

Distribution of Nitrogen Ions Generated in the Electrochemical Oxidation of Nitrogen Containing Organic Compounds

C.C. Jara,^{1,*} C.A. Martínez-Huitle,² R.A. Torres-Palma³

¹ Escuela de Ingeniería Química, Pontificia Universidad Católica de Valparaíso, Avda. Brasil 2147, 2362804 Valparaíso, Chile

² DiSTAM, University of Milan, via Celoria 2, CAP-20133 Milan, Italy

³ Grupo de Electroquímica, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, A. A. 1226, Medellín, Colombia

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Abstract

The electro-oxidation, over platinized titanium and ruthenium oxide anodes, of nitrogen containing molecules (urea, reactive Blue 4 dye, acetonitrile, formamide, guanidine and pyridazine) was investigated, monitoring the products distribution. The N-mineralization leads to have inorganic pollutants ($\text{NH}_3/\text{NH}_4^+$ and/or $\text{NO}_2^-/\text{NO}_3^-$). Amidic and aminic compounds react both in homogeneous (acid hydrolysis) and in heterogeneous phase (direct electrooxidation) with a rate depending on the original state of oxidation of nitrogen. Heterocyclic and multiple-bond carbon-nitrogen molecules were effectively converted with negligible mineralization of nitrogen due to the stability of their first oxidation intermediates. The obtained results (high rate of nitrate generation) evidence the need of coupling of the direct electrooxidation with other process to limit the nitrate concentration to an accepted level; in accordance, dialysis (of the ammonia cation) and indirect oxidation (chlorine-mediated) were proved to be valid alternatives.

Keywords: electrochemical oxidation, conductive metal-oxide anodes, organic nitrogen, ammonia, nitrates.

Introduction

The intensification of industrial activities, after the latter half of the XIX century, has inevitably caused severe environmental pollution with dramatic consequences in atmosphere, waters, and soils. The consequent restrictions imposed by new legislations require effective initiatives for pollution reduction, not only in gaseous emissions and soils, but also adequate decontamination in

* Corresponding author. E-mail address: carlos.carlesi@ucv.cl

both drinking and industrial waters. Typically, in the case of the latter, different classes of pollutants may have accumulated, in natural water sources, during long periods of uncontrolled waste disposal and reclamation may represent a serious technological problem. Due to the very extremely diverse features of pollution phenomena, universal strategies of reclamation have not been found [1].

An alternative can be the application of electrochemical technologies for wastewater treatment, benefiting from advantages such as versatility, environmental compatibility and potential cost effectiveness, among others. At present, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost, but sometimes they are more efficient and compact. The development, design and application of electrochemical technologies in water and wastewater treatment have been focused on particularly in some technologies such as electrodeposition, electrocoagulation, electroflocculation and electrooxidation.

Table 1. Principal characteristics of the electrochemical processes: Direct and Indirect Electrochemical Oxidation [1].

	Direct oxidation	Indirect oxidation, also called mediated electrochemical oxidation
<i>Objective</i>	The complete oxidation of organics to CO ₂ or the conversion of the toxic organics to biocompatible compounds	
<i>Method</i>	Water is passed through anodic compartment of one or more electrochemical cells with specific features.	Anodically and/or cathodically formed oxidants (Cl ₂ , HClO, H ₂ O ₂ , O ₃ , Fenton's reagent, peroxodisulphate but also Ag ^{III/I} , Ce ^{IV/III}) react with organic substrates
<i>Factors</i>	Current, pH, temperature, anodic material, Faradaic processes	Current, pH, Faradaic processes, nature of the oxidants
<i>Mechanism</i>	Heterogeneous electrocatalytic process involving transfer of substrate from bulk solution to the electrode surface or within the double layer and exchange of electrons between the electrode and the substrate.	Homogeneous electrocatalysis of the substrate does not exchange electrons with the electrode directly, but with some intermediates or mediators. Electron transfers and chemical reactions can then take place in the bulk solution.

During the last two decades, the electrochemical oxidation has been considered a promising alternative to eliminate the organic and inorganic compounds from fresh, drinking and waste waters [1, 2]. This method has been considered of practical interest, particularly when the wastewater contains bio-refractory

organic pollutants or micro-toxic substances, which are not amenable for an effective biological abatement. The main objective of the electrochemical wastewater treatment is the complete oxidation of organics to CO₂ [3] or, at least, their conversion to biodegradable compounds [4].

