



# Influence of bicarbonate, other anions and carbon dioxide in the activity of Pd-Cu catalysts for nitrate reduction in drinking water

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## ABSTRACT

Synthetic and commercial drinking waters with different composition were studied as reaction media to study the influence of salts in NO<sub>3</sub> catalytic reduction using a Pd-Cu catalyst supported on a carbon black. As a general trend, a decrease in NO<sub>3</sub> conversion and an increase in NH<sub>4</sub><sup>+</sup> selectivity were observed for high HCO<sub>3</sub><sup>-</sup> concentration media in mixed salts waters. Literature has commonly ascribed HCO<sub>3</sub><sup>-</sup> effect to competitive adsorption with NO<sub>3</sub>. However, in the current work, the mechanism for effect HCO<sub>3</sub><sup>-</sup> is reconsidered basis on HCO<sub>2</sub> formation during NO<sub>3</sub> catalytic reduction, here reported for the first time. HCO<sub>2</sub> formation indicates that hydrogenation of HCO<sub>3</sub><sup>-</sup> occurs in addition to adsorption. Likewise, decomposition of HCO<sub>2</sub> on the catalysts surface releases hydrogen leading to increased spill-over and relevant hydrogenation of NO<sub>3</sub> to NH<sub>4</sub><sup>+</sup>. The presence of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> reduces NH<sub>4</sub><sup>+</sup> selectivity due to competition for active sites and lower HCO<sub>2</sub> generation. Furthermore, it was observed that the use of CO<sub>2</sub> as buffer also contribute to the hydrogenation of NO<sub>3</sub> to NH<sub>4</sub><sup>+</sup> through HCO<sub>2</sub> route.

## 1. Introduction

Nitrate (NO<sub>3</sub><sup>-</sup>) is a common contaminant in surface and groundwater. The pollution by nitrate is mainly caused by anthropogenic activities, such as the combustion of fossil fuels, excessive use of nitrogen-rich fertilizers, intensive animal farming and discharge of wastewater [1–4]. There is a concern about NO<sub>3</sub><sup>-</sup> accumulation in drinking water because it can produce diverse diseases such as methemoglobinemia (blue baby syndrome), caused by nitrite (NO<sub>2</sub><sup>-</sup>) produced in the human body from NO<sub>3</sub><sup>-</sup>, and even cancer [5]. NO<sub>3</sub><sup>-</sup> is also associated with respiratory infection and alteration of thyroid metabolism induced by conversion of NO<sub>3</sub><sup>-</sup> to nitrous compounds [6]. To minimize the adverse health impacts of NO<sub>3</sub><sup>-</sup>, EU regulation establishes 50, 0.1 and 0.5 mg/L as the maximum permitted concentration in drinking water for NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and ammonium (NH<sub>4</sub><sup>+</sup>), respectively [7]. There are several technologies commercially available for the treatment of water contaminated with NO<sub>3</sub><sup>-</sup>, including biological denitrification, reverse osmosis, and ion exchange [2,3,8]. These techniques present disadvantages in their application to drinking water. For instance, reverse osmosis and ion exchange produce effluents with high NO<sub>3</sub><sup>-</sup> concentration, which usually require a post-treatment [9]. Alternative techniques such as photocatalytic reduction, zero-valent iron reduction, electrochemical reduction and catalytic chemical reduction have received increasing attention [5].

Catalytic chemical reduction with hydrogen (H<sub>2</sub>) is an interesting technology to reduce NO<sub>3</sub><sup>-</sup> concentration in water that is free from secondary effluents. The reaction mechanism consists of NO<sub>3</sub><sup>-</sup> reduction to nitrogen (N<sub>2</sub>), involving nitrous compounds intermediates such as NO<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> as unwanted by-product. The most accepted mechanism for the NO<sub>3</sub><sup>-</sup> hydrogenation over a bimetallic catalyst is shown in Fig. 1. It consists of a first stage in which H<sub>2</sub> dissociates on the noble metal sites and NO<sub>3</sub><sup>-</sup> is adsorbed on promoter metal sites, in this step NO<sub>3</sub><sup>-</sup> is reduced to NO<sub>2</sub><sup>-</sup>. This intermediate species is then adsorbed on monometallic noble metal sites where it is hydrogenated to other intermediate species. The final products, NH<sub>4</sub><sup>+</sup> or N<sub>2</sub>, depend on the pathway in which NO<sub>2</sub><sup>-</sup> is reduced [10].

Diverse kinds of metal phases and supports have been studied to improve activity, and particularly to achieve high selectivity towards N<sub>2</sub>. The use of both monometallic and bimetallic catalysts has been investigated, being the second the most active for NO<sub>3</sub><sup>-</sup> reduction. The active phase of bimetallic catalysts is usually composed of a noble metal and a promoter metal. The pairs that showed the best performance are those formed by noble metals such as Pd and Pt, and promoter metals such as Cu, Sn and In [5]. In a recent work it has been found that Pd-Cu catalysts supported on carbon-based supports such as activated carbon, carbon nanofibers and carbon blacks showed almost complete NO<sub>3</sub><sup>-</sup> conversion due to the textural properties and structure of these materials

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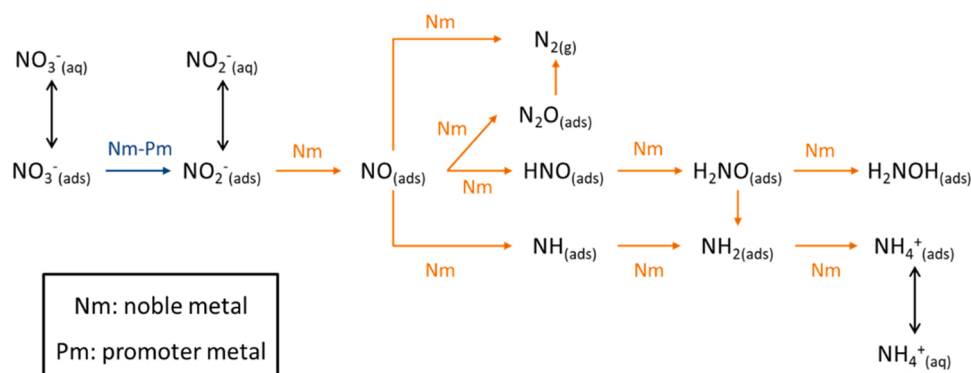


Fig. 1. Mechanism  $\text{NO}_3^-$  reduction over bimetallic catalyst. Adapted from Martínez et al. [5].

[11].

Most studies on catalytic chemical reaction have been conducted with  $\text{NO}_3^-$  solutions in deionized water, however a more thorough study is needed on the effect of ions present in water on catalytic activity. Several authors have reported that salts commonly present in natural waters sources decrease catalytic activity and even lead to deactivation. Thus, Palomares et al. [12] studied  $\text{NO}_3^-$  reduction in a continuous reactor using polluted water with high conductivity and presence of Ca and sulphate ( $\text{SO}_4^{2-}$ ) salts. They found that Pd-Sn catalyst achieved total  $\text{NO}_3^-$  conversion during 8 h and then a progressive decrease in  $\text{NO}_3^-$  conversion took place. This decrease in the catalytic activity was ascribed to the deactivation of the catalyst due to the precipitation of Ca salts on the catalyst surface blocking the active sites. Furthermore, a high  $\text{SO}_4^{2-}$  concentration in the polluted water also caused the deactivation of the catalyst by poisoning of Pd active sites by the sulphur species. Other anions have also been shown to have a negative influence on  $\text{NO}_3^-$  reduction catalysts [13–16]. Wang et al. [15] reported on the behaviour of a Pd-Cu/AC catalyst in the presence of chloride ( $\text{Cl}^-$ ) ion, which was shown to be adsorbed on the metallic Cu sites inhibiting  $\text{NO}_3^-$  reduction to  $\text{NO}_2^-$ . The blockage of active sites also led to a decrease of both  $\text{NO}_3^-$  conversion and  $\text{N}_2$  selectivity, because of the altered ratio between N and H species adsorbed on the catalyst surface [17].

Bicarbonate ( $\text{HCO}_3^-$ ) has also been found to have a negative effect on catalytic activity. Pintar et al. [18] reported one of the first studies about salts effects in  $\text{NO}_3^-$  reduction, carrying out reaction tests in water with  $\text{HCO}_3^-$  concentration in the 0–500 mg/L range. They observed a decrease in  $\text{NO}_3^-$  disappearance rate and an increase in  $\text{NH}_4^+$  selectivity as  $\text{HCO}_3^-$  concentration increased. The behaviour was attributed to competitive adsorption on the active sites due to similarities in the structures of  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  ions, both with planar structure and angles between the N–O and C–O bonds equal to  $120^\circ$ . In recent studies concerning  $\text{HCO}_3^-$  influence on  $\text{NO}_3^-$  reduction, other authors confirmed that its effect is greater than that of other ions present in drinking water [14,17–19]. Nevertheless, to the best of our knowledge, there are no studies deepening on the nature of this negative interference in the catalytic reduction of  $\text{NO}_3^-$ .

