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This is an **author produced version** of a paper published in:

Separation and Purification Technology 255 (2021): 117766

**DOI:** <https://doi.org/10.1016/j.seppur.2020.117766>

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# Effect of water composition on catalytic reduction of nitrate

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## Abstract

This work studies catalytic reduction of nitrate with bimetallic catalysts supported on  $\gamma$ -alumina (Pd-Sn/ $\text{Al}_2\text{O}_3$  and Pd-In/ $\text{Al}_2\text{O}_3$ ). Pd-Sn/ $\text{Al}_2\text{O}_3$  yielded higher  $\text{NO}_3^-$  conversion and selectivity towards  $\text{N}_2$  than Pd-In/ $\text{Al}_2\text{O}_3$  in synthetic water (deionized water with 100 mg/L  $\text{NO}_3^-$ ). The Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst showed highly stable behaviour, without signs of deactivation upon ten consecutive runs of 6 h each, where almost equal low selectivity to  $\text{NH}_4^+$  (absence of  $\text{NO}_2^-$ ) was maintained at high nearly constant nitrate conversion ( $\approx 90\%$ ). The presence of anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) in the reaction medium decreased  $\text{NO}_3^-$  conversion and the selectivity towards  $\text{N}_2$ . Chloride showed a moderately negative effect at relatively low concentration. The effect of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  was more pronounced, being the second the most detrimental to the catalytic activity. The selectivity towards  $\text{N}_2$  was also negatively affected by the presence of those anions following the sequence  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ . However, the joint presence of  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  with  $\text{HCO}_3^-$  reduced the negative effect of the latter. The Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst also showed high activity in  $\text{NO}_3^-$  reduction from drinking waters of weak mineralization, with a slightly increase of the selectivity towards  $\text{NH}_4^+$  with respect to the obtained in deionized water with  $\text{NO}_3^-$  as the only anion.

**Keywords:** catalytic nitrate reduction; drinking water; anions; bimetallic catalysts.

## 1. Introduction

The presence of nitrate in water bodies represents a growing problem worldwide caused mainly by uncontrolled use of nitrogen fertilizers in the intensive agriculture. Human consumption of water containing nitrate and its reduced forms (nitrite and ammonium) causes serious health problems, including methemoglobinemia, reproductive and developmental disorders and different types of cancer [1-3]. Thus, the EU regulations (Directive 91/676/EEC) [4] set maximum concentrations of 50, 0.1 and 0.5 mg/L for  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ , respectively in drinking water. The World Health Organization (WHO) recommends a limit of 10 mg/L N- $\text{NO}_3^-$  (44 mg/L  $\text{NO}_3^-$ ) in drinking water [5].

Ion exchange [6,7], electrodialysis [8] and reverse osmosis [9] are currently the most commercially available techniques for nitrate removal. However, they give rise to highly concentrated rejects requiring post-treatments to minimize environmental damages, thus implying the corresponding extra costs [10, 11]. Biological nitrification-denitrification is an effective technique for nitrate removal, but not practicable for drinking water due to microbial contamination [12]. Catalytic reduction is being investigated in the last decades as a potential solution avoiding the drawbacks of the aforementioned treatments. This technology is addressed to convert  $\text{NO}_3^-$  into harmless gaseous  $\text{N}_2$  using a reducing agent such as  $\text{H}_2$ , without generating any secondary waste. However, the formation of  $\text{NO}_2^-$  and  $\text{NH}_4^+$  has been so far its main limitation avoiding practical use [13, 14]. Besides, ions commonly present in natural waters can produce catalyst deactivation, which is also a critical issue regarding potential application [15-18].

Both mono- and bimetallic catalysts have been tested for nitrate reduction [10, 11, 19, 20], being the second more active [21-23]. These consist of a promoter metal, being Cu [22, 24, 25], Sn [22, 26-30] and In [25, 27, 31, 32] the most widely used, and a noble

metal, most commonly Pd [31, 33-36]. Different supports have been used, being  $\gamma$ - $\text{Al}_2\text{O}_3$  [27, 32, 37-39],  $\text{TiO}_2$  [32, 40-42] and activated carbon (AC) [21, 31, 43, 44] the most frequent.  $\text{Al}_2\text{O}_3$  is considered a passive support because it does not have reducible capacity, and therefore it does not participate directly in the reduction process [11]. Experiments carried out in natural waters with Pd-Sn/ $\text{Al}_2\text{O}_3$  and Pd-Cu/ $\text{Al}_2\text{O}_3$  catalysts have shown  $\text{NO}_3^-$  conversion values higher than 90 % [18, 45-47]. Nevertheless, the selectivity towards  $\text{NH}_4^+$  seems to be higher using the Pd-Cu pair [45-47]. The most impressive results (complete nitrate conversion and 100 % of selectivity to  $\text{N}_2$ ) were obtained using a Mg/Al-hydrotalcite catalysts [48].

The nitrate reduction by bimetallic catalysts consists of a multi-step redox reaction where a promoter metal, a noble metal and a reducing agent are involved [11, 29, 49-52]. The reaction occurs when  $\text{NO}_3^-$  ions and hydrogen, both adsorbed on the bimetallic catalyst surface get in contact [10]. Firstly,  $\text{NO}_3^-$  is reduced to nitrite on bimetallic active sites, being oxidised the promoter metal. In contrast, the role of the noble metal is activating hydrogen, allowing the *in situ* reduction of the second metal to the initial state. Secondly,  $\text{NO}_2^-$  is reduced on the surface of noble metal to NO as the key intermediate in the generation of  $\text{N}_2$  or  $\text{NH}_4^+$ . This time, the noble metal itself can reduce the nitrite ions by activated hydrogen [10].