Attempts for an electrochemical oxidation/destruction treatment for waste or wastewater can be subdivided in two important categories: direct oxidation at the anode, and indirect oxidation using appropriate electrochemically-formed oxidants [1].

According to information in Table 1, while the electron transfer takes place between electrodes and decomposable species in direct electrochemical oxidation, indirect oxidation mainly uses electrochemically generated species as mediators for the destruction of organic compounds.

For indirect electro-oxidation, destruction of organic compounds by anodically generated chlorine and hypochlorite is well known [1]. A particularly interesting case is that of active-chlorine mediation, which has been reported in several papers [5-12]. The interest for this path to electrochemical incineration is due to two reasons: (i) the ubiquitous presence of chloride ions in a lot of effluents and natural waters, which makes the involvement of active chlorine in anodic processes in these media, inevitable; (ii) the chemistry and electrochemistry of chlorine higher oxidation states at pH not far from neutrality, makes their use as incineration mediator of some practical interest. On the other hand, among the cited bio-refractory organic pollutants, N-containing compounds belong to a very crucial group, mainly imputable to the fact that nitrogen constitutes a key element of the nutrient cycle. Moreover, a large number of anthropogenic compounds (i.e. pesticides, drugs, detergents and dyes) contain one or more nitrogen atoms.

The great majority of scientific works in the area of electro-oxidation of organics has been focused on monitoring, during electrolysis, the degree of carbon mineralization towards carbon dioxide (TOC elimination). In the particular case of the nitrogen contained in organic compounds, N can be converted during oxidation treatment into either NH₃/NH₄⁺, in nitrate and nitrite ions, or eventually to N₂. The concentration levels of ammonia, nitrates and nitrites represent important parameters of the quality of water for both industrial application or potable use; although they can be completely removed by biological processes, a great interest exists in alternative treatments for their removal from waters. In this context, advanced oxidation processes (AOPs), including electrochemical techniques, are of major interest.

The aim of the present investigation is the study of the nitrogen ions distribution deriving from mineralization of nitrogen during direct electrooxidation treatment of organic molecules over conductive metal-oxide anodes in a divided electrochemical reactor.

Although anodes with a high overpotential for oxygen evolution (i.e. doped SnO₂ [13] - or doped Diamond [14]) present higher current efficiency in conversion processes, the use of conductive metal oxide anodes (including mixed oxides) has been reported in many scientific works [15-18] due to their availability,

synthesis reproducibility and dimensional stability. This last factor is crucial in waste water treatment applications.

Experimental

A series of electrolysis runs were carried out by monitoring the behaviour of the oxidation by-products. A synthetic solution (4 litres for each run) was prepared using the pure grade (Aldrich) chemical reagents (urea, reactive Blue 4 dye, acetonitrile, formamide, guanidine and pyridazine) – Fig. 1.

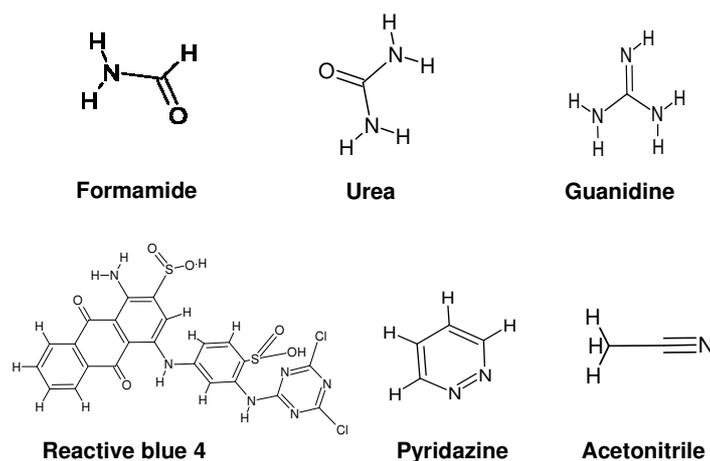


Figure 1. Investigated compounds.

The electrochemical oxidation experiments of organic compounds were carried out in a divided cell [19, 20] 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 runs were carried out isothermally ($30 \pm 2 \text{ }^\circ\text{C}$), controlled by means of a water cooling system placed within the mixing tank. A stainless steel plate was employed as cathode while platinized titanium or DSA type (Ruthenium oxide) were used as anodes. 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) method. All the final concentrations were established using colorimetric determination by means of the Orbeco-Hellige water analysis system (model 975-MP); in addition, UV-Visible spectra (Unicam UV₂, double ray) and chromatographic analysis (Varian Pro Star double pump HPLC equipped with UV-VIS diode array detector) were

performed in the case of cyclic compounds, to monitoring the behaviour of organics degradation.

