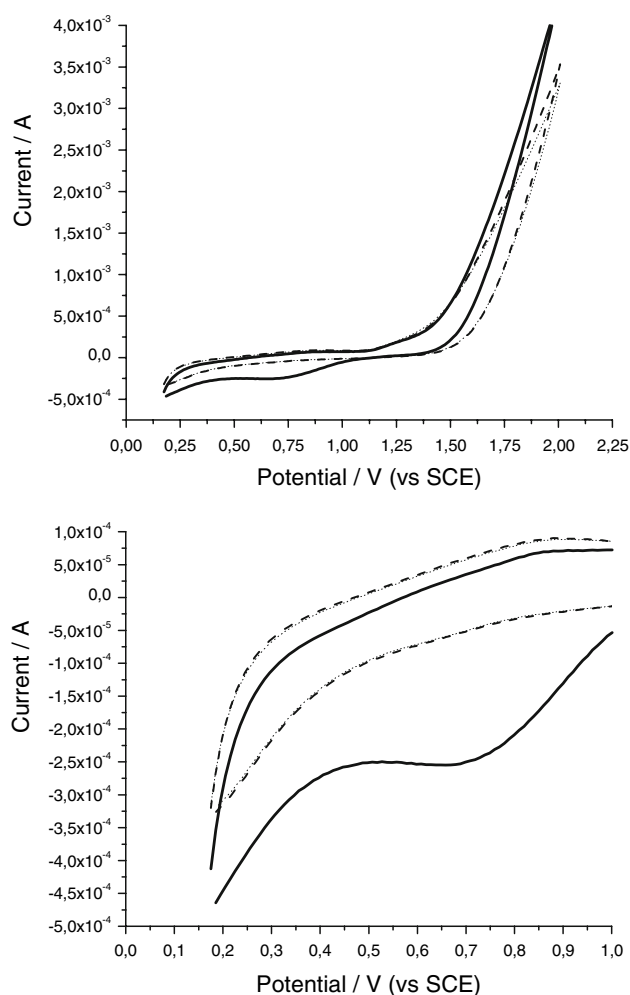


Fig. 8 Cyclic voltammetry of neutral solution (NaCl 0.02 M electrolyte) containing urea (2 g L^{-1}) and urea (2 g L^{-1}) plus 20 mg L^{-1} of nitrate (upper graph). Enlargement of reduction zone (lower graph). Potential scan rate 100 mV s^{-1}

depresses the anodic current, by blocking the sites for chlorine and oxygen evolution. Particularly, the lower graph indicates the reduction zone where the presence of adsorbed urea also blocks the reduction of oxygen species; in this case (neutral pH) the influence of the presence of nitrates is negligible.

The behaviour in a highly acidic environment (0.05 M HCl) is shown in Fig. 9. The influence of urea is similar to that observed in the previous case, but in the reduction zone (see lower graph) the clear influence exerted by the nitrate is seen. This implies that an anodic interaction between nitrates and adsorbed species (urea, Cl, H^+) has occurred. The data obtained here are not enough to determine a reaction mechanism related to this interaction. However, they are in agreement with the experimental results using the divided electrochemical cell in the electrooxidation of urea.