The catalytic reduction of  $\text{NO}_3^-$  in natural water is usually accompanied by catalyst deactivation, due to the presence of some ionic species. A competitive adsorption of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  on the active metal sites has been observed [15-18, 45]. Consequently, the N/H ratio on the catalyst surface is reduced, favouring the formation of  $\text{NH}_4^+$  [53]. Moreover, fouling of the catalyst by precipitation of calcium salts and sulfur compounds can also affect the catalytic activity [45]. However, the effect of the most common ions

of natural waters on catalytic nitrate reduction is still controversial and more clarifying research is needed [10].

The aim of this study is to evaluate the behaviour of  $\text{Al}_2\text{O}_3$ -supported Pd-Sn and Pd-In catalysts in nitrate reduction using synthetic water samples with different concentrations of common anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) as well as commercial drinking waters spiked with  $\text{NO}_3^-$ .

## 2. Experimental

### *2.1. Preparation and characterization of catalysts*

$\text{Al}_2\text{O}_3$  ( $\gamma$ ) spheres (SASOL Germany,  $d = 1.06$  mm) were used as support to prepare bimetallic catalysts of Pd-Sn and Pd-In with 0.5 % wt. Pd and 5 % of the accompanying metal by sequential impregnation. In order to avoid the possible overlapped of the Pd surface by Sn or In, the promoter metal was impregnated in the first place. Solution of  $\text{SnCl}_2$  (Sigma Aldrich, 99.99 %) in methanol (Scharlau, 99.9 %) and  $\text{In}(\text{NO}_3)_3$  (Sigma Aldrich, 99.99 %) in deionized water were used for impregnation of the support (1 mL/g<sub>support</sub> in both cases) in a rotary evaporator at 70 °C. The pressure was 200 mbar and atmospheric for the salts dissolved in water and methanol, respectively. The impregnated materials were dried overnight at 60 °C and calcined at 500 °C for 2 h. Later, Pd impregnation was performed with  $\text{Na}_2\text{PdCl}_4$  (Sigma Aldrich, 99.99 %) solution in deionized water (1 mL/g support), followed by evaporation in a rotary evaporator, dried and calcined under the same above conditions.

The metal content of the catalysts was analyzed by ICP-MS (NexION 300XX, Perkin-Elmer). The porous texture was assessed from the  $\text{N}_2$  adsorption–desorption isotherms at

77 K using a Micromeritics Tristar 3020 automated volumetric gas adsorption equipment. The samples were previously outgassed at 150 °C for 20 h by using a Micromeritics VacPrep 061 degassing system under vacuum. The content of C, H, N and S of the catalysts was determined by elemental analysis with a LECO CHNS-932 analyzer. Room temperature powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance A25 diffractometer with a Bragg Brentano configuration and a lineal detector Lynxeye (Bruker). X-ray photoelectron spectroscopy (XPS) spectra was obtained with a Physical Electronics 5700C Multitechnique instrument using MgK $\alpha$  radiation (1253.6 eV).

## 2.2. Nitrate aqueous samples

Four types of nitrate aqueous samples were tested. The first one was prepared with milliQ water and NaNO<sub>3</sub> (Panreac, 99 %), with a NO<sub>3</sub><sup>-</sup> concentration of 100 mg/L, denoted as W0. Secondly, to determine the individual effect of some commonly anions present in natural waters on the catalytic reduction of nitrate, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> aqueous solutions were prepared dissolving NaCl (Panreac, >99 %), Na<sub>2</sub>SO<sub>4</sub> (Panreac, >99 %) and NaHCO<sub>3</sub> (Sigma Aldrich, >99 %), respectively, in milliQ water and adding 100 mg/L of NO<sub>3</sub><sup>-</sup> (W1-W10). Besides, mixtures of these anions were tested and the samples denoted as M1-M6, whose concentrations appear in the Table 1. Finally, six commercial drinking waters (DW1-DW6) were used after NO<sub>3</sub><sup>-</sup> spiking at 100 mg/L. The analyses of the commercial drinking waters tested are shown in Table 2.

	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)
W0	-	-	-
W1	20	-	-
W2	50	-	-
W3	200	-	-
W4	-	10	-
W5	-	20	-
W6	-	100	-
W7	-	400	-
W8	-	-	100
W9	-	-	200
W10	-	-	400
M1	-	10	200
M2	-	20	200
M3	-	100	200
M4	10	-	200
M5	20	-	200
M6	100	-	200

**Table 1.** Concentration of tested anions in the aqueous samples.

Drinking water	Dry residue 180°C (mg/L)	Hardness (mg CaCO <sub>3</sub> /L)	pH	Conductivity (µS/cm)	Cations (mg/L)					Anions (mg/L)				
					Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
DW1	260	264	7.5	493	5.8	0.8	62.9	25.9	0.4	2.5	-	7.3	22.6	255.1
DW2	12	14	6.1	32	3.0	0.2	3.9	1.1	0.4	6.7	-	-	2.6	8.9
DW3	197	36	6.8	319	57.9	2.3	9.3	3.1	0.4	4.2	-	8.4	6.1	162.6
DW4	273	518	8.2	800	12.0	1.0	171.1	21.9	0.6	5.0	-	16.3	379.7	128.8
DW5	521	257	8.2	874	89.4	1.3	76.3	16.1	0.4	5.3	-	169.8	39.1	244.0
DW6	14	14	6.0	58	5.0	0.4	3.1	1.5	0.7	2.0	-	7.1	8.6	13.0