Results and discussions

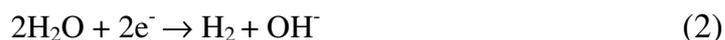
Direct electrooxidation

In the case of direct electrooxidation runs, sodium sulphate 0.02 N was selected as supporting electrolyte, since a negligible electro-generation of bulk oxidising agents (e.g., peroxodisulphates) derives from its use [21] and, in this case, the conversion kinetics could only be ascribed to direct oxidation over the anode surface.

In the electrochemical runs, the pH value in the anodic compartment naturally decreases logarithmically (from ca. 7.0 reach 2.0 after 2 hours of the run) because of water oxidation,



At the same time, the cathodic reactions increase the pH of this compartment logarithmically (reaching the value of 12 after 2 hours)



The results obtained in the electrolytic runs for each molecule, that are described below, were analogous for the two types of tested anodes in term of electrochemical mechanisms, varying only the rate of nitrate generation. The DSA electrode showed worse organic oxidation rate, due mainly to the increase in the oxygen evolution reaction rate (the side reaction) and consequently lesser final amount of nitrates, while the total amount of ammonia remains the same as with Ti/Pt anode.

Urea oxidation

The maximum concentrations of N-ions after 2 hours of electrolysis of urea solution are shown in Fig. 2. The higher the current density, the higher the reaction rate, while, from the superposition of the n-ions generation curves at different currents (not shown here), it is possible to conclude that the mechanism remains the same. According to the reactions below, the generation of ammonia, in the anodic chamber can be due to both hydrolysis (equation 3) in homogeneous phase and heterogeneous reaction (at the anode) with superior oxides on the anode surface (equation 4).



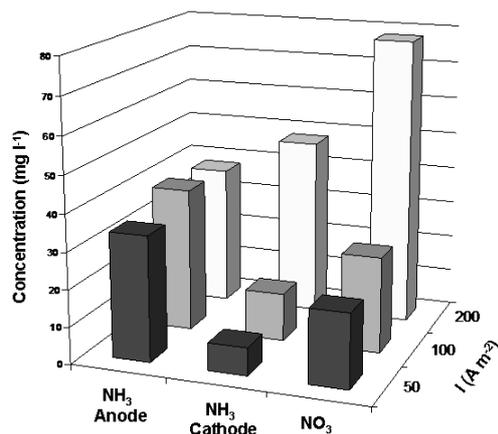


Figure 2. Maximum concentration of N-ions after 2 hours of electrolysis of urea solution (2 g L^{-1}) at different current densities (I). Ti/Pt anode, electrolyte Na_2SO_4 0.02 N . (NO_3) represents the concentration of NO_3 measured in the anodic compartment, while (NH_3 cat.) and (NH_3 an.) represent the ammonia in the cathodic (dialyzed) and anodic compartments, respectively.

Since the anodic compartment is characterised by a low pH value, the generated ammonia quickly becomes an ammonium ion. This ion can flow to the cathodic chamber through the cationic membrane, and then the concentration of NH_4^+ in the anodic chamber reaches a limiting value. Ammonia is regenerated in the cathodic chamber due to the presence of a basic media (equation 5).



Moreover, in this compartment ammonia can be only accumulated without reduction reaction at the cathode, since nitrogen is in its most reduced state. Comparing these results with those obtained by photocatalytic studies [22] on the oxidative treatment of urea, the ammonium/nitrate ratio in the electrochemical processes is higher; this is mainly due to the cited two paths in the electrochemical conversion of the molecule, whereas in the photo-catalytic case the degradation is mainly due to the attack of OH radicals [23] and, at neutral pH value, the contribution of hydrolysis is negligible.

Guanidine oxidation

For this molecule, the profiles of the NO_3 and NH_3 concentration-time curves are similar to that obtained in the case of the urea. The main difference between the two molecules is the presence of double bond carbon-NH in Guanidine. In fact, this bond inhibits the heterogeneous reaction at anode surface, since a higher number of steps (higher oxides at the anode) are requested to complete the oxidation to nitrate formation; then, the $\text{NH}_3/\text{NO}_3^-$ ratio is higher than that related to urea electrooxidation.

