Nitrate reduction by electrochemical processes using copper electrode: evaluating operational parameters aiming low nitrite formation

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ABSTRACT

This work aims to present different electroreduction and electrocatalytic processes configurations to treat nitrate contaminated water. The parameters tested were: current density, cell potential, electrode potential, pH values, cell type and catalyst use. It was found that the nitrite ion is present in all process variations used, being the resulted nitrite concentration higher in an alkaline pH. The increase in current density on galvanostatic operation mode provides a greater reduction of nitrate (64%, 1.4 mA cm$^{-2}$) if compared to the potentiostatic (20%) and constant cell potential (37%) configurations. In a dual-chamber cell was tested the nitrate reduction with current density of 1.4 mA cm$^{-2}$, being obtained the NO$_3$ reduction of 85%. The use of single chamber cell presented 32 ± 3% of nitrate reduction, indicating that in this cell type the nitrate reduction is smaller than in dual-chamber cell (64%). The presence of Pd catalyst with 3.1% wt. decreased the nitrite (1.0 N-mg L$^{-1}$) and increased the gaseous compounds (9.4 N-mg L$^{-1}$) formation. The best configuration showed that, by fixing the current density, a highest nitrate reduction is obtained and the pH presents a significant influence during the tests. The use of catalyst decreased the nitrite and enhanced the gaseous compounds formation.

Key words: copper electrode, electrocatalysis, electroreduction, nitrate reduction, operational parameters, Pd catalyst

HIGHLIGHTS

- The electroreduction can be used to treat contaminated water with a high nitrate concentration.
- Galvanostatic mode promotes a high nitrate reduction.
- The increase of the current density improves the nitrate reduction.
- The Pd catalyst decreases the nitrite and increases the formation of the gaseous compounds.
- This system does not need a catalyst separation stage of water after reaction.

INTRODUCTION

Nitrate (NO$_3$(aq)) is an ion present in surface and groundwater and its presence in these systems can cause damage to the environment (Smith & Schindler 2009; Wang et al. 2021) and to human health (Cameron et al. 2013; Wang et al. 2021). Among different methods used for the treatment of water contaminated with nitrate, the membrane separation processes (MSP) stand out. However, MSP generate a concentrated solution (Sahli et al. 2008), transferring the problem to a residue that needs to be properly treated or stored.

Other options for the treatment of water contaminated with nitrates are the electroreduction and the catalytic processes, where the nitrate ion (NO$_3$(aq)) can be reduced to nitrogen gas (N$_2$(g)). To use the electroreduction process in industrial scale it is necessary to study the different operational parameters that can influence the system, as each operational characteristic may have an effect on the ion removal efficiency and on the different products that can be formed, such as ammonium (NH$_4$(aq)), nitrite (NO$_2$(aq)) and gaseous compounds (ideally nitrogen gas) (Beltrame et al. 2018). Among different parameters, pH, current density, cell (Beltrame et al. 2018) and electrode potential can affect the nitrate ion reduction and, consequently, the products formation (Reyter et al. 2008; Su et al. 2016; Xu et al. 2018). On the other hand, in the catalytic processes, the parameters that influence the reduction efficiency are: the type of catalyst support, reducing agent, pH, composition of the catalyst active phase, type of reactor, among others (Martínez et al. 2017).
To improve conversion or selectivity, a combined process, the electrocatalysis, may be used, to increase the efficiency of the global process, when compared to using them separately (electroreduction or catalysis). For electroreduction and electrocatalytic processes, the electrode material is also an important parameter. Several electrodes can be used to propitiate the nitrate reduction, such as nickel (Simpson & Johnson 2004; Gwak et al. 2019) and iron (Jonoush et al. 2020). However, copper (Pérez-Gallent et al. 2017; Beltrame et al. 2019) is the one the most used, due to the similarity of the energy levels of the copper ‘d’-orbital with the nitrate Lumo π* molecular orbital (Garcia-Segura et al. 2018).

In the electrochemical reduction of nitrate, the electrokinetic is generally slow, due to the high energy of the lowest unoccupied π molecular orbital of nitrate, which makes the injection of charge into this orbital unfavorable. However, due to the similarity in energy levels of the ‘d’ orbitals of some metals, such as copper, and the unoccupied π molecular orbital of nitrate, these metals present the ability to promote the electrochemical reduction of NO3− (Garcia-Segura et al. 2018), transferring electrons more easily to the adsorbed nitrate, and favoring the nitrate electroreduction (Khomutov & Stamkulov 1971; Huang et al. 1990). Thus, it was chosen to use the copper electrode due to its low cost, high stability, catalytic activity (Zhang et al. 2019) and high corrosion resistance. Dortsiou et al. (2013) used, for instance, a Sn like electrode and, even with good selectivity for nitrogen, an electrode corrosion was observed (Dortsiou et al. 2013).

For the electrocatalytic reduction of nitrate, there are studies that focus on the modification of the surface of the electrodes with the use of nanoparticles of a noble metal, for instance, palladium (Pd) (Estudillo-Wong et al. 2011; Zhang et al. 2014) and also non-noble metals (Ye et al. 2020). A distinct approach is the addition of the catalyst not in the electrode surface, but in the cathode compartment of the reactor (Beltrame et al. 2019, 2020).