**Table 2.** Characterization of the commercial drinking waters tested.



### 2.3. *Semi-batch runs*

The catalytic tests in semi-batch mode were performed in glass reactors (250 mL capacity), placed in a thermostatic bath, at 25 °C and atmospheric pressure. To avoid mass-transfer limitations, the catalyst was pulverized (< 0.08 mm) and magnetic stirring (700 rpm) was maintained. The initial concentration of  $\text{NO}_3^-$  was 100 mg/L in all cases and the catalyst concentration 1 g/L. The catalyst was previously reduced under  $\text{H}_2$  flow (20 NmL/min) at 100 °C for 1 h and  $\text{N}_2$  was then passed. The catalyst (0.2 g) was placed in the reactor with 200 mL of the  $\text{NO}_3^-$  solution. A  $\text{CO}_2$  flow (25 NmL/min) was passed for 20 min before  $\text{H}_2$  feeding, being the initial pH 4. During the nitrate reduction experiments  $\text{H}_2$  and  $\text{CO}_2$  (50 NmL/min, 1:1) were continuously fed. Samples were periodically withdrawn from the reactor and filtered through regenerated cellulose filters (pore diameter of 0.45  $\mu\text{m}$ ). To learn on the stability of the catalysts, ten consecutive runs were carried out under the same conditions in glass reactors of 1 L capacity. Between runs, the catalyst was recovered by decantation and dried overnight under vacuum at 60 °C. This process allowed recovering around 90 % of the catalyst used in the previous test. To maintain the catalyst concentration (1 g/L), the  $\text{NO}_3^-$  solution volume was reduced 10 % each cycle.  $\text{NO}_3^-$  conversion and  $\text{NH}_4^+$  selectivity values were reported as the average of three replicate determinations, being the standard deviation less than 10 % in all cases.

### 2.4. *Analytical methods*

The reaction samples were analysed by Ion Chromatography on a Metrohm 882 Compact IC plus chromatograph.  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were determined using a Metrosep A Supp 5 column, with a mobile phase flow of 0.7 mL/min of  $\text{Na}_2\text{CO}_3$  (3.2 mM) and  $\text{NaHCO}_3$  (1.0 mM). For  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , a Metrosep C4 column was used with 0.9 mL/min of  $\text{C}_7\text{H}_5\text{NO}_4$  (0.7 mM) and  $\text{HNO}_3$  (1.7 mM) as mobile phase. Total

nitrogen (TN) was analyzed in a Shimadzu Total Organic Carbon Analyzer (TOC-VCPM) with total nitrogen measuring unit.  $\text{HCO}_3^-$  concentration was determined by titration (TitroMatic 1S/2S titrator Karl Fischer) as alkalinity expressed in mg/L  $\text{CaCO}_3$ . Conductivity and pH were measured by a conductivity meter (GLP 31, CRISON) and a pH-meter (GLP 21, CRISON), respectively. For the commercial drinking waters, the dry residue was determined by weight difference, after evaporating 100 mL of sample for 4 h at 180°C. Hardness was calculated from the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations, analyzed by ionic chromatography (Metrohm 790 IC), following the APHA method 2340B.

### 3. Results and discussion

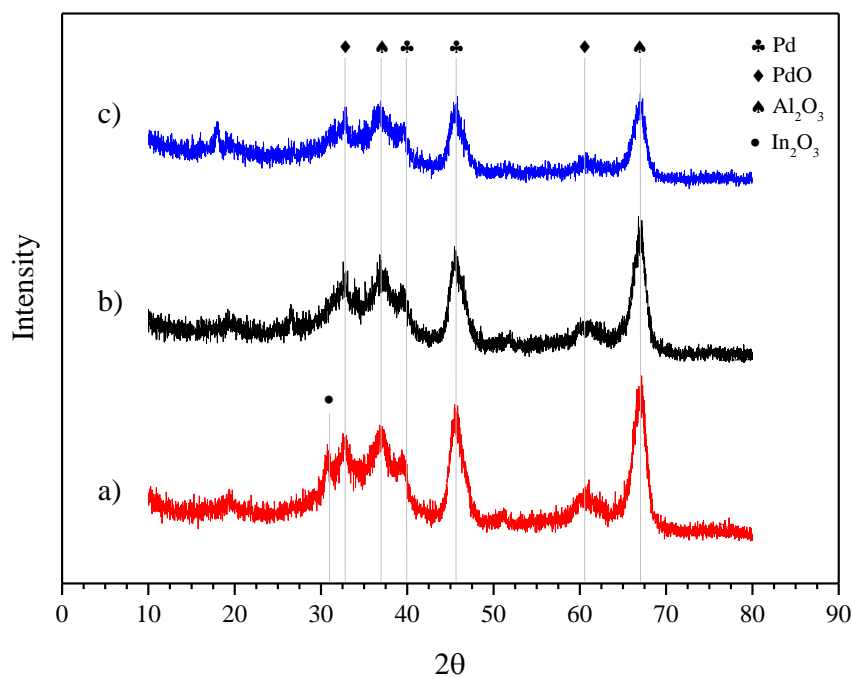
#### 3.1. Catalysts characterization

Table 3 collects the metal content and BET surface area of the catalysts prepared. The Pd content is close to the nominal value in both cases, confirming an effective impregnation, while some deviations can be seen for the accompanying metals, more significant in the case of In. The BET surface area values were quite similar and only little lower than that of the support (158  $\text{m}^2/\text{g}$ ), so that the incorporation of the metallic phases did not imply any significant modification of the porous texture.