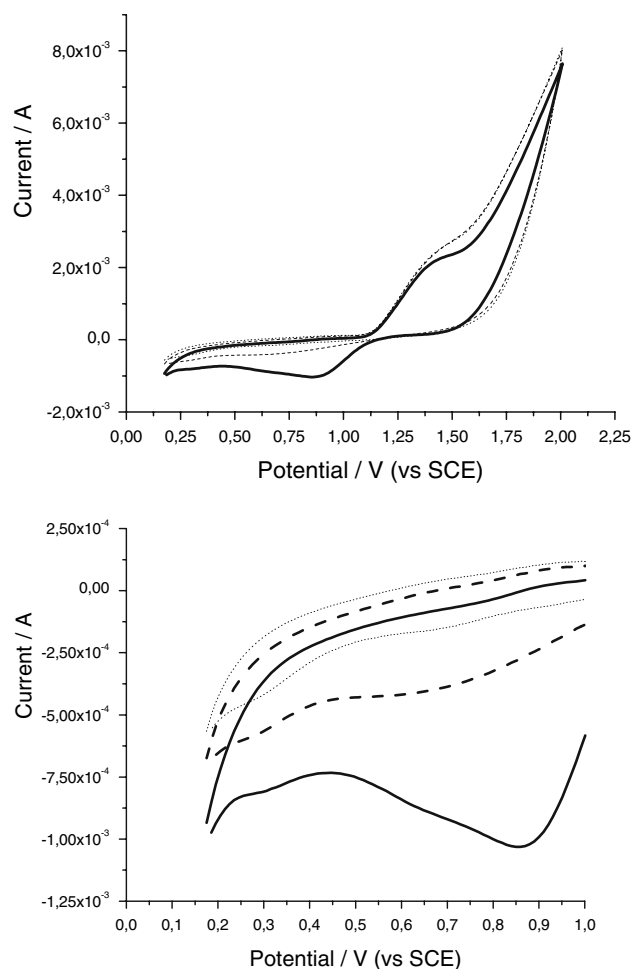


Fig. 9 Cyclic voltammetry on a acid solution (HCl 0.02 M electrolyte) containing urea (2 g L^{-1}) (dash curve) and urea (2 g L^{-1}) plus 20 mg L^{-1} of nitrate (dotted curve) (upper graph). Enlargement of reduction zone (lower graph). Potential scan rate 100 mV s^{-1}

4 Conclusions

Ionic by-products of urea electro-oxidation were monitored in a divided electrochemical cell, in which direct-indirect electro-oxidation was coupled with electro-dialysis. A large difference in the nitrogen evolution was experimentally observed in the electrolysis carried out with an electrolyte containing sodium sulphate and chloride.

The following conclusions can be drawn:

- At high current densities, total inhibition of nitrate formation was not possible. Nevertheless, an apparent reduction in the maximum amount of this species was achieved by increasing the chloride salt concentration, thereby promoting chlorine evolution which acts as a competitive anodic reaction.
- Nitrates generated by homogeneous reaction with “active chlorine” contribute to a relatively low extent

to the anodic generation of nitrates. Consequently, an optimum value of both chloride concentration and imposed current density for the minimization of nitrate generation were determined. These values were also dependent on pH and the ratio total nitrogen/active chlorine.

- In the presence of chloride salt, a direct electrode reaction (acid catalysed) yielding mainly molecular nitrogen was observed for a urea concentration of 2 g L^{-1} .
- A possible reaction mechanism related to the urea-nitrate-chloride anodic interaction was proposed based on the results of voltammetric analyses. Further investigations are though needed to confirm this hypothesis.

Acknowledgements We acknowledge fruitful discussions with Dr. Rodrigo Henriquez from the Chemistry Department of the Pontificia Universidad Catolica de Valparaiso, Chile, as well as the financial support of Regione Piemonte, Italy (Project: “Monitoraggio e rigenerazione dell’acqua nelle missioni spaziali”, 2004 N°182/2006) and Fondecyt N°11070219 (2007) Republic of Chile.

References

1. Di Giulio S, Carlesi Jara C, Fino D, Saracco G, Specchia V, Spinelli P (2007) *Ind Eng Chem Res* 46:6783
2. Paidar M, Bouzek K, Bergmann H (2002) *Chem Eng J* 85:99
3. Simka W, Piotrowski J, Nawrat G (2007) *Electrochim Acta* 52:5696
4. Kraft A, Stadelmann M, Blaschke M, Kreysig D, Sandt B, Schroöder F, Rennau J (1999) *J Appl Electrochem* 29:861
5. Mogyoródy F (2006) *J Appl Electrochem* 36:635
6. Cabeza A, Primo O, Urtiaga AM, Ortiz I (2006) In: e-proceeding of the first European congress on environmental applications of Advanced Oxidation Processes (EAAOP-1) Chania, Greece, p 270
7. Jafvert C, Valentine R (1992) *Environ Sci Technol* 3:577
8. Project Monitoraggio e rigenerazione dell’acqua nelle missioni spaziali, funded by Regione Piemonte 2004 N°182/2006
9. Saracco G, Solarino L, Specchia V, Maja M (2001) *Chem Eng Sci* 56:1571
10. Carlesi Jara C, Fino D, Saracco G, Specchia V, Spinelli P (2007) *Appl Catal B: Environ* 70:479
11. Bezerra A, Desa E, Nart F (1997) *J Phys Chem B* 33:6443
12. Wright JC, Michaels AS, Appleby AJ (1986) *AIChE Journal* 9:1450
13. Fernández JL, Genneero de Chialvo MR, Chialvo AC (2002) *Electrochim Acta* 47:1145