In electroreduction, the energy that is given to the system promotes water hydrolysis, forming hydrogen gas (H2(g)) and oxygen gas (O2(g)). The hydrogen formed acts as a reducing agent on the copper surface, promoting the reduction of nitrate to nitrite and reducing nitrite to ammonium or gaseous compounds (Bosko et al. 2014):

\[
2\text{NO}_3^-(aq) + 5\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{OH}^-(aq) + 4\text{H}_2\text{O}(l) \tag{1}
\]

\[
2\text{NO}_3^-(aq) + 8\text{H}_2(g) \rightarrow 2\text{NH}_4^+(aq) + 4\text{OH}^-(aq) + 2\text{H}_2\text{O}(l) \tag{2}
\]

The reactions 1 and 2 demonstrate that the nitrate ion reduction generates hydroxyl, promoting an increase of the pH value, what increases the selectivity of the reaction towards the production of the ammonium ion, NH4+(aq), instead of N2(g) (Tokazhanov et al. 2020). The desirable product of nitrate reduction in drinking water is the nitrogen gas, though the byproducts ammonium or nitrite are obtained in electrochemical treatments (Garcia-Segura et al. 2018).

It is a challenge to find an ideal operational parameter to obtain the nitrate electroreduction: in this sense, some parameters should be analyzed, such as current density, pH values, operation mode, cell potential, cell type and catalyst use. Therefore, in this paper, operational parameters for nitrate electroreduction process were studied, aiming low nitrite ion formation, by using the copper electrode to increase the ammonium and gaseous compounds production. For this, the following parameters were studied: current density, pH, cell potential, electrode potential and cell type. Three operational mode were evaluated: galvanostatic, potentiostatic and constant cell potential. In the galvanostatic mode, different current densities were fixed, while in the potentiostatic mode the cathode potential was fixed (Garcia-Segura et al. 2018). In the constant cell potential operational mode, the cell potential was fixed along the experiments.

At last, the influence of Pd catalyst in the nitrate reduction was also tested. It is important to highlight that usually palladium catalyst supported on alumina is used in the powder form to reduce nitrate (Martínez et al. 2017; Tokazhanov et al. 2020), being necessary a subsequent unitary operation to separate the catalyst of the nitrate solution.

At this work, the catalyst was placed close to the copper electrode, and not added on the nitrate solution. Therefore, there was no need for a further filtration step to separate the catalyst from the solution, yielding a novel electrocatalytic system.

**EXPERIMENTAL**

**Work solutions**

Two different sodium nitrate solutions, with 600 mg L−1 (135.5 N-mg L−1) or 100 mg L−1 (22.5 N-mg L−1) (NaNO3 > 99%, Reagen, Brazil), were used to study the nitrate ion reduction. A sulphate solution of 1,400 mg L−1 (Labsynth, Brazil) was used to maintain the system conductivity when a dual chamber cell was
used. In some cases, when a single chamber cell was used, a sulphate solution (300 mg L$^{-1}$) was also added as electrolyte. Palladium chloride P.A (PdCl$_2$ Neon, Brazil) was used in the pellet's catalyst synthesis. Alumina (Ketjen CK300) with 198 m$^2$ g$^{-1}$ surface area and 0.5 mL g$^{-1}$ pore volume was used as support in the pellet's synthesis (1.2% wt. and 3.1% wt.). All solutions were prepared with distilled and deionized water. When the pH was adjusted, solutions of H$_2$SO$_4$ 3 mol L$^{-1}$ (Dinâmica, Brazil) or NaOH 3 mol L$^{-1}$ (Dinâmica, Brazil) were used.

**Experimental setup**

A single chamber cell (SCC) and a dual-chamber cell (DCC) (Beltrame et al. 2018), separated by a cationic membrane (HDX 100, supplied by Hidrodex$^*$) with 16 cm$^2$, were used in the experiments. For both cells, an electrode of Ti70/TiO$_2$30RuO$_2$ (geometric area of 15 cm$^2$) and an electrode of copper (15 cm$^2$) were used as anode and cathode, respectively. For the SCC, 170 mL of NaNO$_3$ solution was utilized. In the DCC, the sodium nitrate solution was placed in the cathodic compartment, whereas on the anodic side, sodium sulphate was used. The volume of the solution in each chamber was 170 mL.

The catalyst preparation was accomplished with the methodology used by Beltrame et al. (2020) and as briefly explained here: alumina pellets, PdCl$_2$ (0.056 M) and HCl (0.1 M) were added in a Beaker with magnetic stirring and heated until 80 °C, being the temperature maintained until all the solution was evaporated. Then, the pellets were calcined (500 °C for 4 hours) and activated with hydrazine (1 M) for one hour and at 40 °C. The catalyst was washed and dried for 12 hours at 80 °C. The palladium catalyst (0.25 g inside a 100% polyester fabric bag with geometric area of 30 cm$^2$) was placed in the cell near the copper electrode. This mode of configuration was chosen instead of carrying out an electrode synthesis, or using the catalyst as a power form, because it is a simple way of scaling up the process. The catalyst can be placed near the electrode and withdrawn when necessary, without a separation step, such as filtration, for instance.