Catalyst	Metal content (wt %)			$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )
	Sn	In	Pd	
Pd-Sn/ $\text{Al}_2\text{O}_3$	4.31	-	0.48	149
Pd-In/ $\text{Al}_2\text{O}_3$	-	3.46	0.47	155

**Table 3.** Metal content and BET surface area ( $S_{\text{BET}}$ ) of the bimetallic catalysts.

XRD analysis was performed to determine the structural features and mineral phases for a) Pd-In/ $\text{Al}_2\text{O}_3$  fresh catalyst, b) Pd-Sn/ $\text{Al}_2\text{O}_3$  fresh catalyst and c) Pd-Sn/ $\text{Al}_2\text{O}_3$  after ten reaction runs. The XRD diffractograms are depicted in Fig 1. The characteristic peaks of palladium oxide (PdO) and palladium metallic (Pd) are observed in all samples appearing the oxidized form at  $33.4^\circ$  and  $60.9^\circ$  [27, 30, 36], and the metallic form at  $40.1^\circ$  and  $46.7^\circ$  [25, 31, 37]. No diffraction lines for crystalline Sn or tin oxides ( $\text{SnO}_x$ ) were observed [18, 47], whereas characteristic peak of indium oxide ( $\text{In}_2\text{O}_3$ ) is detected at  $31.5^\circ$  [54]. Finally, it can be observed a lightly decrease of intensity in the Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst after ten successive runs respecting to the fresh catalyst. This loss of intensity was not associated with the metal leaching insomuch as the TXRF analysis showed a negligible difference in the metal content between both samples.



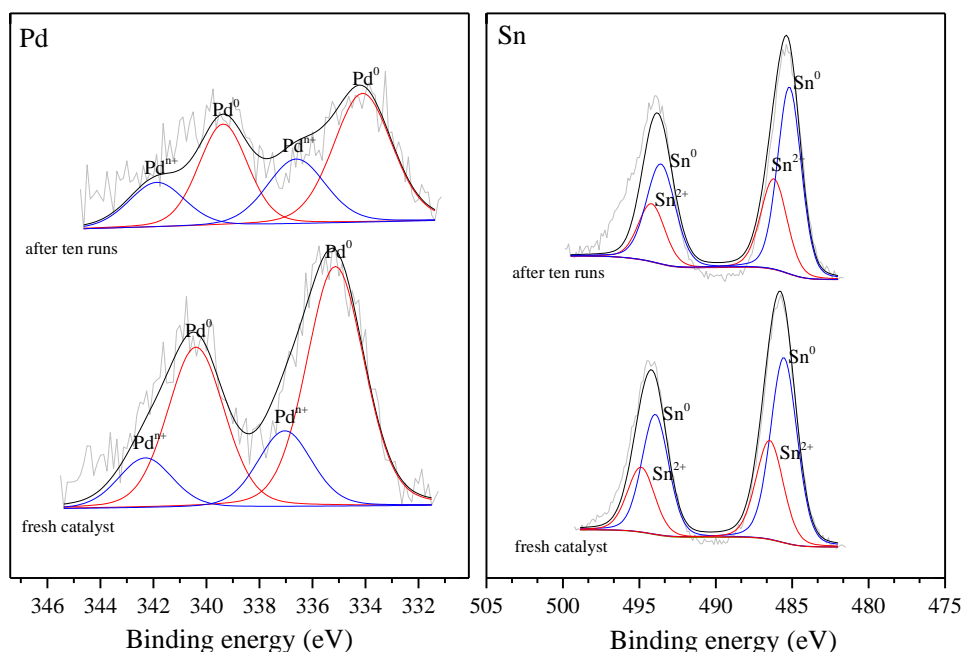
**Fig. 1** XRD diffractograms of a) fresh Pd-In/ $\text{Al}_2\text{O}_3$  catalyst, b) fresh Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst and c) Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst after ten successive runs of 6 h each.

In order to obtain information about the evolution of the oxidation state of the active phases on the catalyst surface, X-ray photoelectron spectroscopy studies of Pd-Sn/ $\text{Al}_2\text{O}_3$

fresh catalyst and Pd-Sn/Al<sub>2</sub>O<sub>3</sub> after ten reaction runs were performed. Surface atomic concentration and XPS spectra of studied samples are depicted in Table 4 and Fig 2, respectively. As can be observed, Sn concentration is not affected by the consecutively reaction runs, around 7 % in both samples. However, Pd content on the catalyst surface seems to be lightly affected, reducing its content in a 37 %. This could be due to a loss of metal or, most probably, by the Pd covering on the catalyst surface. On the other hand, regarding metal oxidation species, the reduced one is in both samples the predominant, although in the case of Pd, the proportions decrease slightly with the use of the catalyst in reaction.

	Pd-Sn/Al <sub>2</sub> O <sub>3</sub> fresh catalyst	Pd-Sn/Al <sub>2</sub> O <sub>3</sub> after ten runs
C (%)	8.5	6.4
O (%)	45.0	47.6
Al (%)	38.9	38.5
Pd (%)	0.8	0.5
Pd <sup>0</sup> (%)	77.1	66.5
Pd <sup>n+</sup> (%)	22.9	33.4
Sn (%)	6.9	7.0
Sn <sup>0</sup> (%)	64.5	65.1
Sn <sup>2+</sup> (%)	35.5	34.9