In the current work the effect of salts on  $\text{NO}_3^-$  reduction using a Pd-Cu catalyst supported on carbon black is investigated, with a focus on the reaction mechanism and fate of  $\text{HCO}_3^-$ . Reduction experiments are carried out using synthetic and commercial drinking waters with diverse ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) spiked with  $\text{NO}_3^-$ . The  $\text{HCO}_3^-$  concentration in water resources is highly variable and largely depending on water source characteristics. Different studies have reported  $\text{HCO}_3^-$  concentration values ranging from a few tens to more than 500 mg/L [20,21]. Therefore, to analyse the  $\text{HCO}_3^-$  effect, it was chosen to work with commercial drinking water and considering this wide range of concentrations.

## 2. Experimental

### 2.1. Materials

$\text{PdCl}_2$  (> 99.9%),  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  (> 99.9%), 2,6-Pyridinedicarboxylic acid (> 99.5%),  $\text{CaCl}_2$  (> 99.5%),  $\text{MgSO}_4$  (> 99.5%) and Formate Standard for IC (> 99.96%) were provided by Sigma-Aldrich.  $\text{NaCl}$  (99.5%),  $\text{NaNO}_3$  (99%),  $\text{NaNO}_2$  (98%),  $\text{NH}_4\text{Cl}$  (99.5%),  $\text{Na}_2\text{CO}_3$  (99%),  $\text{NaHCO}_3$  (99.5%) and  $\text{HNO}_3$  (65%) were supplied by Panreac.  $\text{H}_2$  (> 99.999%) and  $\text{CO}_2$  (> 99.99%) were supplied by Nippon gases. Carbon black ENSACO350G (ENS350) was purchased from Timcal.

### 2.2. Catalyst preparation and characterization

The commercial carbon black ENS350 was used as support to prepare Pd-Cu bimetallic catalysts by successive wet impregnation with metal salt solutions of Pd ( $\text{PdCl}_2$ ) and Cu ( $\text{CuCl}_2 \cdot 0.2 \text{H}_2\text{O}$ ). The nominal load of metallic phase in the catalyst was 5% (wt.) and the Pd:Cu ratio was 2:1 (wt). The metal solution of Pd was prepared in 0.1 M HCl and then was mixed with 1 g of support in a rotary-evaporator at  $70^\circ\text{C}$ , 200 rpm and 150 mbar until dryness. Then impregnation of Cu solution, which was prepared in milli-Q water, was carried out following the same procedure. After impregnation, the catalyst was dried in an oven at  $60^\circ\text{C}$  for 24 h, calcined at  $200^\circ\text{C}$  for 2 h in air atmosphere, and finally reduced at  $200^\circ\text{C}$  under  $\text{H}_2$  flow for 1 h (25 N mL/min). In a former study that compared different calcination and reduction temperatures for Pd-Cu catalysts supported on a carbon material, it was found that the optimum calcination and reduction temperature for these catalysts was  $200^\circ\text{C}$ , due to high conversion results were obtained when tested in catalytic assays [22]. Accordingly,  $200^\circ\text{C}$  was selected as calcination and reduction temperatures for the catalyst synthesized in the current work. The support and catalyst were characterised as described in a previous work [11]. The support showed a surface area of  $770 \text{ m}^2 \text{g}^{-1}$ . The catalyst characterization by Transmission Electron Microscopy (TEM), using JEOL JEM 2100 with EDS, Oxford instruments and ImageJ software for the measure of nanoparticles mean diameter. The results showed good metal dispersion with a mean nanoparticle size and standard deviation of 1.4 nm and 0.6 nm, respectively [11]. Elemental maps of the catalyst were obtained by energy dispersed X-ray spectroscopy (EDX) coupled to a FEI Talos F200X microscope. Furthermore, in the present work the fresh and used catalysts were characterized by X-ray Photoelectron Spectroscopy (XPS), using K-Alpha Thermo Scientific equipped with an AlK $\alpha$  X-Ray excitation source, 1486.68 eV. XPSPEAK v4.1 software was used to determine the proportion of zero-valent and electro-deficient metal species on the catalyst surface.

**Table 1**

Composition of the water samples tested.

Waters tested	Na <sup>+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)
MW	—	—	—	—	—	—
SW1	—	0.8	2.8	0.6	13.4	—
SW2	21.3	—	13.2	55.6	52.1	—
DW1	2.0	2.9	0.4	0.8	5.9	< 5
DW2	2.0	92.4	2.7	3.8	6.8	274
DW3	21.0	88.0	23.0	39.8	52.8	298

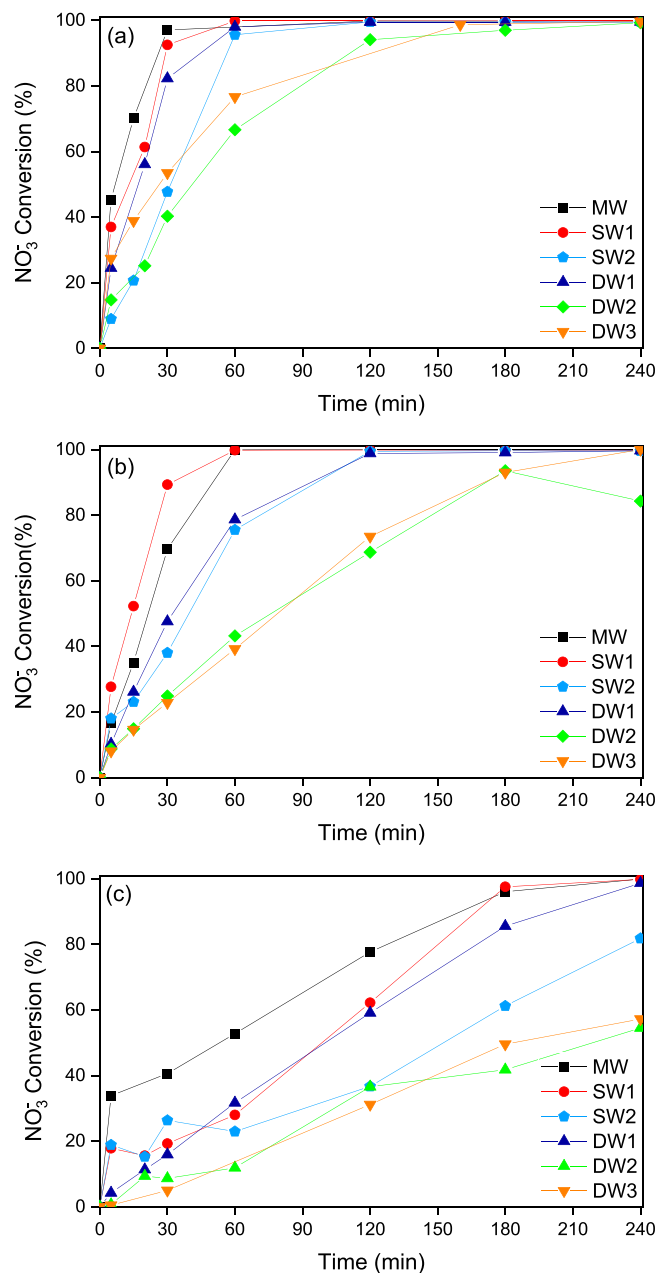
### 2.3. Water samples composition

To analyse the ions effect on the catalytic activity, some water solutions with different composition were prepared. Firstly, synthetic waters with low ions concentration (SW1) and high ions concentration (SW2) were prepared without addition of bicarbonate. These solutions were prepared dissolving CaCl<sub>2</sub>, MgSO<sub>4</sub> and NaCl, in milli-Q water. Additionally, a series of commercial drinking waters with a wide range of ions concentrations (DW1, DW2 and DW3) were tested. The pH values of the synthetic and commercial drinking waters used in this study are in the range of 7–8. The characterization of the water samples tested can be seen in Table 1. Milli-Q water was used as blank (MW). The results for the blank correspond to the experiments reported in previous study using milli-Q water [11].

### 2.4. Catalyst evaluation

The NO<sub>3</sub><sup>-</sup> catalytic reduction tests were carried out in a jacketed glass reactor at 30 °C and atmospheric pressure. An amount of catalyst (60 mg) was placed into the reactor with 140 mL of synthetic or drinking water under vigorous stirring (800 rpm). The reaction medium was buffered by use of CO<sub>2</sub>. H<sub>2</sub> (50 N mL/min) and CO<sub>2</sub> (50 N mL/min) were bubbled from 30 min before zero reaction time. Then, 10 mL of a concentrated solution of NO<sub>3</sub><sup>-</sup> were added at zero reaction time in order to have an initial concentration of 100 mg/L. Gas flow was maintained constant throughout the reaction (4 h), but different H<sub>2</sub> flow rates from 1 to 50 N mL/min were tested in different experiments. In addition, NO<sub>3</sub><sup>-</sup> adsorption tests were performed in the presence and absence of HCO<sub>3</sub><sup>-</sup> to analyse its effect on the catalytic behaviour. In these tests, the catalyst (60 mg), milli-Q water and CO<sub>2</sub> (50 N mL/min) were brought into contact under stirring (800 rpm) for 30 min before starting the reaction. The test in HCO<sub>3</sub><sup>-</sup> absence was conducted with an initial NO<sub>3</sub><sup>-</sup> concentration of 100 mg/L. The adsorption test in HCO<sub>3</sub><sup>-</sup> presence was carried out using a 100 mg/L initial concentration of each anion. A HCO<sub>2</sub><sup>-</sup> decomposition test in the NO<sub>3</sub><sup>-</sup> presence was also performed, both anions with an initial concentration of 100 mg/L. HCO<sub>2</sub><sup>-</sup> decomposition tests were carried out under the same operating conditions as the NO<sub>3</sub><sup>-</sup> catalytic reduction test, but only CO<sub>2</sub> flow (50 N mL/min) was used. Due to the buffer effect produced by the CO<sub>2</sub>, all tests performed showed pH values in the range of 6.5–7, despite the addition of the different salts. Some experiments were duplicated and an error of less than 10% was obtained in all of them.