**Polarization curves**

Different current density, cell and electrode potentials can be used to provide the nitrate electroreduction. Therefore, polarization curves were carried out aiming to obtain values of current density and potentials that can be applied in the NO$_3$(-aq) reduction. Current–voltage curves (CVC) were carried out in the cationic membrane, monitoring the cell (by DC Power Source) and electrode potential. Besides, voltammetry curves were also accomplished. All polarization and voltammetry curves were made with the nitrate concentration of 600 mg L$^{-1}$ (135.5 N-mg L$^{-1}$).

**Current–voltage curves (CVC)**

The Current–voltage curves were constructed using the DCC. In the first moment, in order to minimize the membrane polarization phenomena, it was determined the limiting current of the cationic membrane by polarization curves (Buzzi et al. 2013; Bittencourt et al. 2017). Current increments were applied using a DC power source, for 120 seconds, with a space of 180 seconds without electrical current. Then, the difference of the membrane potential was measured, as well as, during the CVC construction, the cathode and the cell potential. The cathode potential was obtained using Luggin’s capillary with Ag/AgCl as a reference electrode. Figure S1 (see supplementary material) shows the scheme used to obtain the values of current density and potentials.

**Cyclic voltammetry**

A cyclic voltammetry was accomplished to investigate a specific current and potential that furthers the nitrate ion reduction. The voltammetry was made in a typical cell with three electrodes in conjunction (Autolab model PGCTAT 302N). The reference electrode was Ag/AgCl (saturated), the working electrode was copper and the counter electrode was platinum.

**Electroreduction experiments**

In a first moment the Equation (3) (Plethcher 1982) was used to determine the time of reaction:

$$t = \frac{m \cdot n \cdot F}{I \cdot M_w} \quad (3)$$

where 'm' is the initial concentration of nitrate in the solution (0.6 g L$^{-1}$ of nitrate), ‘F’ is the Fadaray Constant (96,485 C mol$^{-1}$), ‘$M_w$’ is the nitrate molecular mass, ‘I’ is the current (A) and ‘n’ is the electron number from the
limiting step of the reaction, which in this case was used the value 2 (reaction of nitrate reduction to nitrite: \( \text{NO}_3^{(aq)} + \text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{NO}_2^{(aq)} + 2\text{OH}^{(aq)} \)). The final value calculated was 5.2 hours, so all tests were performed for a period of 6 hours. Besides, all electroreduction assays were performed in SCC or DCC cell configurations, magnetically stirred (800 rpm–1,000 rpm) and performed at room temperature (25 °C). Tests in galvanostatic and potentiostatic modes were carried out, besides the experiments with the application of constant cell potential. In galvanostatic mode, the current density was fixed during the experiments and this operational mode is the most appropriate when it is not necessary a high process control; also, it can be easily applied in industrial scale (García-Segura et al. 2018). By this mode, a study about how the different current densities can influence nitrate reduction and the products formed was conducted. Then, studies on the adjustment of pH during the experiments were done. The pH measurements and adjustments were performed by a PHTEK pH measurer (model PH-3B).

In potentiostatic mode, based on the values obtained in the cyclic voltammetry, the potential of the copper electrode was fixed, with the use of a Luggin capillary with Ag/AgCl reference electrode and with an Autolab model PGCTAT 302N potentiostat.

Experiments with a kept constant cell potential were also accomplished to evaluate the influence of this parameter.

Table 1 presents the summary of experiments carried out. After the procedures with the concentrated solution containing 600 mg L\(^{-1}\) of nitrate (135.5 N-mg L\(^{-1}\)), tests were carried out reducing the initial concentration of nitrate to 100 mg L\(^{-1}\) (22.5 N-mg L\(^{-1}\)), aiming to simulate groundwater contaminated with this ion. In these tests, Pd catalysts with different metallic charges were also used.

### Calculations and analysis

Initial and final samples from the cathodic compartment were collected to determine the nitrate, nitrite and ammonium concentrations by ion chromatography (DIONEX ICS 3000 Chromatograph). The results of nitrate reduction were expressed as conversion rate \( X(\%) \) (Equation 4):

\[
X(\%) = \left[ 1 - \left( \frac{C_t}{C_0} \right) \right] \cdot 100 \tag{4}
\]

where \( C_0 \) is the concentration of nitrate (N-mg L\(^{-1}\)) at the beginning of the reduction process and \( C_t \) is the concentration (N-mg L\(^{-1}\)) of nitrates at time \( t \) (six hours).

The calculations of products formation were carried out considering the analyzed \( \text{NO}_3^{(aq)} \), \( \text{NO}_2^{(aq)} \) and \( \text{NH}_4^{(aq)} \) concentrations and the calculated N-gaseous compounds concentration (obtained by mass balance). The mass