**Table 4.** Surface atomic concentration (%) of studied samples.

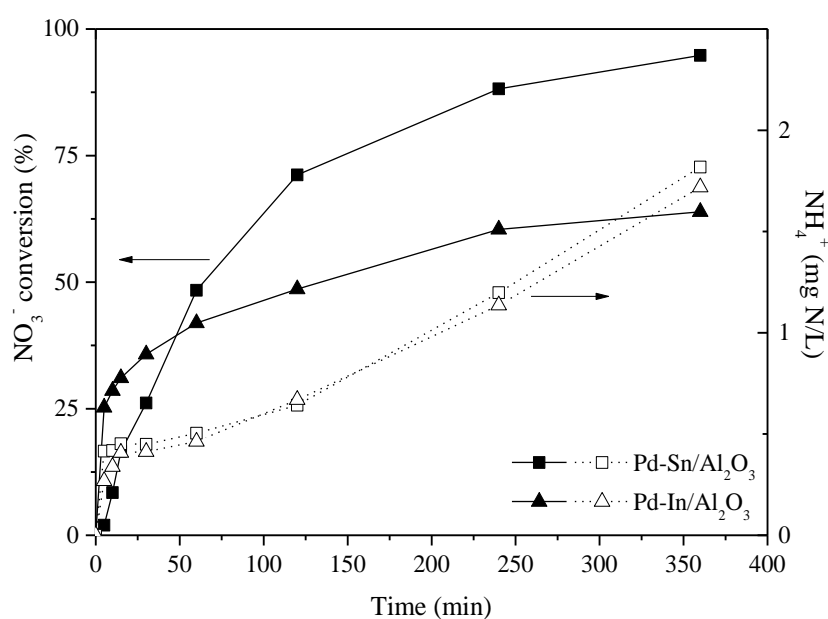


**Fig. 2** XPS spectra of Pd (3d) and Sn (3d<sub>5/2</sub>) of Pd-Sn/Al<sub>2</sub>O<sub>3</sub> fresh catalyst and Pd-Sn/Al<sub>2</sub>O<sub>3</sub> after ten reaction runs.

### 3.2. Performance of the catalysts

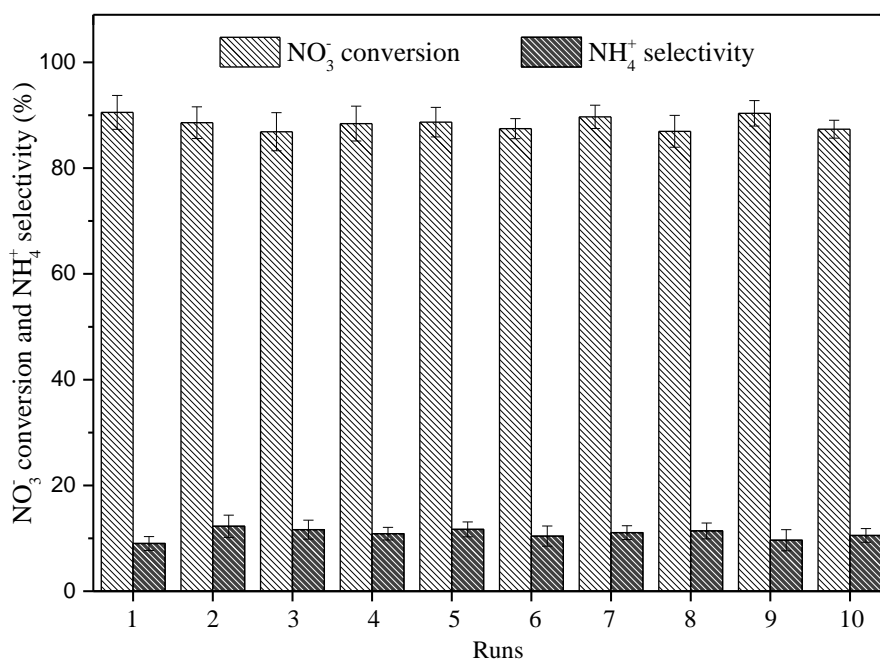
Fig. 3 shows the time course of nitrate conversion and NH<sub>4</sub><sup>+</sup> formation upon the catalytic reaction. Nitrite was not detected. The Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst shows higher activity for nitrate reduction and also higher selectivity towards N<sub>2</sub>. In about one-hour reaction time this catalyst reached 50 % nitrate conversion, which, taking into account the initial NO<sub>3</sub><sup>-</sup> concentration in the synthetic water sample (100 mg/L), would be below the limit value of EU regulation (50 mg/L). At that 50 % conversion, the selectivity to N<sub>2</sub> was somewhat above 95 % and the concentration of ammonium 0.5 mg N/L, almost the allowed limit value established by EU (0.5 mg/L NH<sub>4</sub><sup>+</sup> or 0.4 mg N-NH<sub>4</sub><sup>+</sup>/L) [4]. It has to be considered that the starting nitrate concentration used in our experiments is well above the most frequent values found in surface and groundwater bodies. Even at as high as 95 % nitrate conversion the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst yielded almost 92 % selectivity towards N<sub>2</sub>, with no

nitrite detected in water. Pizarro et al. [27] observed complete nitrate conversion with both Pd-Sn/Al<sub>2</sub>O<sub>3</sub> and Pd-In/Al<sub>2</sub>O<sub>3</sub> (5-1.25 wt %) under similar reaction conditions. However, the selectivity to NH<sub>4</sub><sup>+</sup> at that conversion was much higher than the obtained in the current study (34 and 56 % for Pd-In and Pd-Sn catalysts, respectively). On the other hand, Al-Bahri et al. [24] obtained 8.3 % selectivity to NH<sub>4</sub><sup>+</sup> at 70 % nitrate conversion with a Pd-In/AC catalyst, significantly better than that of a Pd-Sn/AC catalyst (5-2.5 wt %).



**Fig. 3** Time course of NO<sub>3</sub><sup>-</sup> conversion (full symbols) and NH<sub>4</sub><sup>+</sup> concentration (empty symbols) with the catalysts tested.