Formamide oxidation

The same behaviour found for guanidine (in terms of anions ratio) was obtained for formamide (Fig. 3). The fast initial conversion observed is mainly due to the presence of easily extractable hydrogen bonded to the carbon.

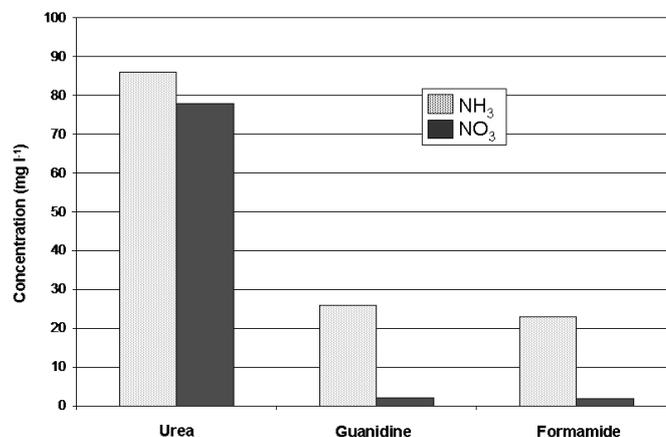


Figure 3. Maximum concentrations of N-ions after 2 hours of electrolysis of urea solution (starting concentration: 2 g L⁻¹), guanidine (starting concentration: 0.5 g L⁻¹), and formamide (starting concentration: 7.33 g L⁻¹). Anode: Ti\Pt, electrolyte: Na₂SO₄ 0.02 N, applied current density: 200 A m⁻².

Piridazine oxidation

The original molecule was effectively converted. Notwithstanding this, the rate of inorganics nitrogen ion generation was very low. The nitrate ion was not found in the products. This last result seems to be linked to the low oxidation state of the nitrogen in the starting molecule, as referred in the photocatalytic oxidation studies [22].

Reactive Blue 4 oxidation

The original molecule was effectively converted, evidenced by a decolouration of the solution. Chromatographic analysis permits to determinate that during the electrooxidation this molecule was broken up into three fragments: amino-anthraquinon-sulphonic acid, aminobenzene-sulphonic acid and the triazinic ring. This last structure (the reactive part of the dye), that contains the main part of nitrogen, turned out to be very persistent against the electrooxidative treatment, and then a negligible mineralization of nitrogen was obtained. In spite of the mentioned low mineralization of the nitrogen, the rapid decolouration observed during the electro-oxidation is an important result, since colour is a pollution factor for the wastewaters of the textile industry and, for this case, toxicity and biodegradability tests should be carried out in order to be sure that the electrochemical treatment transforms the initial pollutant in environmental friendly intermediates [24].

Acetonitrile oxidation

Acetonitrile shows a negligible reactivity. The stability of this molecule is due to the presence of a triple bond between carbon and nitrogen. In fact, the high stability of these molecules renders it useful for a wide range of applications as solvent in the electrochemistry field. The eventual oxidation of acetonitrile brings about the formation of cyanate, a very hard-to-oxidize molecule even by OH radicals.

Indirect coupled electrooxidation

As demonstrated, direct electrooxidation of nitrogen-containing molecules could enable, on the one hand, to have an oxidative conversion of a variety of organic molecules, but, alternatively, 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 [25].

In the case of direct electrochemical treatment, the inhibition of nitrate formation in a highly oxidizing process seems to be difficult, as well as the removal of nitrates 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 at the anodic chamber of the divided cell, thereby enabling a combined process of direct-indirect electrooxidation coupled with electrodialysis. This pathway was devised under the assumption that chlorine and nitrates generation might be competing processes.

In the oxidation of urea, in presence of sodium chloride, when operating 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. Dichloramine generation is linear with respect to the electric charge level passed and mono-chloro amine is quickly transformed to di-chloro amine.

Nitrates are thus generated from two routes: i) the direct-homogeneous electrooxidation of ammonia, and ii) a parallel homogeneous reaction between the electro-generated "active chlorine" and the nitrogen-containing molecules, according to a reaction which is not fully understood [26].

As the chloride salt concentration rises, chloramine formation starts to compete with nitrate generation, reducing the maximum amount of nitrates obtained after two hours of electrolysis time (Fig. 4) and the amount of recovered ammonia rises, as a consequence of the enhanced urea degradation (via the homogeneous path).