| Cell type | Operational mode | Parameter influence | Conditions |
|-----------|------------------|---------------------|------------|
| DCC       | Cell potential fixed | Experimental potentials | 7 and 9 V |
| DCC       | Potentiostatic   |                      | -0.9 V \(_{\text{Ag}/\text{AgCl}}\) |
| DCC       | Galvanostatic    | Current density      | 0.8 mA cm\(^{-2}\) |
|           |                  |                     | 1.2 mA cm\(^{-2}\) |
|           |                  |                     | 1.4 mA cm\(^{-2}\) |
| SCC       | Galvanostatic    | Cell type and current density | 1.2 mA cm\(^{-2}\) |
|           |                  |                     | 1.4 mA cm\(^{-2}\) |
| DCC       | Galvanostatic    | Initial pH           | 2.5 |
|           |                  |                     | 4.0 |
|           |                  |                     | 6.5 |
| DCC       | Galvanostatic    | pH adjustment        | 3–3.5 |
|           |                  |                     | 6–6.5 |
|           |                  |                     | 9–9.5 |
| DCC       | Galvanostatic    | Use of catalyst, 100 mg L\(^{-1}\) and 1.4 mA cm\(^{-2}\) | Without catalyst |
|           |                  |                     | With Pd 1.2% wt. |
|           |                  |                     | With Pd 3.1% wt. |
balance was calculated by subtracting, from the initial nitrate concentration, the nitrite, ammonium and nitrate present in the solution after six hours of experimental tests, considering that all other products formed are gaseous compounds and that, according to the Pourbaix Diagram (1963), the N₂O and NO oxides formation is not likely at the experimental pH and electrodes potential, being these compounds only intermediary products (Abdallah et al. 2014). Also, N₂O and NO are unstable subproducts and can be easily reduced to nitrogen (Zhang et al. 2019).

Catalysts characterization
To determine the composition and surface morphology of the materials used in this study, the catalysts were characterized by SEM and EDS, using a Phenom-World scanning electron microscope, equipped with an energy dispersive analytical system, operated with 15 kV of radiation.

RESULTS AND DISCUSSION
Determination of current density, and cell and electrode potentials
Current–voltage curves
In Figure 1(a), the Current–voltage curves in the cationic membrane can be seen. The limiting current density value, defined by the intersection of the tangents of the first and second region (Buzzi et al. 2013) was 1.57 mA cm⁻². The use of current densities smaller than the limiting one (i < iₘₚ) can minimize the concentration polarization phenomena in the membrane/solution interface (Moura et al. 2012). So, in a first moment, to minimize the effect of membrane polarization, the current density applied in the electroreduction tests was 1.2 mA cm⁻², which corresponds to the 85% of the limiting current density value obtained in the CVC.

By the CVC construction the cathode potential (copper electrode potential) was monitored (Figure 1(b)). At this experiment, inflections in 0.64 Vₜₐ and 0.75 Vₜₐ were observed. Analyzing these values at the Pourbaix

![Graph](image-url)
Diagram (1963), and by pH 11 it was possible to observe that ammonium or nitrogen formation would be possible.

These values of cathode potential, according to the CVC obtained, correspond to 7 and 9 V in the cell potential. The current density values obtained in these potentials were 0.4 and 0.5 mA cm\(^{-2}\), respectively. These values of current density indicate that the membrane polarization phenomena will not occur (Bosko et al. 2014), since these current density values are lower than the \(i_{\text{lim}}\). Therefore, cell potentials of 7 and 9 V were also chosen for essays with constant cell potential.

**Cyclic voltammetry**

The voltammetry presents a peak in the coordinate 1.4 mA cm\(^{-2}\) and \(-0.85\) V\(_{\text{Ag/AgCl}}\) (Figure S2 in supplementary material), indicating the nitrate reduction to other nitrogen products. Then, electroreduction tests were also made in galvanostatic mode applying 1.4 mA cm\(^{-2}\) and in potentiostatic mode applying a cathode (electrode) potential of \(-0.9\) V\(_{\text{Ag/AgCl}}\).

**Nitrate reduction reactions in a dual-chamber cell (DCC)**

**Cell potential effect**

One operational way to carry out nitrate electroreduction is fixing the cell potential. To carry out these tests, the cell potential was fixed in 7 and 9 V, according to data obtained in the CVC. When a cell potential of 7 V was used, the nitrate was reduced 25 ± 3%, while with 9 V, the reduction was of 37 ± 5%. When applying a cell potential of 7 V, the initial current density was of 0.4 ± 0.1 mA cm\(^{-2}\) and the final was of 0.58 ± 0.1 mA cm\(^{-2}\), while at 9 V the initial value was of 0.62 ± 0.1 mA cm\(^{-2}\) and the final value of 1.0 ± 0.1 mA cm\(^{-2}\). These values of current density can explain the low nitrate reduction obtained in this variation since, probably, the hydrogen generated was not sufficient to provide the nitrate reduction, being necessary more time to occur this reaction.

On the gaseous compound's formation (Figure 2), the formation was similar in both potentials, being higher on 9 V (10 ± 2 N-mg L\(^{-1}\)) and this probably occurs due to higher hydrogen formation in the higher current density (Zhang et al. 2016). The ammonium formed was lower in both variations and this also probably happens as a result of lower values of current densities reached.