The catalytic performance was monitored by taking liquid samples for determination of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>2</sub><sup>-</sup> concentration. Liquid samples withdrawn from the reactor were filtered (PTFE filter, pore size 0.45 µm) prior to analysis by ionic chromatography (Metrohm 882 Compact IC plus anion and cation). A Metrosep C6 column using a 1.7 mM HNO<sub>3</sub> + 1.7 mM 2,6-Pyridinedicarboxylic acid eluent (0.9 mL/min) was used for cation separation and a Metrosep A Supp 5 column and 3.2 mM Na<sub>2</sub>CO<sub>3</sub> + 1 mM NaHCO<sub>3</sub> eluent (0.7 mL/min) was used for anion separation. Moreover, HCO<sub>3</sub><sup>-</sup> concentration was calculated from the inorganic carbon (IC) of the liquid samples measured using a TOC-VCSH apparatus (Shimadzu). The catalyst behaviour is analysed by means of the results of NO<sub>3</sub><sup>-</sup> conversion, selectivity towards NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> calculated by



**Fig. 2.** NO<sub>3</sub><sup>-</sup> conversion vs reaction time for different waters and H<sub>2</sub> flows: (a) 50 N mL/min; (b) 5 N mL/min; (c) 1 N mL/min ([NO<sub>3</sub>]<sub>0</sub> = 100 mg/L, CO<sub>2</sub> flow: 50 N mL/min, 0.4 g/L of catalyst).

means of Eqs. (1)–(3). In these equations  $n_{i,t=0}$  is represented as the initial concentration of each ion and  $n_{i,t}$  as the concentration at time  $t$  (min) of each ion.

$$X_{NO_3}(\%) = \frac{n_{NO_3,t=0} - n_{NO_3,t}}{n_{NO_3,t=0}} \cdot 100 \quad (1)$$

$$S_{NO_2}(\%) = \frac{n_{NO_2,t}}{n_{NO_3,t=0} - n_{NO_3,t}} \cdot 100 \quad (2)$$

$$S_{NH_4^+}(\%) = \frac{n_{NH_4^+,t}}{n_{NO_3,t=0} - n_{NO_3,t}} \cdot 100 \quad (3)$$

### 3. Results and discussion

#### 3.1. Effect of ions on the catalyst's performance

Fig. 2 depicts NO<sub>3</sub> conversion vs reaction time for all waters tested at different H<sub>2</sub> flows (1–50 N mL/min). SW1 reactions exhibited similar behaviour to MW, with a total conversion at the end of the experiment (4 h), suggesting that at low concentration Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> have a minor influence on the catalyst activity. The experiments with SW2, whose main feature is a higher content in SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup>, showed diminished NO<sub>3</sub> reduction rate in comparison to SW1, in good agreement with previous works [14,15,23]. In general, Cl<sup>−</sup> showed a greater negative effect than SO<sub>4</sub><sup>2−</sup> on both NO<sub>3</sub> conversion and N<sub>2</sub> selectivity [13,15,16, 23]. Hirayama and Kamiya [23] compared Pd-Cu and Pd-Sn catalyst, both supported on alumina, in experiments carried out with aqueous solutions containing 50 mg/L of NO<sub>3</sub> and different concentration of Cl<sup>−</sup> and SO<sub>4</sub><sup>2−</sup>, in the range of 0–220 mg/L and 0–580 mg/L, respectively. They observed noticeable changes in NO<sub>3</sub> decomposition rate and selectivity in the Cl<sup>−</sup> presence for both catalysts. The behaviour was mainly associated with the adsorption of Cl<sup>−</sup> on the active sites of the catalysts, thus, provoking a decrease in nitrogen species adsorption on active sites [15]. This effect took place in a greater extent in Pd-Cu catalyst, even at low Cl<sup>−</sup> concentration (< 28.4 mg/L). According to Cl<sup>−</sup> adsorption isotherms performed by Wang et al. [15], the impact of Cl<sup>−</sup> on these catalysts is due to its higher affinity for Cu sites compared to other promoter metals such as Sn. The Cl<sup>−</sup> effect on the activity of Pd-Cu catalysts has also been observed in other reactions such as trichloroethylene hydrodechlorination [24]. Besides, it was observed that isolated monometallic Cu nanoparticles not interacting with Pd nanoparticles were poisoned with Cl<sup>−</sup> faster and in a greater extent. On the contrary, H<sub>2</sub> spillover from Pd sites contribute to the elimination of Cl<sup>−</sup> species [25, 26]. Hirayama and Kamiya [23] reported a 50% decrease in NO<sub>3</sub> reduction rate in water with a Cl<sup>−</sup> concentration of 28.4 mg/L and a NO<sub>3</sub>:metallic phase ratio ca. 23:1. Sanchis et al. [19] reported a 10% decrease in NO<sub>3</sub> conversion, using a higher Cl<sup>−</sup> concentration (50 mg/L) and a lower NO<sub>3</sub>:metallic phase ratio of 1.8:1, which indicates that a higher metal phase concentration reduces the effect of high Cl<sup>−</sup> concentration. The low loss of activity of the Pd-Cu/ENS350 catalyst in experiments with SW2 water, with a Cl<sup>−</sup> concentration of 55.6 mg/L, could be related to the low ratio between NO<sub>3</sub> initial concentration and metal phase. A decrease in NO<sub>3</sub> reduction activity in SW2 water (82% conversion after 4 h) was only observed clearly when H<sub>2</sub> flow was reduced to 1 N mL/min (Fig. 2c). This observation can be related to lower availability of H<sub>2</sub> for spillover onto Cu sites poisoned by Cl<sup>−</sup>, since in the case of SW1 water a much lower decrease in activity was found for a H<sub>2</sub> flow rate of 1 N mL/min.

Regarding the effect of HCO<sub>3</sub><sup>−</sup>, a non-significant decrease in NO<sub>3</sub> removal rate was observed when HCO<sub>3</sub><sup>−</sup> concentration was low (DW1 water). However, a high HCO<sub>3</sub><sup>−</sup> concentration (DW2 and DW3 waters) led to a drastic decrease in the catalytic activity for all the H<sub>2</sub> flows used. Final values of NO<sub>3</sub> conversion decreased to around 50% when 1 N mL/min H<sub>2</sub> flow was used. Therefore, HCO<sub>3</sub><sup>−</sup> exhibited a much larger influence on catalytic performance than SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup>, in good agreement with the literature [14,17–19]. Sanchis et al. [19] observed a decrease in NO<sub>3</sub> conversion of around 45% when comparing experiments in deionized water and in water with a HCO<sub>3</sub><sup>−</sup> concentration of 200 mg/L. Likewise, when waters with higher ratio [SO<sub>4</sub><sup>2−</sup>]/[HCO<sub>3</sub><sup>−</sup>] or [Cl<sup>−</sup>]/[HCO<sub>3</sub><sup>−</sup>] were tested the decrease in activity was slightly lower (41% and 30%, respectively). Therefore, SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup> could reduce the negative effect of HCO<sub>3</sub><sup>−</sup> on catalyst behaviour, probably due to competitive adsorption at active sites. For this reason, Pd-Cu/ENS350 catalyst showed a similar performance in the reactions where DW2 and DW3 waters were used, with a slight variation of NO<sub>3</sub> conversion (2.7%) for DW3, especially when a 1 N mL/min H<sub>2</sub> flow was used.