The increase in chloride concentration causes the amount of recovered ammonia to be slowly incremented and the level of dichloramine to be greater. On the other hand an increase of current density (up to $200 - 300 \text{ A m}^{-2}$ range) leads to an enhancement on the initial levels of nitrates, the maximum level of dichloramine remains almost the same but the recovered ammonia rises significantly mainly as a consequence of the increase of the cell potential (electric field) and the enhancement in the urea oxidation rate.

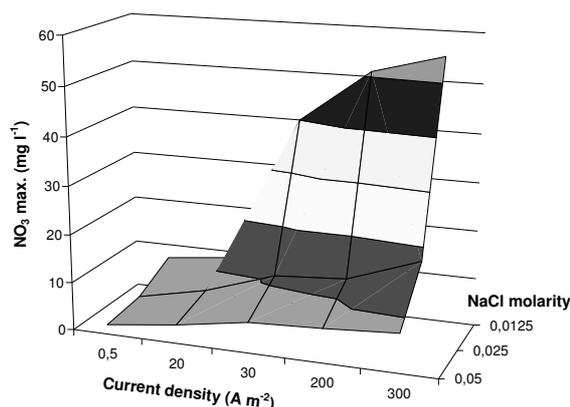


Figure 4. Maximum concentrations of nitrate ions after 2 hours of electrolysis of urea solution (2 g L^{-1}) in presence of different concentrations of chloride salt and different applied current densities. Anode: Ti\Pt.

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

Conclusions

The distribution of ionic nitrogen inorganic species derived from the direct electrooxidation over conductive metal oxide was monitored. The $\text{NH}_3/\text{NO}_3^-$ ratio mainly depends on the original chemical structure that also influences the extent of inorganic nitrogen formation. The most meaningful differences between the electrochemical oxidation regards other AOPs (i.e., photocatalysis, ozonation, etc.) come from the contribution of a homogeneous reaction (acid hydrolysis), which affects principally amide, and amine molecules. This hydrolysis (continuous acidification) is present in minor importance in the others AOPs, since pH of the whole solution does not change or changes slowly. As a consequence, the reaction rate of molecules is faster in the electrochemical case for amidic and aminic compounds, and the $\text{NH}_3/\text{NO}_3^-$ ratio is higher than in others AOPs.

The problem of high concentration of nitrate generated by the electrolytic process was tried to be solved by coupling direct-indirect electro-oxidation and electro-dialysis, in the divided cell, in which the total inhibition of nitrate formation was not possible. Nevertheless, an apparent reduction of the maximum amount of this species was enabled by increasing the chloride salt concentration, thereby promoting the chlorine evolution reaction that acts as a competitive anodic reaction. In addition, nitrates generated by homogeneous reaction with “active chlorine” contribute to a relatively low extent of the anodic generation of nitrates. Consequently, an optimum value of both chloride concentration and imposed current density for limiting the maximum nitrate concentration can be

determined, which is also dependent on other experimental conditions such as pH and the ratio between total nitrogen and active chlorine.

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Resumen

El presente estudio se centró en la monitorización de la distribución de nitrógeno en los productos de oxidación de compuestos orgánicos nitrogenados (urea, colorante Blue 4, acetonitrilo, formamida, guanidina y piridazina) sobre ánodos de titanio platinado y de óxidos de rutenio. La mineralización del nitrógeno produce contaminantes inorgánicos ($\text{NH}_3/\text{NH}_4^+$ y/o $\text{NO}_2^-/\text{NO}_3^-$). Los compuestos amídicos y amínicos reaccionan tanto en fase homogénea (hidrólisis acida) como en fase heterogénea (electrooxidación directa), con una velocidad que depende del estado inicial de oxidación del nitrógeno en la molécula orgánica. Las moléculas con enlaces múltiples y heterocíclicos fueron convertidas eficazmente con una mineralización del nitrógeno despreciable, dada la elevada estabilidad de los compuestos intermedios de su oxidación. Los resultados obtenidos (elevada producción de nitratos) evidencian la necesidad de acoplar la electrooxidación directa con otros procesos para, de esta forma, limitar la concentración de nitratos a niveles aceptables. Los procesos estudiados, diálisis (del catión amonio) más oxidación indirecta (mediante cloro activo), demostraron ser alternativas validas para este objetivo.

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