**Electrode potential effect: potentiostatic mode**

Several electrode potentials were used with a copper electrode on the literature, for instance (Reyter et al. 2008) applied values of of \(-0.9\) V, \(-1.1\) V and \(-1.4\) V vs. Hg/HgO obtaining the total relative conversion of nitrate with

![Figure 2](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.215/895329/wst2021215.pdf)

**Figure 2** | Effect of constant cell potential in the nitrate reduction and compounds formed. Initial nitrate concentration: 600 mg L\(^{-1}\) (135.5 N-mg L\(^{-1}\)), 6 h of experiment.
−1.4 V and total ammonia formation, with 250 hours of electrolysis reduction and 0.1 M NaNO₃ in 1 M NaOH solution (Reyter et al. 2008). The experiments conducted in this paper were performed applying an electrode potential of −0.9 V_{Ag/AgCl} (−0.96 V_{Hg/HgO}), being this value determined by the cyclic voltammetry results. The results show that, at the end of the 6 hours of experiments, 20 ± 3% of the nitrate was reduced. The low value can be attributed to values of current density (Figure 3) reached in this operational parameter, that decreased during the experiment. It is possible to notice that this value of reduction was similar to the one obtained when the cell potential was fixed in 7 V and the initial current density was 0.4 mA cm⁻².

Figure 4 shows the products formation by nitrate reduction, where practically the same values were found to the nitrite, ammonium and gaseous compounds. Studies indicate that in a potential of −1.1 E/V_{Ag/AgCl} there is a predominance in the reduction of nitrate to the nitrite ion in an alkaline medium (Cattarin 1992), while in higher potentials (−1.3 V_{Ag/AgCl}) the main product formed is ammonia. According to Xu et al. (2018) the different products selectivity is related to the demands of electrons for each product formation. For instance, Kuang et al. (2018) tested a nitrate reduction in the range of −1.2 to −3.0 V_{Ag/AgCl} (initial nitrate concentration of 50 N-mg L⁻¹ with 1.0 g L⁻¹ of Na₂SO₄ and Cu like electrode) and observed the highest faradaic efficiency to nitrite (44.6%) and ammonium (17.3%) when a potential of −1.2 V was applied, considering that in more negative potentials these products formation decreased.

It should be noted that the experiments performed in the potentiostatic mode are be used when greater control of the nitrate reduction is required because only the redox reactions that are thermodynamically possible in an ‘E’ potential occurred. However, to obtain this greater control of the process, three electrodes are required: a working electrode, a counter electrode and a reference electrode. Therefore, the galvanostatic mode, although having

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**Figure 3** | Current density as a function of time. Conditions: constant cathode potential of −0.9 V_{Ag/AgCl}; 6 h: initial nitrate concentration of 600 mg L⁻¹.

**Figure 4** | Concentration of nitrogen compounds as function of the applied cathode potential (−0.9 V_{Ag/AgCl}). Initial nitrate concentration: 600 mg L⁻¹ (135.3 N-mg L⁻¹). 6 h of experiment.
as a characteristic a smaller control of the chemical reactions occurring during the nitrate reduction, presents
applicability in industrial operations (García-Segura et al. 2018).

After performing these experiments, it is noted that in addition to the potential of the electrode and cell, the
current densities reached are an important parameter in nitrate reducing, associated to the hydrogen evolution
and to its role as a reducing agent. Then, tests were accomplished in galvanostatic mode setting the current density
during the experiment.

**Current density effect: galvanostatic mode**

Several current density values were applied according to the literature, such as 0.89, 2, 5, 25, 50 and 100 mA cm⁻²
(Prasad et al. 2005; Kim et al. 2015; Zhang et al. 2016). However, in this study, the current density was based on
the polarization curves and cyclic voltammetry. Then, tests were made with 0.8 mA cm⁻² (current density below
the limiting value found in the membrane CVC), 1.2 mA cm⁻² and 1.4 mA cm⁻². It can be observed (Figure 5(a))
that the lowest nitrate reduction occurs at the lower current density (28 ± 3%, with 0.8 mA cm⁻²). The highest
nitrate reduction, 64 ± 3%, occurred in the current density of 1.4 mA cm⁻², while in 1.2 mA cm⁻², a reduction
of 52 ± 2% was attained. This can be associated with the higher hydrogen content generated in higher current
densities (Zhang et al. 2016). Figure 5(b) shows the products formation in each current density applied.

The nitrite ion was formed in all current densities studied and the ammonium formation was detected in minor
quantities. The presence of nitrite in solution may be explained due to the capacity of nitrate to adsorb in the sur-
faced of copper electrode, then the NO₃⁻ is reduced to NO₂⁻ (Xu et al. 2018; Zhang et al. 2021), but this ion is
not efficiently reduced to gaseous compounds in the Cu surface. Besides, the presence of N-nitrite may be also
related to the pH of the solution, alkaline in this experimental variation, considering that in these pH values
the NO₂⁻ formation is favored (Hörold et al. 1993). The N-ammonium formation was practically constant,
between 11 and 18 N-mg L⁻¹, in all variations, however it was possible to identify greater formation at the highest
applied current density. The highest current density presented an increased formation of gaseous compounds
(25 ± 3 N-mg L⁻¹).

**Influence of cell type**

Aiming to compare the difference between nitrate reduction in a divided (DCC) and a single electroreduction cell
(SCC), the NO₃⁻ removal applying an electroreduction cell without membrane, in galvanostatic mode, with the
current densities of 1.2 or 1.4 mA cm⁻², was tested. On Table 2, it can be noticed that the nitrate reduction was
lower when the membrane was not used.