The results above show the crossed effect of anions concentration and H<sub>2</sub> availability in the reaction medium. The lower effect of anions

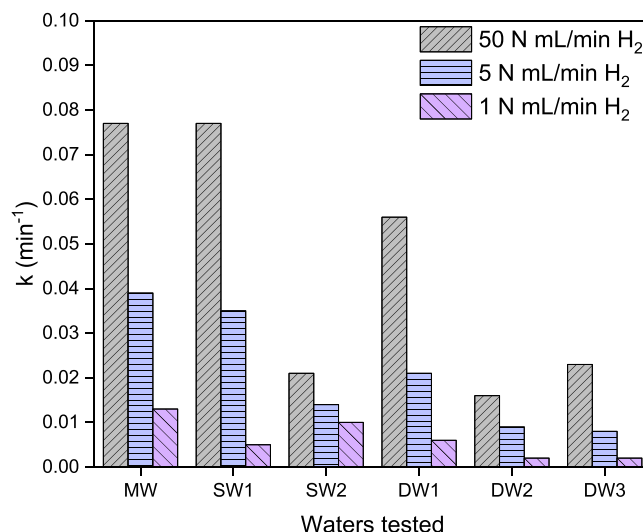


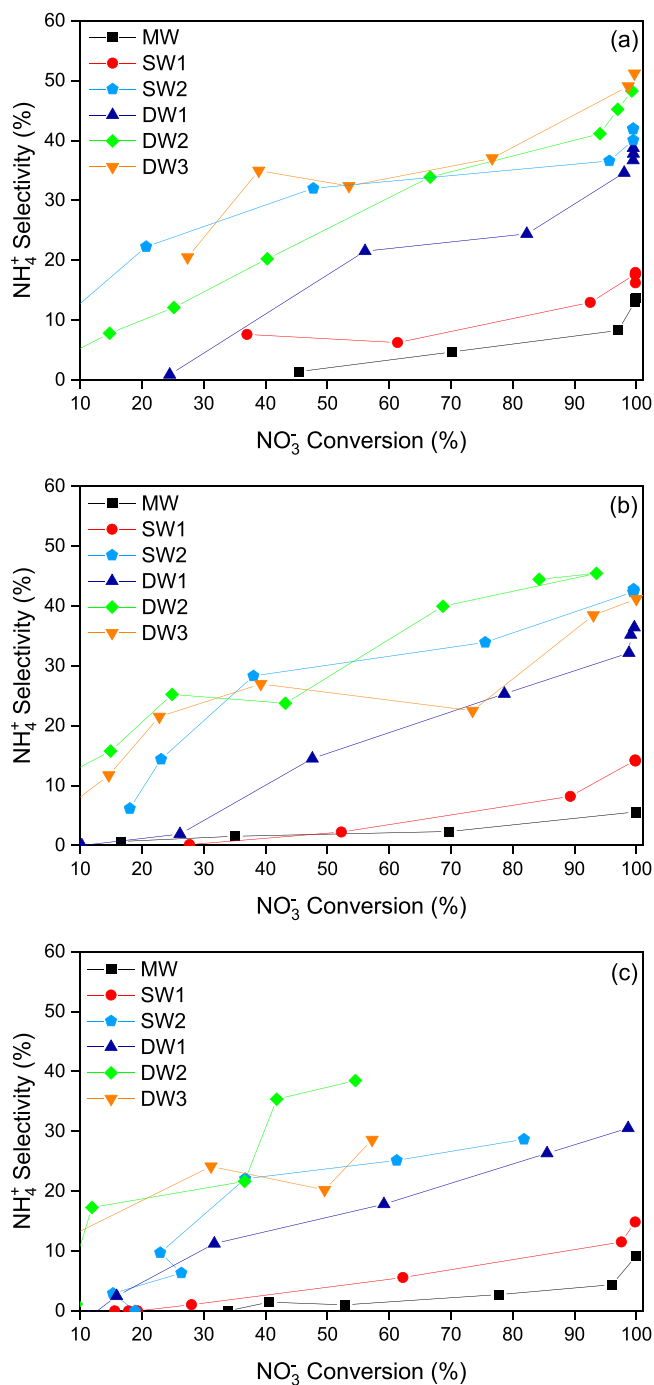
Fig. 3. Kinetic constant for tested waters at H<sub>2</sub> flows of 50, 5 and 1 N mL/min.

observed for high H<sub>2</sub> may indicate both better reduction of the Cu by hydrogen spill-over from Pd, and competitive adsorption of H<sub>2</sub> for the active sites. These attenuation mechanisms become weaker when H<sub>2</sub> flow decreases to 1 N mL/min due to H<sub>2</sub> concentration decrease in the catalyst surface. In a previous work, the influence of H<sub>2</sub> availability and mass transfer regime was assessed through parameters such as Carberry number (gas-liquid and liquid-solid) for external mass transfer and Weisz-Prater criterion for internal diffusion limitations. In that previous work [11], experiments with Pd-Cu/ENS350 catalyst in deionized water using the same experimental setup showed that NO<sub>3</sub> conversion and NH<sub>4</sub><sup>+</sup> selectivity decreased substantially when H<sub>2</sub> flow was reduced to 1 N mL/min. Limitations in H<sub>2</sub> mass transfer in these conditions were also suggested by Carberry number values greater than 0.5 for gas-liquid H<sub>2</sub> transfer. The decrease of H<sub>2</sub> availability at the catalyst surface was shown as a tool to reduce generation of NH<sub>4</sub><sup>+</sup>, but this strategy seems to be limited to waters with low salt content. For a better insight on the salts effect in the NO<sub>3</sub> conversion, the calculation of the kinetic constants was carried out fitting Ln [NO<sub>3</sub>] vs time data to a pseudo first order kinetics equation. For this calculation, only the data corresponding to conversions values lower than 50% were considered. The resulting kinetic constants for all the reactions with the tested waters and different H<sub>2</sub> flow rates can be seen in Fig. 3. The constants are in the range of 0.016–0.077 min<sup>−1</sup> for 50 N mL/min H<sub>2</sub>, 0.08–0.03 min<sup>−1</sup> for 5 N mL/min H<sub>2</sub> and 0.002–0.014 min<sup>−1</sup> for 1 N mL/min H<sub>2</sub>.

NO<sub>2</sub> concentration was found to be very low (< 1 mg/L) in all reactions, and negligible for reaction times longer than 30 min, for this reason, the discussion is focused on the NH<sub>4</sub><sup>+</sup> selectivity. Fig. 4 shows selectivity towards NH<sub>4</sub><sup>+</sup> vs NO<sub>3</sub> conversion for the experiments with all the waters tested. As in the case of NO<sub>3</sub> conversion, selectivity was affected by the presence of ions in the reaction medium. NH<sub>4</sub><sup>+</sup> selectivity in tests in MW water was lower than 14% for all H<sub>2</sub> flows studied, even at complete NO<sub>3</sub> conversion. In the experiments with SW1 water (low anion content, no HCO<sub>3</sub><sup>−</sup>) slightly higher values of selectivity towards NH<sub>4</sub><sup>+</sup> of up to 16.2% were observed at complete NO<sub>3</sub> conversion (Fig. 4a). In contrast, SW2 (high anions content, no HCO<sub>3</sub><sup>−</sup>) showed substantially higher NH<sub>4</sub><sup>+</sup> formation, which can be attributed to the effect of SO<sub>4</sub><sup>2−</sup> and Cl<sup>−</sup> on selectivity. The anions effect on NH<sub>4</sub><sup>+</sup> selectivity is generally related to competitive adsorption on the metallic phase of the catalyst, as previously explained. This can result in a few number of active sites available for adsorption of N intermediate species. Therefore, the H/N ratio would increase at the catalyst surface since the H<sub>2</sub> flow rate is kept constant during the reaction. This variation in the H/N ratio would lead to a higher NH<sub>4</sub><sup>+</sup> formation during the reaction.

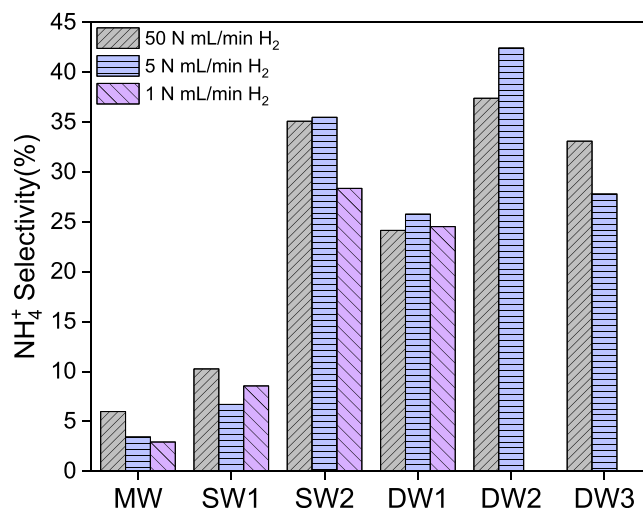
The experiments in waters with low ions concentration but different





**Fig. 4.** Selectivity to  $\text{NH}_4^+$  vs  $\text{NO}_3^-$  conversion for different waters and  $\text{H}_2$  flows: (a) 50 N mL/min; (b) 5 N mL/min; (c) 1 N mL/min ( $[\text{NO}_3^-]_0 = 100 \text{ mg/L}$ ,  $\text{CO}_2$  flow: 50 N mL/min, 0.4 g/L of catalyst).

type of ions, SW1 and DW1, show relevant differences for all  $\text{H}_2$  flows tested. SW1 experiments showed a  $\text{NH}_4^+$  selectivity in the range of 6.7%–10.3% for 80%  $\text{NO}_3^-$  conversion, while DW1 exhibited values in the range between 24.1% and 25.8%. This difference shows that even small amounts of  $\text{HCO}_3^-$  can affect negatively to selectivity. The increase in  $\text{NH}_4^+$  formation has been traditionally attributed to competition for Cu active sites between  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ , leading to lower production of N intermediates (e.g.  $\text{NO}_2^-$ ) and thus higher H/N ratio at Pd active sites leading to overreduction [10,19,23]. However, Fig. 4 shows that large differences between production of  $\text{NH}_4^+$  in SW1 and DW1 water also occur at low  $\text{H}_2$  flow. This observation also suggests interaction between



**Fig. 5.** Selectivity to  $\text{NH}_4^+$  for tested waters at 80% of  $\text{NO}_3^-$  conversion\*.

**Table 2**

$\text{NO}_3^-$  conversion and  $\text{NH}_4^+$  selectivity for reactions using Pd-Cu/ENS350, for all waters tested at different  $\text{H}_2$  flows.

