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Title: State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates

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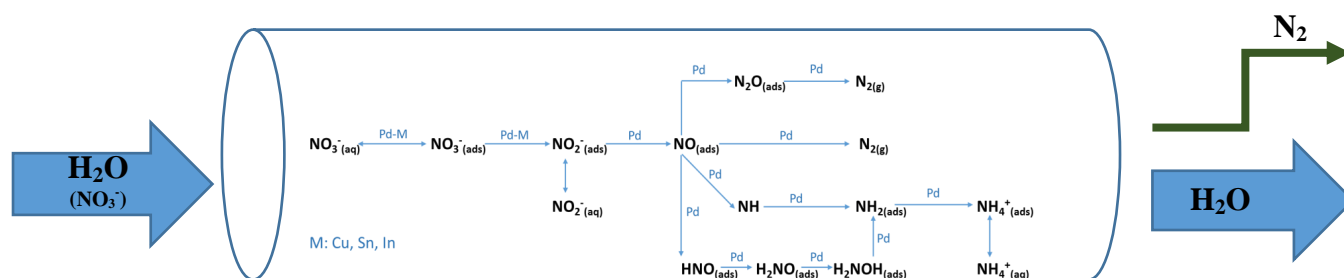# State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates.

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Graphical abstract

$NO_3^-{}_{(aq)}$ $\xrightarrow{Pd-M}$ $NO_3^-{}_{(ads)}$ $\xrightarrow{Pd-M}$ $NO_2^-{}_{(ads)}$ $\xrightarrow{Pd}$ $NO_{(ads)}$

$NO_2^-{}_{(aq)}$

$N_2O_{(ads)}$ $\xrightarrow{Pd}$ $N_{2(g)}$

$\xrightarrow{Pd}$ $N_{2(g)}$

NH $\xrightarrow{Pd}$ $NH_{2(ads)}$ $\xrightarrow{Pd}$ $NH_4^+{}_{(ads)}$

$HNO_{(ads)}$ $\xrightarrow{Pd}$ $H_2NO_{(ads)}$ $\xrightarrow{Pd}$ $H_2NOH_{(ads)}$ $NH_4^+{}_{(aq)}$

M: Cu, Sn, In

H_2O
(NO_3^-)

N_2

H_2O

HIGHLIGHTS

Catalytic and electrocatalytic reduction of aqueous nitrates overview

Mechanisms of Nitrate reduction to nitrogen

Catalysts, operating conditions and reactor configuration assessment

INDEX

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ABSTRACT

Keywords: Nitrate, Catalytic Reduction, Electrocatalytic Reduction, Groundwater

Nitrate pollution of groundwater, which is mainly caused by the application of nitrogen-based fertilizers in intensive agriculture, is a widespread problem all over the world and a potential risk for public health. Reverse osmosis, ion exchange and electrodialysis are currently used for water denitrification, yielding a highly concentrated reject water that requires economic and environmental costs for disposal. Nitrate reduction technologies that are able to convert nitrate into inert nitrogen gas have appeared that are promising, cost effective and environmentally friendly. Among these technologies, attention has been focused on i) the chemical reduction over mono- and bimetallic catalysts with hydrogen as the reducing agent and ii) electrocatalytic reduction processes over metallic anodes. Although selectivity values towards N_2 of greater than 90% are achieved with both technologies, the undesired formation of ammonium as a reaction by-product is still the main drawback preventing their implementation at larger scales. For this reason, the development of new catalytic and electrodic materials as well as novel reactor configurations to avoid ammonium formation have been extensively investigated in the last few years to increase the effectiveness and competitiveness of both technologies. In this paper, an overview of the current state-of-the-art of both catalytic reduction and electroreduction of nitrates is presented, highlighting their potential and their main drawbacks along with guidelines for future research.

1. INTRODUCTION

In the past several centuries, demand for clean drinking water has risen significantly. Pollution of groundwater, which represents the main drinking water source, is becoming a global problem. Nitrate pollution of aquifers, caused mainly by the application of nitrogen-based fertilizers in intensive agriculture, is one of the most widespread causes for groundwater contamination in many countries due to the rapid progress of their agricultural and industrial activities. Nitrate can pose a health risk for humans because the human body reduces it to nitrite, which may cause metahemoglobinemia, also known as "blue baby syndrome", and transforms it into the precursor of carcinogenic nitrous amine. For these reasons, the European Union and the United States of America limit the concentration of nitrogen compounds in drinking water. For example, The Nitrate Directive (EC, 1991) is the European legislation that sets maximum concentrations of 50, 0.1 and 0.5 ppm for NO_3^-, NO_2^- and NH_4^+, respectively. Even lower limits have been recommended by The World Health Organization: 10, 0.03, and 0.4 ppm for NO_3^-, NO_2^- and NH_4^+, respectively.

Currently, nitrate removal from drinking water is carried out mainly by several commercially available physicochemical technologies such as electrodialysis (ED), reverse osmosis (RO) or ion exchange (IE). However, concentrated nitrate brine is produced by these physicochemical processes, requiring post-treatment of the effluents with high associated costs. Another possibility to remove nitrates from water is the use of biological denitrification, which reduces the nitrates to nitrogen using microorganisms in a biological reactor. Although highly concentrated nitrate waste streams are avoided, the possibility of bacterial contamination of the drinking water or the sludge formed during the process make biological denitrification not competitive for nitrate removal when compared against physicochemical processes.