![Figure 5](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.215/895329/wst2021215.pdf)

**Figure 5** | Influence of current density in galvanostatic mode in the nitrate reduction with 600 mg L⁻¹ of nitrate (135.5 N-mg L⁻¹).
6 h of experiment. (a) reduction of nitrate as a function of the applied current density. (b) concentration of nitrogen compounds as a function of applied current density.
In a single cell, the reactions of reduction and oxidation can occur simultaneously at the cathode and anode electrode surfaces, respectively (Ding et al. 2015; Martínez et al. 2017). When the membrane was not used, the nitrate can be reduced to nitrite in the cathode electrode and reoxidized nitrate on the anode electrode (See Figure S3 in supplementary material). Therefore, the reaction is not completed to nitrogen gas. These reactions that occurred in the electrodes explain the low values of nitrate reduction. About the products, it is possible to identify a similar formation of ammonium and gaseous compounds when a current density of 1.4 mA cm\(^{-2}\) was applied. However, with both applied current densities, there was a predominance of nitrite formation, being the value formed similar to ammonium when 1.2 mA cm\(^{-2}\) was used.

**pH adjustment during the experiments: galvanostatic mode in DCC**

The pH value is very important to the nitrogen reaction. As the better values of nitrate reduction were obtained in galvanostatic mode, different values of pH adjustment were tested during these experiments. To all variations, without pH adjustment, the final values of pH were acid in the anodic compartment (pH = 2.0) and alkaline in the cathodic one (pH = 11.5), this happening due to the reactions (Equations (5) and (6)) occurring in the electrodes (Mook et al. 2012):

**Cathode:**

\[ 2H^+_{(aq)} + 2e^- \rightarrow H_2(g) \quad (5) \]

**Anode:**

\[ 2H_2O(l) \rightarrow 4H^+_{(aq)} + O_2(g) + 4e^- \quad (6) \]

These values of pH influence the products formation, as studies show that in an alkaline medium the main product formed is the nitrite ion (Reyter et al. 2008; Beltrame et al. 2019), in comparison to the acid media, in which the ammonium is more present in the solution (Xing et al. 1990). Taking that into consideration, tests were made applying a current density of 1.2 mA cm\(^{-2}\), adjusting constantly the cathodic solution’s pH during the

![Figure 6](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.215/895329/wst2021215.pdf)

**Figure 6** | Influence of pH adjusted in the nitrate reduction. Conditions: nitrate solution of 600 mg L\(^{-1}\) (135.5 N-mg L\(^{-1}\)), current density of 1.2 mA cm\(^{-2}\), 6 h of experiment.
experiments, adding sulfuric acid (acid pH) or sodium hydroxide (alkaline pH). The results showed that the nitrate reduction increased with increasing pH, being observed a reduction of 23 ± 2% to pH 3–3.5, a reduction of 33 ± 3% to pH 6–6.5 and a reduction of 54 ± 3% to 9–9.5 (Figure 6). The decrease of nitrate reduction in lower pH occurs due to the presence of ions in the solution, such as sulphate from the added sulfuric acid (Huang et al. 2013), competing with the nitrate reduction and blocking the catalytic sites from copper electrodes.

The formation of gaseous compounds increased with increasing pH (Figure 6), but there was no significant difference between using pH 6–6.5 and 9–9.5. The nitrite formation was lower in the acid pH and this was already reported by Garcia-Segura et al. (2018).

Xing et al. (1990) presented in their studies that in more alkaline conditions the reduction produces mainly nitrite, whereas with higher proton concentrations (H+) a major N2(g) or NH4(aq) formation may happen. In alkaline conditions, it is favorable the adsorption of oxidized materials, such as OH− and Ox− in the electrode and the presence of these oxides reduces the amount of available active centers of the copper electrode, which hinders the adsorption of nitrate onto the Cu surface (Martínez et al. 2017; Zhang et al. 2019).

Although the method used to regulate the pH at this work did not present itself as ideal, considering the possible adsorption of sulphate or oxidized materials in the electrode, blocking the active sites of the copper, the results showed that there is a decrease in the formation of the nitrite ion at acidic pH.

**Initial pH adjustment: galvanostatic mode**

The influence of the initial pH in the nitrate solution (135.5 N-mg L−1) was studied using a current density of 1.4 mA cm−2. The initial pH was adjusted with sulfuric acid 3 M and the current was chosen because it was obtained in the CV analysis and propitiated a good reproducibly (low standard deviation) in the experiments. Table 3 presents the results of nitrate reduction and nitrogen compounds formation using the initial pH at 2.5, 4.0 and 6.5. The nitrate reduction was 56 ± 2% to pH 2.5; 60 ± 2% to 4.0 and 64 ± 3% to 6.5, and the products formed when the initial pH was 2.5 and 4.0 were similar. Besides, the formation of the gaseous compounds was very analogous at these pH values. Therefore, it can be concluded that the initial pH, in this case, does not present a variable that can cause significant alteration on the nitrate ion reduction when the electroreduction cell operates in galvanostatic mode.

On the products side, a lot of nitrite was formed in the different initial pH and the highest gaseous compounds formation was obtained with initial pH of 6.5. Li et al. (2010) studied the effect of initial pH on nitrate electroreduction using an iron electrode and the authors concluded that using the initial pH of 3.0; 5.0; 7.0; 9.0 and 11.0 the electrochemical reduction of nitrate was similar for all the variations. Similar values of final reduction may be justified because of the rapid formation of hydroxyls during the nitrate reduction reactions (Equations (1) and (2)) that are occurring. This formation of OH− favors the pH increase in all studied variations, with the main final value in the cathodic compartment being equal to 11.5.