		50 mL/min $\text{H}_2$	5 mL/min $\text{H}_2$	1 mL/min $\text{H}_2$
MW	$\text{NO}_3^-$ Conversion (240 min)	100%	100%	99.9%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	5.9%	3.4%	2.9%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	2.0%	1.9%	1.1%
SW1	$\text{NO}_3^-$ Conversion (240 min)	99.9%	99.8%	99.8%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	10.3%	6.7%	8.6%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	6.8%	2.2%	3.9%
SW2	$\text{NO}_3^-$ Conversion (240 min)	99.5%	99.6%	81.8%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	35.0%	35.5%	28.4%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	32.2%	30.1%	23.7%
DW1	$\text{NO}_3^-$ Conversion (240 min)	99.5%	99.7%	98.7%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	24.2%	25.8%	24.5%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	23.9%	15.4%	15.6%
DW2	$\text{NO}_3^-$ Conversion (240 min)	99.3%	84.3%	54.5%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	37.4%	42.5%	— <sup>a</sup>
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	25.3%	28.1%	37.4%
DW3	$\text{NO}_3^-$ Conversion (240 min)	99.7%	99.9%	57.2%
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 80\%$ )	33.1%	27.8%	— <sup>a</sup>
	$\text{NH}_4^+$ Selectivity ( $X_{\text{NO}_3^-} = 50\%$ )	33.0%	25.6%	20.7%

<sup>a</sup>  $\text{NH}_4^+$  selectivity is not calculated because  $\text{NO}_3^-$  conversion was less than 80% of DW2 and DW3 tests at 1 N mL/min of  $\text{H}_2$ .

$\text{HCO}_3^-$  and Pd, beyond the adsorption of  $\text{HCO}_3^-$  and the effect of H/N ratio at the catalyst surface, since important  $\text{NH}_4^+$  generation was observed even when  $\text{H}_2$  was decreased.

The experiments in DW2 water, with a slightly higher concentration of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , and much larger of  $\text{HCO}_3^-$ , showed  $\text{NH}_4^+$  selectivity in the range 37.4%–42.5% for a  $\text{NO}_3^-$  conversion of 80%, evidencing again the major effect of  $\text{HCO}_3^-$ . In the case of DW3,  $\text{NH}_4^+$  selectivity values were in the range 27.8%–33.1% (Fig. 5). Thus, DW2 and DW3 experiments showed some differences in selectivity towards  $\text{NH}_4^+$  despite containing a similar  $\text{HCO}_3^-$  concentration, indicating the role of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  in

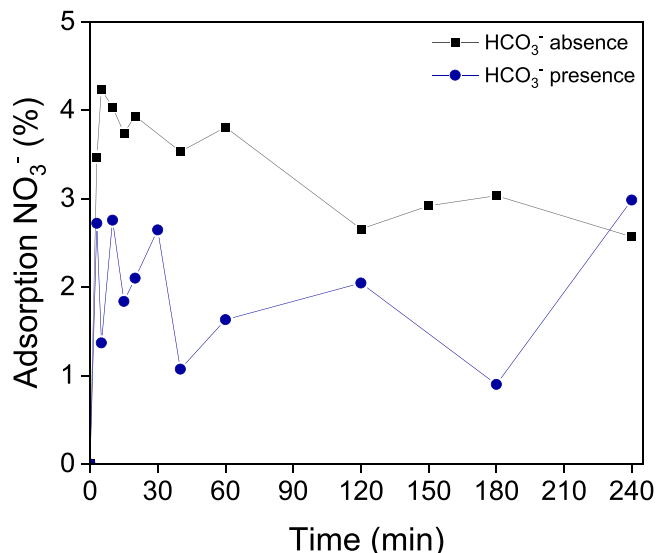


Fig. 6. NO<sub>3</sub><sup>-</sup> adsorption in absence ([NO<sub>3</sub>]<sub>0</sub> = 100 mg/L, CO<sub>2</sub> flow: 50 N mL/min) and presence ([NO<sub>3</sub>]<sub>0</sub> = [HCO<sub>3</sub>]<sub>0</sub> = 100 mg/L, CO<sub>2</sub> flow: 50 N mL/min) of HCO<sub>3</sub><sup>-</sup> in the medium reaction using milli-Q water.

attenuating the effect of HCO<sub>3</sub><sup>-</sup>, even at high HCO<sub>3</sub><sup>-</sup> concentration. This effect may be related to the adsorption competition between HCO<sub>3</sub><sup>-</sup> and the other anions in the reaction medium as SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>. Likewise, the results shows that although poisoning by HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> has been attributed to adsorption on active sites in all cases, different additional mechanisms are involved.

\*DW2 and DW3 tests at 1 N mL/min of H<sub>2</sub> are not represented as the NO<sub>3</sub><sup>-</sup> conversion was less than 80%.

As a summary, it can be seen in Table 2, NO<sub>3</sub><sup>-</sup> conversions to final reaction time (240 min), NH<sub>4</sub><sup>+</sup> selectivity at 80% and 50% of NO<sub>3</sub><sup>-</sup> conversion for all the waters tested at 50, 5 and 1 N mL/min of H<sub>2</sub> flow.

### 3.2. Bicarbonate effect on nitrate reduction

Several authors have studied the influence of the ions naturally occurring in water on NO<sub>3</sub><sup>-</sup> catalytic reduction, agreeing that the ones with the most important negative effect are anions [19,23]. Furthermore, according to different investigations, it has been found a prevailing influence of HCO<sub>3</sub><sup>-</sup> in NO<sub>3</sub><sup>-</sup> reduction [14,17,19]. In order to deepen into the effect of HCO<sub>3</sub><sup>-</sup> on the reaction, a series of adsorption and reaction tests were performed in the presence and absence of this. Fig. 6 depicts the experiments of NO<sub>3</sub><sup>-</sup> adsorption in absence of H<sub>2</sub>. In the presence of HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> was adsorbed to a lesser extent, showing the

competitive adsorption between these anions for the catalytic centres. In reaction experiments, NO<sub>3</sub><sup>-</sup> conversion (Fig. 7a) was also affected by the presence of HCO<sub>3</sub><sup>-</sup>, which increased the time needed to achieve complete conversion. In addition, the selectivity towards NH<sub>4</sub><sup>+</sup> (Fig. 7b) showed an increase in presence of HCO<sub>3</sub><sup>-</sup>. When HCO<sub>3</sub><sup>-</sup> was added as at 10 min reaction time, NO<sub>3</sub><sup>-</sup> conversion became slower and a sharp increase in NH<sub>4</sub><sup>+</sup> generation took place. In the reaction where HCO<sub>3</sub><sup>-</sup> was added as a pulse, a sudden change in pH values from 5.8 to 6.8 was observed due to the pulse. Interestingly, the selectivity to NH<sub>4</sub><sup>+</sup> remained high the rest of the reaction in spite of being buffering with CO<sub>2</sub>. This suggests that the increase in OH<sup>-</sup> concentration could result in more extent blockage of active sites on the catalyst surface thus hindering the adsorption of the nitrogen species [5].



In addition to adsorption, the fate of HCO<sub>3</sub><sup>-</sup> in the reaction system was studied. A significant concentration of formate ion (HCO<sub>2</sub><sup>-</sup>) was detected in all the experiments, evidencing reduction of HCO<sub>3</sub><sup>-</sup>. Fig. 8 shows HCO<sub>2</sub><sup>-</sup> concentration vs reaction time for the NO<sub>3</sub><sup>-</sup> reduction tests in different waters. The formation of HCO<sub>2</sub><sup>-</sup> at the end of the reaction was higher in the experiment using DW2, which has a higher HCO<sub>3</sub><sup>-</sup> concentration. In the experiment with DW3, with HCO<sub>3</sub><sup>-</sup> concentration similar to DW2 but higher concentration of other anions, a lower HCO<sub>2</sub><sup>-</sup> formation was used. This behaviour is related with the presence Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in DW3 water, resulting also in competition with HCO<sub>3</sub><sup>-</sup> for adsorption on the active sites, and decreasing the generation of HCO<sub>2</sub><sup>-</sup>.