Fig. 4 shows the performance of the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst in terms of NO<sub>3</sub><sup>-</sup> conversion and the selectivity towards NH<sub>4</sub><sup>+</sup> upon ten successive batch runs of 6 h each. Nitrite was, again, not detected. As can be seen, the catalyst showed a highly stable behaviour, without signs of deactivation under the experimental conditions used, maintaining almost equally low levels of NH<sub>4</sub><sup>+</sup> at fairly high nitrate conversion ( $\cong 90$  %).



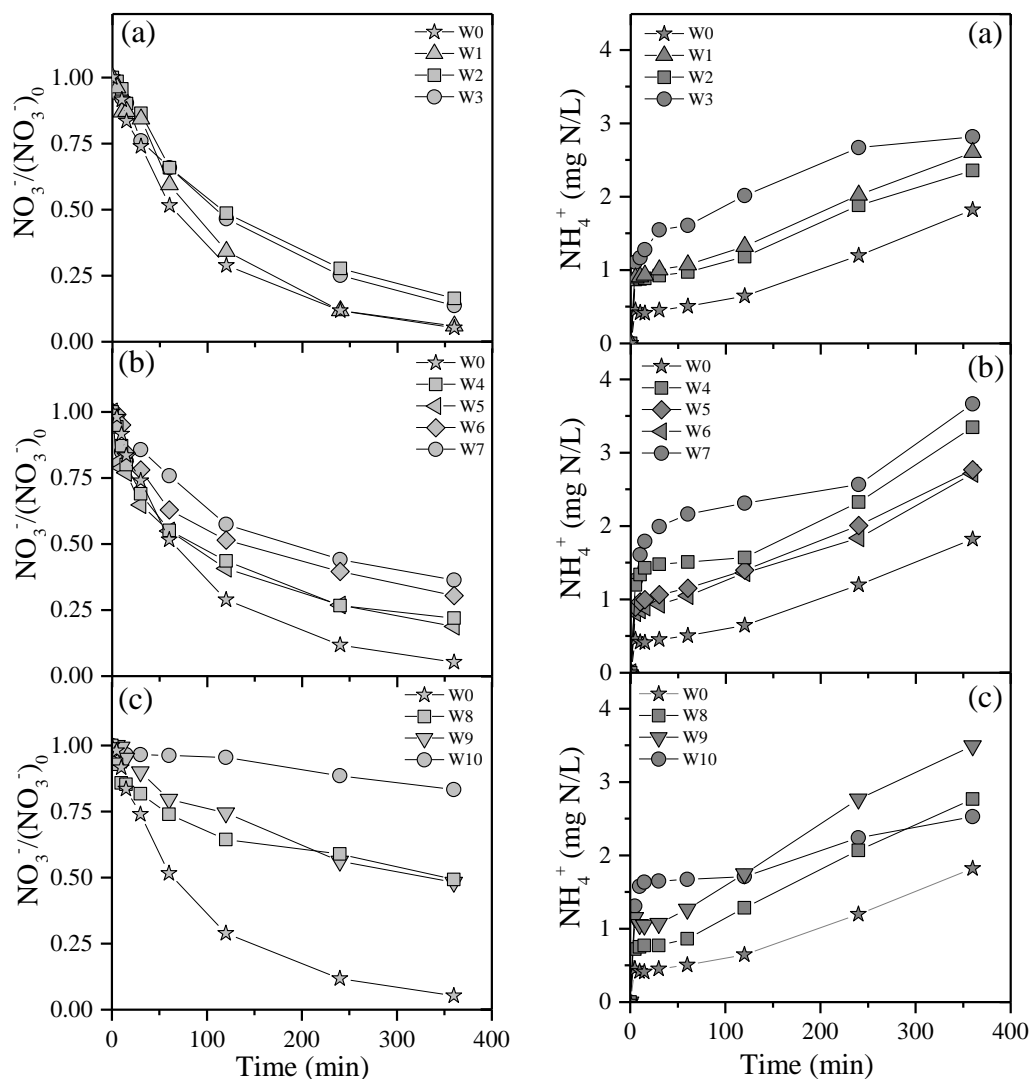
**Fig. 4** Performance of the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst upon ten successive runs of 6 h each.

### 3.3. Effect of anions on the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalytic performance

Fig. 5 depicts the time course of NO<sub>3</sub><sup>-</sup> removal and the concentration of NH<sub>4</sub><sup>+</sup> in the nitrate reduction experiments with the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, using synthetic waters with 100 mg/L starting NO<sub>3</sub><sup>-</sup> concentration spiked with different anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, see Table 1 for nomenclature). For the sake of easily rapid comparison, the results with the nitrate-only sample have been included in all the Figures (W0 sample). Chloride showed a moderately negative effect at relatively low concentration (> 20 mg/L), which, however, did not increase significantly beyond ≈ 50 mg/L in term of nitrate conversion while a monotonically growing effect was observed respect to NH<sub>4</sub><sup>+</sup> formation. Similarly, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions showed negative effects on the performance of the catalyst, more pronounced than Cl<sup>-</sup>, most in particular in the case of bicarbonate. Hirayama and Kamiya [18] observed that the affinity of chloride ion for the Sn sites is lower than for other promoter metals. Therefore, the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst seems to present a relative high

tolerance to  $\text{Cl}^-$  in water. The negative effect of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  ions can be attributed to their competition with  $\text{NO}_3^-$  for the metallic active sites [17]. Partial substitution of nitrate would reduce its surface concentration, thus increasing the H/N ratio and favouring  $\text{NH}_4^+$  formation, while decreasing the probability of recombination of N atoms into molecular  $\text{N}_2$  [53, 55, 56]. Elemental analyses of the catalysts demonstrated the presence of significant amounts of S after the experiments carried out with sulfate-containing samples ( $\approx 1\%$  at 400 mg/L). Meanwhile after the experiments with bicarbonate-containing water, the C content of the catalyst increased with respect to those in absence of that anion (1.4 % at 400 mg/L vs. an average value around 0.8 % when no bicarbonate was present, this last C being attributable to the  $\text{CO}_2$  continuously passed in all the experiments).