**Influence of the initial nitrate concentration and the use of Pd catalyst**

Aiming to evaluate the electroreduction process to treat a MSP concentrate, tests were made with a solution with lower initial nitrate concentration (100 mg L−1–22.5 N-mg L−1), applying the current density of 1.4 mA cm−2 and without pH control (Figure 7). It was possible to notice that the nitrate reduction was higher (85 ± 4%), however the main products formed were nitrite (5.1 ± 1 N-mg L−1) and ammonium (12.6 ± 2 N-mg L−1) ions, with the formation of only 0.7 ± 0.3 of N-gaseous compounds. The highest formation of ammonium in this concentration can occurred associated to the higher value of current density used, being that according to the study presented by Tong et al. (2019).

**Table 3** | Influence of initial pH in the nitrate reduction with nitrate solution of 600 mg L−1 (135.5 N-mg L−1), current density of 1.4 mA cm−2 at pH 2.5, pH 3.9 and pH 6.5

| Initial pH | X (%) | Nitrite formation (N-mg L−1) | Ammonium formation (N-mg L−1) | Gaseous compounds Formation (N-mg L−1) |
|-----------|-------|-----------------------------|-----------------------------|---------------------------------------|
| 2.5       | 56 ± 2% | 50.8 ± 4                     | 10.0 ± 3                    | 15.0 ± 2                              |
| 4.0       | 60 ± 2% | 56.0 ± 2                     | 10.1 ± 1                    | 15.2 ± 3                              |
| 6.5       | 64 ± 3% | 42.3 ± 3                     | 15.3 ± 2                    | 29.1 ± 4                              |

6 h of experiment.
Comparing the values of initial nitrate concentrations applying a current density of 1.4 mA cm\(^{-2}\), it can be inferred that with the smaller initial nitrate concentration (22.5 N-mg L\(^{-1}\)) there was a higher nitrate reduction (85 ± 4%), while with the initial nitrate concentration of 135.5 N-mg L\(^{-1}\) a reduction of 64 ± 3% was achieved. The highest nitrate reduction in the smaller initial nitrate concentration may have occurred because the electrochemical reduction is dependent on an initial adsorption in the cathode surface, since the mass transfer depends on the nitrate diffusion in the electrode by Fick’s Law. In different nitrate concentrations, the active sites of electrode can determine the occurrence or not of NO\(_2\) reduction (da Cunha et al. 1996; de Groot & Koper 2004; Dima et al. 2005; Katsounaros & Kyriacou 2007). At this work, by using a cathodic electrode of copper with 15 cm\(^2\), the active electrode sites can be sufficient to propitiated a major nitrate reduction on 100 mg L\(^{-1}\).

Aiming to minimize the production of nitrite/ammonium and to improve the gaseous compounds formation (Beltrame et al. 2021), a catalyst impregnated with different Pd loads was tested. In the present system, copper is responsible for reducing nitrate; in turn, Pd can reduce the nitrite generated to gaseous compounds or ammonium. In this paper, the catalyst chosen was alumina in the pellets form, impregnated with Pd in the proportions of 1.2% wt. and 3.1% wt. (Figure 7).

The nitrate reduction with catalyst was practically the same of without a catalyst (85 ± 4%), indicating that that the palladium does not act in the nitrate reduction (Rosca et al. 2009). The reduction was of 81 ± 3% when using 1.2% Pd wt. and 83 ± 3% to 3.1% Pd wt. In the presence of the catalyst, a smaller amount of nitrite was observed. The nitrite in the solution was lower when used the catalyst with Pd 3.1% wt. (1.0 ± 0.5 N-mg L\(^{-1}\)) and the ammonium formation was of 8.0 ± 2 N-mg L\(^{-1}\). The presence of the catalyst with Pd 1.2% wt. resulted in the ammonium formation being the same from the one obtained with the variance without catalyst (12.5 ± 2 N-mg L\(^{-1}\)). However, a decrease of the nitrite formation to 3.0 ± 1 N-mg L\(^{-1}\) was noted. The highest gaseous compounds formation was obtained when using a catalyst with Pd 3.1% wt., being attained a value of 9.4 ± 1.5 N-mg L\(^{-1}\). The improve of gaseous compounds formation can be explained due to presence of H\(_{ads}\), that can occur in the presence of catalysts having a high affinity to adsorbed hydrogen, for example, the palladium used in these tests (Chaplin et al. 2012).

In general, the fact that more palladium causes a higher formation of reduction products is in line with the expectations for systems with catalytic nitrite reduction (Bosko et al. 2011). So, the composition, the type of support, structure of the catalyst (Martínez et al. 2017) and the operating parameters define which end-products are favored. The lower presence of nitrite in the solution is due to the reduction of nitrite to ammonium or nitrogen in Pd active sites (Jung et al. 2012; Jung et al. 2014; Hamid et al. 2018; Tokazhanov et al. 2020), according to the reactions 7 and 8.

\[
2\text{NO}_2(aq) + \text{Pd} - 4\text{H}_{ads} \rightarrow \text{Pd}^0 + \text{N}_2(g) + 4\text{OH}^-_{(aq)} \quad (7)
\]

\[
\text{NO}_2(aq) + \text{Pd} - 6\text{H}_{ads} \rightarrow \text{Pd}^0 + \text{NH}_4^+_{(aq)} + 2\text{OH}^-_{(aq)} \quad (8)
\]
Catalysts characterization

Figure 8 shows the SEM micrographs of the materials used in this study. The SEM was used to determine the morphology and disposition of the active phase. The materials composition was quantified by EDS, operated in the surface mapping mode. Also, elemental composition is showed in Table 4.