In the experiments with waters without HCO<sub>3</sub><sup>-</sup> (MW, SW1 and SW2), relevant formation of HCO<sub>2</sub><sup>-</sup> was also observed, which is related to the reduction of HCO<sub>3</sub><sup>-</sup> formed from CO<sub>2</sub> used to buffer the reaction medium. Blank catalytic reaction experiments were carried out in milli-Q water, without added HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, but under CO<sub>2</sub> and variable H<sub>2</sub> flow (50, 5 and 1 N mL/min). The results of these assays (Fig. 9a) show HCO<sub>2</sub><sup>-</sup> formation but reaching lower concentration than in the case of the experiments in the presence of NO<sub>3</sub><sup>-</sup> (MW, Fig. 8). Moreover, an increase in the HCO<sub>3</sub><sup>-</sup> concentration can be seen (Fig. 9b), resulting from dissolved CO<sub>2</sub>:



In the case of the NO<sub>3</sub><sup>-</sup> reduction tests, OH<sup>-</sup> ions are generated according to reactions (4) to (6) and neutralized by the CO<sub>2</sub> buffer, thus

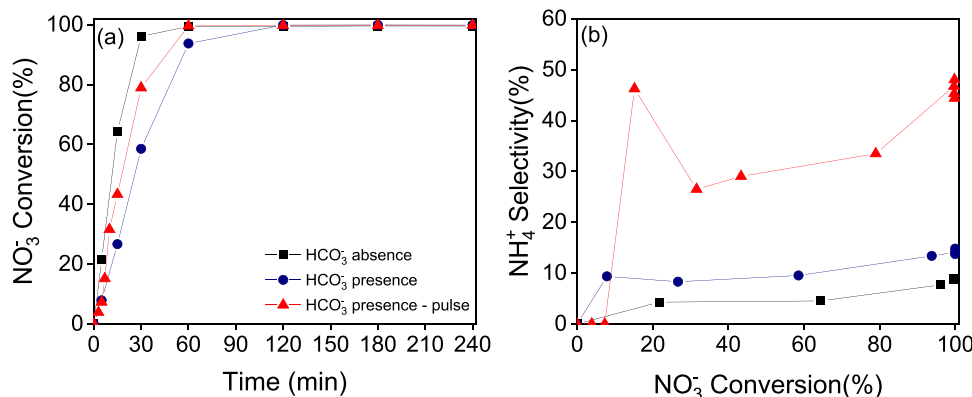
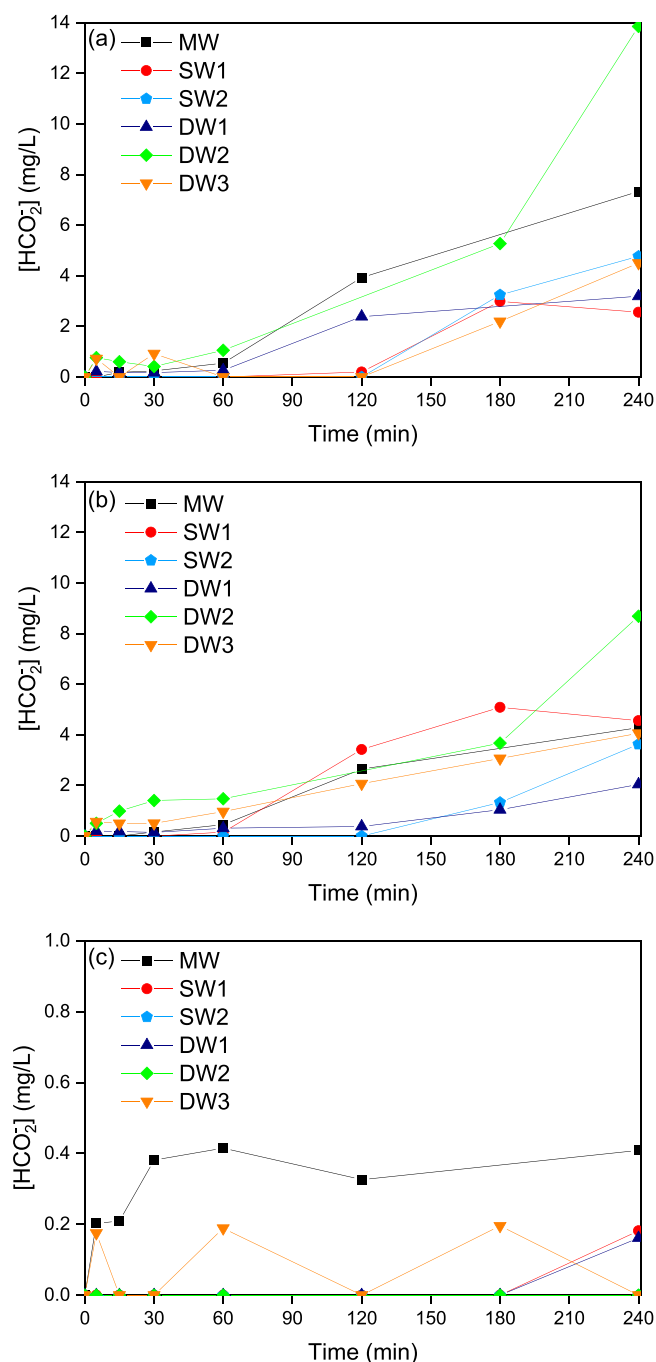


Fig. 7. (a) NO<sub>3</sub><sup>-</sup> conversion vs time reaction and (b) NH<sub>4</sub><sup>+</sup> selectivity vs conversion on NO<sub>3</sub><sup>-</sup> reduction with the catalyst Pd-Cu/ENS350 for assays in absence and presence of HCO<sub>3</sub><sup>-</sup> ([NO<sub>3</sub>]<sub>0</sub> = [HCO<sub>3</sub>]<sub>0</sub> = 100 mg/L, CO<sub>2</sub> flow: 50 N mL/min, H<sub>2</sub> flow: 50 N mL/min) using milli-Q water.



**Fig. 8.** Formation of  $\text{HCO}_2^-$  vs reaction time on nitrate reduction for (a)  $\text{H}_2$  flow: 50 N mL/min; (b)  $\text{H}_2$  flow: 5 N mL/min; (c)  $\text{H}_2$  flow: 1 N mL/min with the catalyst Pd-Cu/ENS350.

increasing the concentration of  $\text{HCO}_3^-$ . This is consistent with higher concentration of  $\text{HCO}_2^-$  observed in those experiments. In addition, in the reduction experiments with a low  $\text{H}_2$  flow of 1 N mL/min (Fig. 8c),  $\text{HCO}_2^-$  concentration was very low for all waters tested. This dependence of  $\text{HCO}_2^-$  on  $\text{H}_2$  availability can also be seen in the blank tests (Fig. 9a), where the  $\text{HCO}_2^-$  concentration was lower in the assays with lower  $\text{H}_2$  flow (1 N mL/min). These results indicate that during the  $\text{NO}_3^-$  catalytic reduction, the presence of  $\text{HCO}_3^-$  results in a parallel reaction, and that  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  compete not only for adsorption on active sites but also for hydrogenation, decreasing  $\text{NO}_3^-$  conversion. This is consistent with the role  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in diminishing  $\text{HCO}_3^-$  adsorption and hence increasing  $\text{NO}_3^-$  conversion.

In the present work,  $\text{HCO}_2^-$  generation from  $\text{HCO}_3^-$  reduction in the  $\text{NO}_3^-$  catalytic reduction in drinking water is reported for the first time, evidencing that not only the commonly accepted  $\text{HCO}_3^-$  adsorption leads to competition with  $\text{NO}_3^-$  molecules for the reaction catalytic sites. In the energy production field,  $\text{HCO}_3^-$  reduction has been reported as a process for  $\text{HCO}_2^-$  generation aiming at its use as  $\text{H}_2$  carrier but at catalyst dose,  $\text{HCO}_3^-$  concentration and reaction times much higher than those used in the catalytic reduction of  $\text{NO}_3^-$  in drinking water. For instance, Stalder et al. [27] reported the  $\text{HCO}_3^-$  reduction towards  $\text{HCO}_2^-$  in presence of  $\text{H}_2$ , using a 5% wt. Pd catalyst supported on materials carbon-based (10 g/L), at ambient conditions. Conversion of 54% was achieved with an initial concentration of  $\text{HCO}_3^-$  of 18.3 g/L, at 90 h of reaction. Using more severe pressure conditions (27 atm), Su et al. [28] obtained a conversion of 95% after 15 h of reaction. Several authors have investigated different catalysts for this process and reported that Pd catalysts exhibited higher values of catalytic activity associated with  $\text{HCO}_3^-$  hydrogenation and recently bimetallic catalyst as Pd-Cu, Pd-Au, Pd-Ag [28–30] have been investigated. The conditions needed are indicative of hampered reaction, therefore, in the case of competence with  $\text{NO}_3^-$  reduction, once  $\text{HCO}_3^-$  is adsorbed renewal of active sites is a slow process that decreases catalytic activity for  $\text{NO}_3^-$  conversion.