**Fig. 5** Effect of  $\text{Cl}^-$  (a),  $\text{SO}_4^{2-}$  (b) and  $\text{HCO}_3^-$  (c) on nitrate reduction with the Pd-Sn/ $\text{Al}_2\text{O}_3$  catalysts.

For the sake of easier comparison, Table 5 summarizes numerical values of  $\text{NO}_3^-$  conversion at 6 h reaction time and the selectivity to  $\text{NH}_4^+$  ( $\text{NO}_2^-$  was never detected) at 50 %  $\text{NO}_3^-$  conversion from the experiments of Figure 3 (W0-W10). Additional experiments with mixtures of those anion are also included as well as the values of the pseudo-first order rate constant of  $\text{NO}_3^-$  disappearance for each experiment. Although no significant negative effect was observed at low chloride concentration in absence of other anions (W1) the simultaneous presence of bicarbonate provoked a strong reduction of

NO<sub>3</sub><sup>-</sup> conversion, even at very low concentration of Cl<sup>-</sup>, and more severe than the observed with HCO<sub>3</sub><sup>-</sup> alone (see W9, M4 and M5). Intriguingly, the negative effect of bicarbonate is more pronounced at lower chloride concentrations. Pintar et al [15] and Theologides et al [53] observed that the presence of Cl<sup>-</sup> in the reaction medium gives place to a modification of the acid sites on the catalyst surface. The same trend can be observed for the SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup> mixtures. The experiments M1 and M2 yielded similar NO<sub>3</sub><sup>-</sup> conversion, being significantly lower than the obtained with the M3 water sample, containing the highest SO<sub>4</sub><sup>2-</sup> concentration. The presence of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> in the reaction medium, produced always an increase of NH<sub>4</sub><sup>+</sup> selectivity, more pronounced in the case of bicarbonate. As can be seen in Table 4, these anions accompanying to NO<sub>3</sub><sup>-</sup> provoked a decrease of the pseudo-first order kinetic constant of nitrate disappearance, that negative effect following the order HCO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>. The presence of these ions causes the decrease of certain active sites available for the adsorption of NO<sub>3</sub><sup>-</sup>, affecting the reaction kinetic. Nevertheless, the occurrence of these anions do not interfere to the reaction mechanism, which follows the same pattern described in previous works [18, 52]. In the first step, the redox reaction begins with the adsorption of NO<sub>3</sub><sup>-</sup> over bimetallic sites (Pd-Sn) on the catalyst surface. Metallic Sn or low-valent Sn<sup>n+</sup> reduces NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> and consequently Sn or low-valent Sn<sup>n+</sup> is oxidized. The oxidized Sn species are then reduced with hydrogen activated on the Pd sites, affording the original Sn species. The intermediate NO<sub>2</sub><sup>-</sup> is then reduced over the Pd site to the final products (N<sub>2</sub> and to a lesser extent NH<sub>4</sub><sup>+</sup>), being Sn not involved in the reaction.

As can be seen, the performance of the bimetallic catalyst depends strongly on the water composition, thus it is difficult to compare results with other studies. However, the trend reported in the literature is the decreasing of the nitrate conversion when the reaction medium is composed by natural water instead synthetic water [15-18, 45, 47, 57], even

leading to the deactivation of the catalyst [45, 47]. Wang et al. [17] observed a stronger negative effect of  $\text{Cl}^-$  over Pd-Cu catalyst supported on  $\text{Al}_2\text{O}_3$  than the obtained in the present study with Pd-Sn/ $\text{Al}_2\text{O}_3$ , reporting a decrease of nitrate reduction from 83 % to 55 % attributed to the presence of 50 mg/L  $\text{Cl}^-$ , and a slight effect of  $\text{SO}_4^{2-}$  provoking a concentration of 50 mg/L a decrease of a 5 % of conversion. Similarly, Palomares et al. [47] observed a reduction of nitrate conversion from 98 %, obtained using distilled water with 100 mg/L  $\text{NO}_3^-$ , to 58 % with natural water (100 mg/L  $\text{NO}_3^-$ , 79 mg/L  $\text{Cl}^-$ , 200 mg/L  $\text{SO}_4^{2-}$ , 50 mg/L  $\text{Na}^+$ , 150 mg/L  $\text{Ca}^{2+}$ , 1000  $\mu\text{S}/\text{cm}$ ) after 100 h of reaction with a Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst.