In the Figure 8(a), the fresh sample of Pd 1.2% catalyst shows Pd particles distributed on the entire surface of the alumina (composition determined by EDS). In Figure 8(c), Pd 3.1% wt., it can be seen that the number of particles is greater and there is also a visible population of agglomerates, compared to the Pd catalyst 1.2% wt. For the catalysts used, Figure 8(b)–8(d), it can be seen that the samples show an increase in the particle size of Pd compared to the fresh samples. This increase was more accentuated in the Pd 3.1% wt. catalyst. All Pd particles are nanometric in size. This reordering is similar to the behavior observed in reactions of catalytic elimination of nitrate in aqueous medium, using the same support and active phase (Zoppas et al. 2018).

Table 4 | Weight concentration of the components found on the surfaces of the catalysts analyzed by SEM

| Weight concentration of the components found on the surfaces of the catalysts analyzed by SEM |
|-----------------------------------------------|-----------------|-----------------|-----------------|
|                                                | Al\(^a\)         | O\(^a\)          | Pd\(^a\)        |
| Fresh Pd 1.2% wt.                             | 52.82           | 45.82           | 1.35            |
| Used Pd 1.2% wt.                              | 55.44           | 42.43           | 2.13            |
| Fresh Pd 3.1% wt.                             | 50.74           | 45.95           | 3.30            |
| Used Pd 3.1% wt.                              | 50.24           | 45.13           | 4.62            |

\(^a\)Weight concentration.
In Table 4, it can be seen the predominance of Al and O, characteristic of the support, in all samples. In addition, it is observed that the composition of the active phase for fresh samples is close to the nominal value Pd 1.2% and 3.1% wt. Furthermore, there is a superficial enrichment of the active phase, indicating that there could be a migration of Pd particles from the inside of the support to the surface.

**Energy consumption**

An important parameter to analyze when applying an electrochemical process is the energy consumption. The Table S1 in supplementary material shows the values of energy consumption obtained in these experiments. With the DCC and 600 mg L$^{-1}$ of nitrate, it can be observed that the values of energy consumption are between 78 and 119 Kwh/N-Kg and these values are in accordance to those obtained on the Zhang et al. (2019) study. The highest values in the SCC (340 Kwh/N-K, 1.4 mA cm$^{-2}$) can be attributed to the fact of the smaller nitrate reduction compared to the one with achieved with the DCC.

The highest values of energy consumption obtained in the initial nitrate concentration of 100 mg L$^{-1}$ (524 Kwh/N-K) can occur as a response to a low nitrate concentration in the solution; also, the reduced presence of ions in the solution can cause a major resistance of the cell, causing a higher consumption of energy. The values of Faradic Current obtained in the nitrite formation in the electroreduction with initial nitrate concentration of 135.5 N-mg L$^{-1}$ and DCC cell are presented in the supplementary material.

**CONCLUSIONS**

This work shows that the electrochemical process to nitrate reduction has potential to be used as a way of treating wastewater with high and low nitrate concentration. With the experiments carried out it was possible to identify and to relate important parameters that can influence in the electrochemical reduction of nitrate aiming low nitrite formation. It was noticed that in an alkaline pH and initial nitrate concentration of 600 mg L$^{-1}$, in all the current densities tested, a high nitrite concentration was formed. By applying 1.4 mA cm$^{-2}$, it was possible to obtain 64% of nitrate reduction. At an alkaline pH, there is a highest reduction of nitrate ion compared to an acid pH, however with adjusted pH in 3–3.5 and 6–6.5 the nitrite formation is practically null.

The initial pH value was not significant for the reduction of nitrate and consequent formation of nitrogen products. The cell with two compartments presented a higher nitrate reduction than the cell with one compartment (32%, 1.4 mA cm$^{-2}$). To the nitrate concentration of 100 mg L$^{-1}$, with and without Pd catalyst, the nitrate reduction was similar (82%); but considering the products formation, with a catalyst of 3.1% wt. Pd, the nitrite formation was only 1.0 N-mg L$^{-1}$ and the gaseous compound formation was of 9.4 N-mg L$^{-1}$.

Lastly, it was possible to notice that operational parameters like current density, type of cell, pH, initial nitrate concentration and catalyst can influence the electrochemical nitrate reduction and, consequently, the products formed, being necessary more studies and tests about this subject.

**ACKNOWLEDGEMENTS**

The financial support of the Brazilian funding agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq/Brazil, Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul FAPERGS/Brazil, Financiadora de Estudos e Projetos -FINEP/Brazil and from the Ibero-American Program on Science and Technology for Development (CYTED) are acknowledged. The authors would like to thank Régis Araujo for the English review.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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Received 12 April 2021; accepted in revised form 25 May 2021. Available online 4 June 2021.