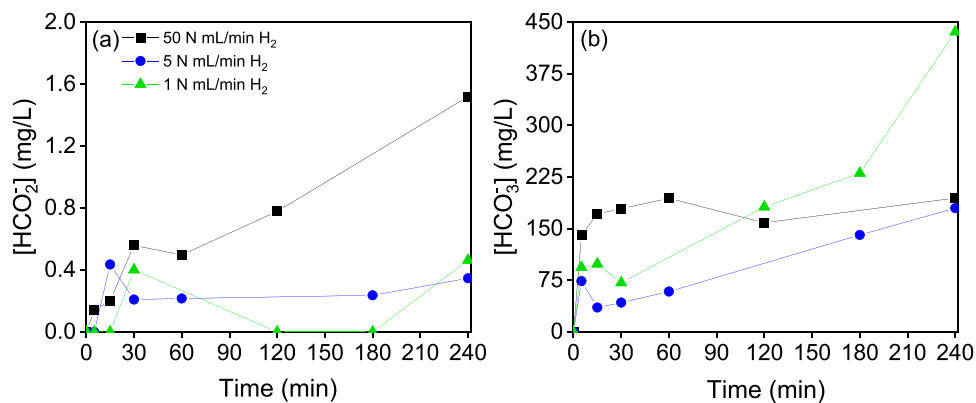
In addition,  $\text{HCO}_2^-$  in presence of Pd based catalyst can decompose into  $\text{H}_2$  and  $\text{CO}_2$  [30]. A  $\text{HCO}_2^-$  decomposition test was performed in the presence of  $\text{NO}_3^-$  and absence of  $\text{H}_2$  (Fig. 10a). Fast decomposition of the  $\text{HCO}_2^-$  added took place, with conversion ca. 91% at the end to the reaction time. Likewise,  $\text{NO}_3^-$  conversion reached 36%, being reduced due to the  $\text{H}_2$  produced by decomposition of  $\text{HCO}_2^-$ . Extremely high selectivity to  $\text{NH}_4^+$  can be observed in Fig. 10b, suggesting that the generation of  $\text{H}_2$  during the decomposition of  $\text{HCO}_2^-$  on the active sites may lead to increased spillover and high H/N ratio, favouring the formation of  $\text{NH}_4^+$ . The selectivity is much higher at low  $\text{NO}_3^-$  conversion values, which is consistent with the higher concentration of  $\text{HCO}_2^-$  in water at short reaction time and hence the higher production of  $\text{H}_2$  on the surface of the catalyst.

### 3.3. Catalysts characterization

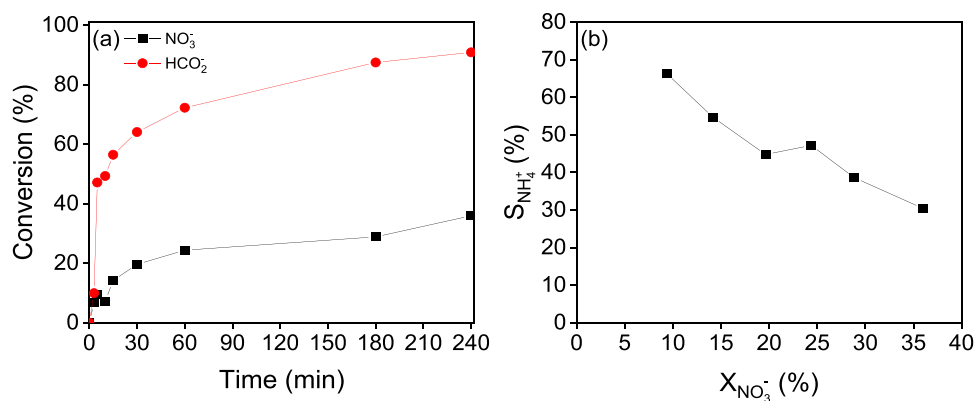
According to EDX images of the fresh catalyst shown in Supplementary Material (Fig. S1), the metallic phase of the catalyst consists mainly of monometallic Pd and Cu nanoparticles with a good dispersion of both metal phases on the carbon support. In some areas Pd is localized forming aggregates of small size, while the Cu is dispersed throughout the support in particles of smaller size that occasionally formed larger agglomerates. According to these images, a minor contribution of nanoalloys could be expected. Therefore, the catalytic behaviour observed cannot be attributed to specific structures, it should be rather considered as the sum of contributions of different Pd-Cu structures.

Fresh and used catalysts corresponding to the reactions using a  $\text{H}_2$  flow of 50 N mL/min were analysed by XPS. Likewise, together with the catalyst used in the reaction with SW2 and performed with a  $\text{H}_2$  flow of 1 N mL/min. The analysis of the Pd  $3d_{5/2}$  level shows two contributions, in the range 335.5–336.2 eV for  $\text{Pd}^0$  and in the range 336.8–337.7 eV for  $\text{Pd}^{n+}$ . Similarly, for the Pd  $3d_{3/2}$  level, these contributions can be seen at 340.8–341.6 eV and 342.5–343.4 eV for  $\text{Pd}^0$  and  $\text{Pd}^{n+}$ , respectively (Fig. 11). At the Cu  $2p_{3/2}$  level, the contributions ascribable to  $\text{Cu}^0$  in the range 932.0–932.7 eV and  $\text{Cu}^{n+}$  in the range 934.0–934.8 eV can be observed (Fig. 12).

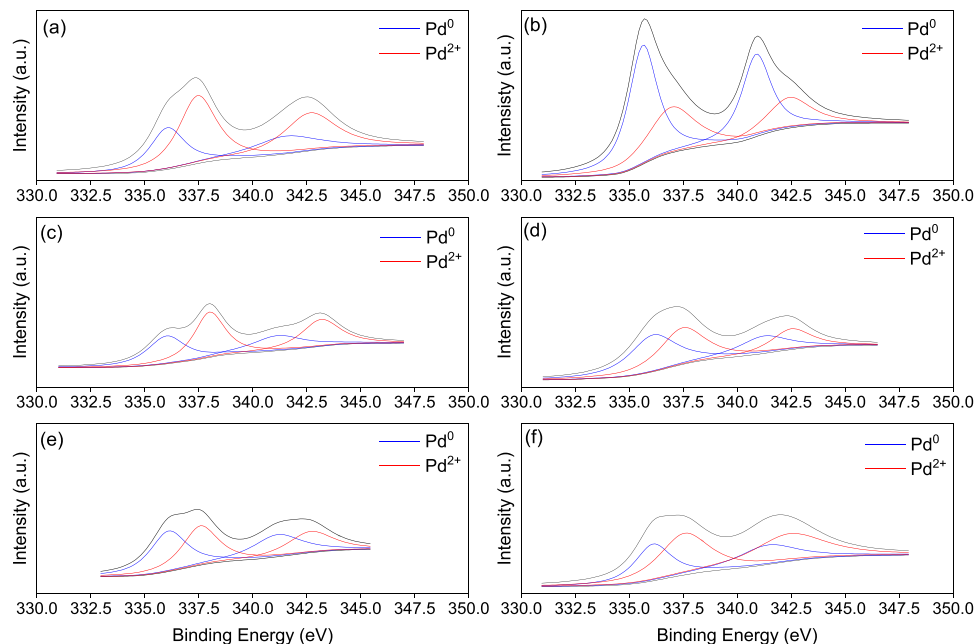
According to the composition of the metal species shown in Table 3, the catalysts were reduced by exposure to  $\text{H}_2$  in the reaction media. A higher reduction of the metal phase was observed for the catalyst used in the absence of  $\text{HCO}_3^-$  (SW1). This reduction may also be related with the higher  $\text{NO}_3^-$  reduction due to higher  $\text{H}_2$  from the metal phase. In studies related to hydrogen adsorption on Pd nanoparticles surface, it has been found that H atoms preferentially adsorb on Pd atoms with high coordination [31]. Therefore, the reduction of the metal phase improves  $\text{H}_2$  adsorption on the Pd sites, increasing  $\text{H}_2$  spillover and thus leading to



**Fig. 9.** Concentration of (a) HCO<sub>2</sub><sup>-</sup> and (b) HCO<sub>3</sub><sup>-</sup> vs assay time for CO<sub>2</sub> flow: 50 N mL/min, H<sub>2</sub> flow: 50, 5 and 1 N mL/min with Pd-Cu/ENS350 catalyst and using milli-Q water.

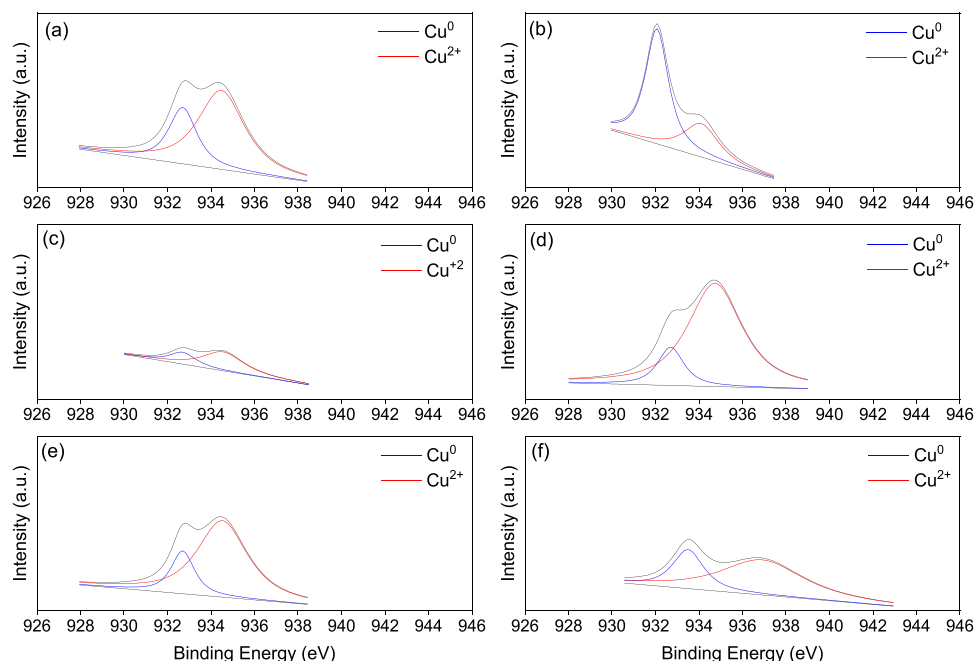


**Fig. 10.** (a) Conversion HCO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> vs time reaction (b) selectivity towards NH<sub>4</sub><sup>+</sup> vs NO<sub>3</sub><sup>-</sup> conversion using milli-Q water, Pd-Cu/ENS350, initial NO<sub>3</sub><sup>-</sup> and HCO<sub>2</sub><sup>-</sup> concentration of 100 mg/L, CO<sub>2</sub> flow of 50 N mL/min.