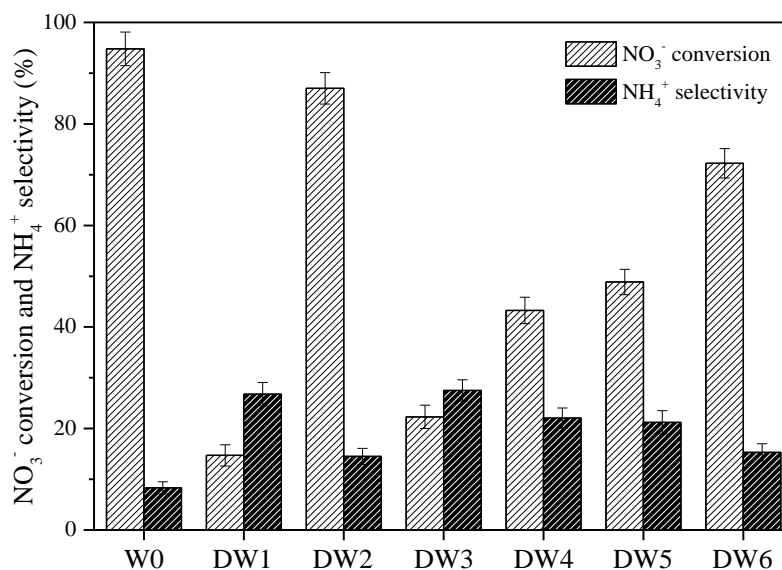
	$\text{NO}_3^-$ conversion (%, 6 h)	$\text{NH}_4^+$ selectivity at 50 % $\text{NO}_3^-$ conversion (%)	$k \cdot 10^3$ ( $\text{min}^{-1}$ )	$R^2$
W0	94.8	4.4	$8.4 \pm 0.26$	0.99
W1	94.0	10.4	$8.1 \pm 0.25$	0.99
W2	83.7	9.9	$5.1 \pm 0.14$	0.99
W3	86.3	16.8	$5.4 \pm 0.14$	0.99
W4	78.1	13.1	$4.2 \pm 0.42$	0.95
W5	81.2	9.5	$4.3 \pm 0.35$	0.96
W6	69.6	12.4	$3.3 \pm 0.33$	0.95
W7	63.7	17.9	$2.8 \pm 0.24$	0.95
W8	50.7	22.8	$1.8 \pm 0.21$	0.96
W9	51.9	28.0	$2.1 \pm 0.13$	0.97
W10	16.7	n.d.	$0.45 \pm 0.031$	0.96
M1	46.7	n.d.	$1.7 \pm 0.15$	0.95
M2	43.1	n.d.	$1.6 \pm 0.13$	0.96
M3	67.3	25.4	$3.2 \pm 0.22$	0.97
M4	31.7	n.d.	$1.0 \pm 0.85$	0.95
M5	41.4	n.d.	$1.4 \pm 0.15$	0.96
M6	55.7	13.9	$2.3 \pm 0.16$	0.96

n.d.: not determined ( $\text{NO}_3^-$  conversion does not reach 50 %)

**Table 5.** Results of nitrate reduction experiments with the Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst in presence of other anions.

### 3.4. Experiments with nitrate-spiked commercial drinking waters

Table 2 collects the analyses of the six commercial drinking waters used in these experiments. All of them were spiked with nitrate to set the initial concentration at 100 mg  $\text{NO}_3^-/\text{L}$ , as in the previous experiments. Figure 6 shows the results obtained with these water samples with the Pd-Sn/ $\text{Al}_2\text{O}_3$  catalyst, in terms of nitrate conversion and selectivity to  $\text{NH}_4^+$  after 6 h reaction time. The highest  $\text{NO}_3^-$  conversion values were obtained for DW2 and DW6, both of very weak salinity. The lowest nitrate removal was observed for the DW1 water, which, although not having the highest salinity combines the highest  $\text{HCO}_3^-$  concentration and a relatively high hardness. However, although DW5 presents similar hardness and  $\text{HCO}_3^-$  concentration values than DW1, the  $\text{NO}_3^-$  conversion was significantly higher. This result could be related to the high  $\text{Cl}^-$  concentration in DW5, which seems to produce an antagonist effect with bicarbonate already observed with the M6 synthetic water sample. Besides, the coexistence of high  $\text{SO}_4^{2-}$  with  $\text{HCO}_3^-$  decreases the negative effect of  $\text{HCO}_3^-$ , as can be observed comparing DW3 and DW4. On the other hand, the selectivity towards  $\text{NH}_4^+$  increased in all drinking water runs compared with only-nitrate sample (W0), being that effect less significant with those of very weak salinity (DW2 and DW6).



**Fig. 6** Results from the catalytic reduction of nitrate in commercial drinking waters with the Pd-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst after 6 h reaction time.

#### 4. Conclusion

Catalytic reduction of nitrate with high selectivity towards N<sub>2</sub> has been successfully performed with a Pd-Sn/Al<sub>2</sub>O<sub>3</sub> (5-0.5 wt %) catalyst. This catalyst showed highly stable behaviour after ten consecutive 6h-batch runs, maintaining almost unchanged low levels of NH<sub>4</sub><sup>+</sup> at nearly constant high nitrate conversion ( $\approx 90\%$ ). The presence of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> in the reaction medium caused some negative effect, especially in the case of HCO<sub>3</sub><sup>-</sup>, which even at low concentrations provoked significant reduction of the catalytic activity and increased the selectivity to ammonium. This enhanced selectivity towards NH<sub>4</sub><sup>+</sup> can be attributed to the decrease of the N/H ratio on the catalyst surface, caused by the competitive adsorption of those anionic species. The joint presence of Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> with HCO<sub>3</sub><sup>-</sup> reduced the negative effect of the latter. Catalytic reduction of NO<sub>3</sub><sup>-</sup> was successfully achieved in commercial drinking waters of low conductivity and hardness but was less effective as the values of those parameters increased.

#### Acknowledgments

The authors wish to thank for the financial support the Spanish MINECO (CTM2016-264 76564-R) and Comunidad de Madrid (BIOTRES-CM, S2018/EMT-4344). I. Sanchis also thanks Comunidad de Madrid for award of a research grant (PEJD-265 2017-PRE/AMB-4616).

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