**Fig. 11.** XPS spectra of Pd<sup>0</sup> and Pd<sup>2+</sup> of Pd-Cu/ENS350 catalyst, for the samples (a) fresh catalyst, catalyst used with (b) SW1, (c) SW2, (d) DW1, (e) DW2 and (f) DW3.





**Fig. 12.** XPS spectra of Cu<sup>0</sup> and Cu<sup>n+</sup> of Pd-Cu/ENS350 catalyst, for the samples (a) fresh catalyst, catalyst used with (b) SW1, (c) SW2, (d) DW1, (e) DW2 and (f) DW3.

**Table 3**

Active phases composition on the catalyst surface for fresh and used Pd-Cu/ENS350 catalysts as determined by XPS (50 N mL H<sub>2</sub>/min, \*: 1 N mL H<sub>2</sub>/min).

Catalyst	Pd <sup>0</sup> (%)	Pd <sup>n+</sup> (%)	Pd <sup>0</sup> /Pd <sup>n+</sup>	Cu <sup>0</sup> (%)	Cu <sup>n+</sup> (%)	Cu <sup>0</sup> /Cu <sup>n+</sup>
Fresh	36.6	63.4	0.6	30.0	70.0	0.4
SW1	62.7	37.3	1.7	69.2	30.8	2.3
SW2 *	43.3	56.7	0.7	28.9	71.1	0.4
DW1	51.4	48.6	1.1	15.1	84.9	0.2
DW2	52.5	47.5	1.1	20.6	79.4	0.3
DW3	37.9	62.1	0.6	29.4	70.6	0.4

better catalyst activity, as it can be observed in the reaction with SW1. Furthermore, Zhang et al. [32] reported that changes in electron density on the surface of Pd atoms can alter the activation energy of NO<sub>2</sub> in reduction and consequently the selectivity. A later work reported that high coordination Pd sites formed more β-hydride (hydrogen dissolved in Pd lattice), which has a larger reducing activity than α-hydride (hydrogen adsorbed on Pd surface). Moreover, this study related the Pd atoms of low coordination with a higher NH<sub>4</sub><sup>+</sup> selectivity due to a low electron density on the surface of Pd atoms [33]. Then, the low NH<sub>4</sub><sup>+</sup> selectivity of the SW1 reactions can also be related to the higher Pd<sup>0</sup>/Pd<sup>n+</sup> ratio. H<sub>2</sub> deficit during the reaction (SW2 experiment) affected the reduction of the catalyst, leading to similar distribution of zero-valent and electro-deficient species is observed for the fresh and used catalyst, and similar Pd<sup>0</sup>/Pd<sup>n+</sup> and Cu<sup>0</sup>/Cu<sup>n+</sup> ratios of 0.6–0.7 and 0.4, respectively.

As a general trend, the catalysts tested in HCO<sub>3</sub><sup>-</sup> presence (DW1, DW2 and DW3) showed a lower Pd<sup>0</sup>/Pd<sup>n+</sup> ratio. As explained above, HCO<sub>3</sub><sup>-</sup> would compete with NO<sub>3</sub><sup>-</sup> for adsorption and reaction on similar active sites, thus also hindering the reduction of the metal phase. This effect is more noticeable in the catalyst used in DW3, with a higher HCO<sub>3</sub><sup>-</sup> concentration, showing similarity with the fresh catalyst in the Pd<sup>0</sup>/Pd<sup>n+</sup> and Cu<sup>0</sup>/Cu<sup>n+</sup> species ratios, 0.6 and 0.4, respectively. Despite H<sub>2</sub> the higher production due to HCO<sub>2</sub> decomposition in water with high HCO<sub>3</sub><sup>-</sup> concentration, no influence in Pd reduction can be inferred, showing that this reaction pathway only influences to the formation of NH<sub>4</sub><sup>+</sup>. On the other hand, according to the literature, NO<sub>3</sub><sup>-</sup> is generally expected to

adsorb on low-coordination active sites. Therefore, it has been assumed that there is competition with HCO<sub>3</sub><sup>-</sup> for these active sites in both Pd and Cu. The competition for the Cu active sites influences the catalyst activity since it hinders the first stage of the reaction. A lower proportion of Cu<sup>0</sup> in the catalysts tested in waters with a higher presence of salts (DW1, DW2 and DW3). The observation suggest that the Cu sites were reduced to a lesser extent, i.e., there is a higher prevalence of electro-deficient species, which seems to contribute to the reduction of catalyst activity. Fig. 12f also shows a displacement of the peak associated to Cu<sup>n+</sup>, in most of the analysed catalysts. This peak, appearing around 934.5 eV, is associated to CuO. However, in the catalyst used with DW3, the peak appears around 936.9 eV, which can be ascribed to the appearance of species related to CuSO<sub>4</sub>. This observation would indicate that SO<sub>4</sub><sup>2-</sup> in high concentrations in the reaction medium can interfere with Cu reduction on the catalyst surface and the redox pair needed for the activity of the catalyst in NO<sub>3</sub><sup>-</sup> reduction. In an interaction study between sulfonic groups and metals, it was found that these groups strongly interact with low coordination sites [34]. Therefore, SO<sub>4</sub><sup>2-</sup> would also adsorb on electrodeficient sites. As explained before, it is expected that HCO<sub>3</sub><sup>-</sup> is also adsorbed on these active sites, therefore SO<sub>4</sub><sup>2-</sup> competition could decrease HCO<sub>3</sub><sup>-</sup> adsorption on the catalyst surface. Yoshinaga et al. [35] explained that sites with low coordination such as edges or corners of the catalyst, favours NH<sub>4</sub><sup>+</sup> production. Then, SO<sub>4</sub><sup>2-</sup> adsorption on these low coordination sites would decrease NH<sub>4</sub><sup>+</sup> formation, as suggested by the comparison of results obtained with DW2 and DW3. These waters have similar HCO<sub>3</sub><sup>-</sup> concentrations but DW3 has a HCO<sub>3</sub><sup>-</sup> concentration similar to that of DW2, but a higher SO<sub>4</sub><sup>2-</sup> concentration that could reduce the negative effect of HCO<sub>3</sub><sup>-</sup> on selectivity.

#### 4. Conclusions

The Pd-Cu catalyst supported on ENS350 showed a high tolerance to salts at low concentration, and even at high concentration nearly complete NO<sub>3</sub><sup>-</sup> conversion was achieved in most of the experiments, particularly when H<sub>2</sub> flow rate was high. However, the presence of salts in the tested waters caused a decrease in NO<sub>3</sub><sup>-</sup> rate elimination, associated to the competitive adsorption of Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> on the metal active sites. In addition to the traditional explanation of the effect of anions, i.e.

competitive adsorption on catalyst active sites, significant formation of HCO<sub>2</sub><sup>-</sup> indicates hydrogenation HCO<sub>3</sub><sup>-</sup> occurring at active sites. The H<sub>2</sub> generated from the decomposition of HCO<sub>2</sub><sup>-</sup> leads to high availability on the catalyst surface and over hydrogenation of NO<sub>3</sub><sup>-</sup> with a disproportionate formation of NH<sub>4</sub><sup>+</sup>. This route contributes significantly to NH<sub>4</sub><sup>+</sup> selectivity, and it is partially suppressed when the concentration of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> as they also compete with HCO<sub>3</sub><sup>-</sup> for active sites. The characterization of catalysts used in experiments with high concentration of HCO<sub>3</sub><sup>-</sup> show a lower proportion of zero valent metallic species, which may also contribute to lower activity. Likewise, formation of species related to CuSO<sub>4</sub> on the catalysts surface in tests with waters with SO<sub>4</sub><sup>2-</sup> may contribute to lower activity as it interferes with the redox pair needed for the reaction. The CO<sub>2</sub> commonly used as buffer also contributes to the formation of HCO<sub>2</sub><sup>-</sup>, due to dissociation of carbonic acid to form HCO<sub>3</sub><sup>-</sup> this may reframe its use as a buffer in the NO<sub>3</sub><sup>-</sup> catalytic reduction.

### CRedit authorship contribution statement

**D.T. Gonzalez:** Investigation, Writing – original draft. **J.A. Baeza:** Writing – review & editing, Validation. **L. Calvo:** Conceptualization, Funding acquisition. **M.A. Gilarranz:** Supervision, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data Availability

Data will be made available on request.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2023.102494](https://doi.org/10.1016/j.jcou.2023.102494).

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