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The global energy and environmental situation has led to increasing demand for green technologies for the sustainable production of clean water that are not energy intensive and with no environmental impact. Jensen et al. [1] provided an overview of the actual management strategies and treatment options for nitrate and nitrite removal, including the cost and common problems of the commercially available technologies which in turn justify research on novel strategies that can improve upon the conventional techniques.

Several emerging technologies capable of reducing NO_3^- to N_2 while avoiding producing a waste stream have been proposed in the last few years. Catalytic hydrogenation of nitrate, studied for the first time by Vorlop et al. [2], appears as one of the most promising technologies. Hörold et al. [3,4] reported in 1993 a widely recognized reaction mechanism based on catalytic reduction over bimetallic catalysts using a noble metal (Pd, Pt) and a transition metal (Cu, Sn, In) in the presence of hydrogen as the reductant [5-7]. Batch reactors with bimetallic catalysts supported on alumina powder have been mostly used to test the reaction performance [5,7-11]. Although total nitrate removal has been reached, the formation of undesirable ammonia is the main drawback of the catalytic reduction. Development of novel catalysts and configurations to improve nitrogen selectivity is the principal challenge to be solved for the catalytic reduction of nitrates to become competitive. With this goal, many research efforts in the last few years have focused on the use of different support materials [12-14], reactor configurations such as catalytic membrane reactors [15-25], and the use of zero valent iron (ZVI) as the catalyst [26,27].

Nitrate electroreduction has also been considered as an alternative to transform nitrates to nitrogen gas in drinking water treatment. Some of the advantages associated with this process are no sludge production, a small area occupied by the plant and relatively

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low investment costs. The reaction mechanism in the electrochemical cell, as described by Paidar et al. [28], depends mainly on the type of the electrocatalytic material, the pH of the solution and the cathode potential. Nitrogen, nitrite and ammonia are obtained as the principal products of the nitrate electroreduction [28]. The selective reduction of nitrate to nitrogen becomes even more difficult when water with a low nitrate concentration, typical in groundwater, is treated. To improve the process performance and selectivity, novel electrodic materials and cell configurations have been widely investigated.

This work aims to give an overview of the state-of-the-art of the most promising nitrate reduction strategies. In particular, this paper focuses on the study of the catalytic reduction and the electroreduction processes due to their high potential to achieve more sustainable nitrate removal. Fundamentals and reaction mechanisms will be explained. The effects of different catalysts, support materials, reactor or cell configurations and the influence of the operation conditions will be analysed and compared. The positive and negative aspects for each technology will be evaluated.

2. CATALYTIC REDUCTION OF NITRATES

2.1 Mechanism of catalytic nitrate reduction

The reaction mechanism of nitrate removal through chemical reduction over bimetallic catalysts has been widely studied by different authors since the nineties [6,7,29-37]. Nitrate reduction is carried out in the presence of hydrogen as a reducing agent over the surface of a catalyst consisting of both a noble metal and a transition metal deposited on a support. Palladium and platinum have been mainly used as the noble metals for nitrate reduction due to their favourable hydrogen adsorption abilities. In addition, the best

activity and selectivity have been achieved with Cu, Sn or In as the promoter metal, Figure 1.

Numerous investigations and discussions have been performed to clarify how the reaction proceeds. A general and detailed mechanism for NO_3^- and NO_2^- reduction by hydrogen as reducing agent in aqueous solutions over mono and bimetallic Pd-M catalysts (square brackets symbolise the active surface centers) that is mostly accepted is as follows [18],

$$NO_3^- + 2M[] \rightarrow [M_2O]_{surf} + NO_2^- \qquad (1)$$
$$H_2 + 2Pd[] \rightarrow 2Pd[H] \qquad (2)$$
$$[M_2O]_{surf} + 2Pd[H] \rightarrow 2M[] + 2Pd[] + H_2O \qquad (3)$$
$$NO_3^- + Pd[H] \rightarrow Pd[NO_2] + OH^- \qquad (4)$$
$$Pd[NO_2] \leftrightarrow NO_2 + Pd[] \qquad (5)$$
$$2\ NO_2 + 2\ OH^- \rightarrow NO_2^- + NO_3^- + H_2O \qquad (6)$$
$$NO_2^- + Pd[H] \rightarrow Pd[NO] + OH^- \qquad (7)$$
$$Pd[NO_2] + Pd[H] \rightarrow Pd[NO] + Pd[OH] \qquad (8)$$
$$Pd[NO] + Pd[] \rightarrow Pd[N] + Pd[O] \qquad (9)$$
$$Pd[O] + 2\ Pd[H] \rightarrow 3\ Pd[] + H_2O \qquad (10)$$
$$Pd[N] + Pd[N] \rightarrow 2Pd[] + N_2 \qquad (11)$$
$$Pd[NO] + Pd[H] \rightarrow Pd[N2O] + H2O \qquad (12)$$
$$Pd[N2O] + Pd[H] \rightarrow Pd[] + H2O + N2 \qquad (13)$$
$$Pd[N] + Pd[H] \rightarrow Pd[NH] + Pd[] \qquad (14)$$
$$Pd[NH] + Pd[NH] \rightarrow N2 + H2 + 2Pd[] \qquad (15)$$
$$Pd[NH] + Pd[H] \leftrightarrow Pd[NH_2] + Pd[] \qquad (16)$$
$$Pd[NH_2] + Pd[H] \rightarrow Pd[NH_3] + Pd[] \qquad (17)$$
$$Pd[NH_3] \rightarrow NH_3 + Pd\ [] \qquad (18)$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (19)$$
$$Pd[OH] + Pd[H] \rightarrow H_2O + 2Pd[] \qquad (20)$$
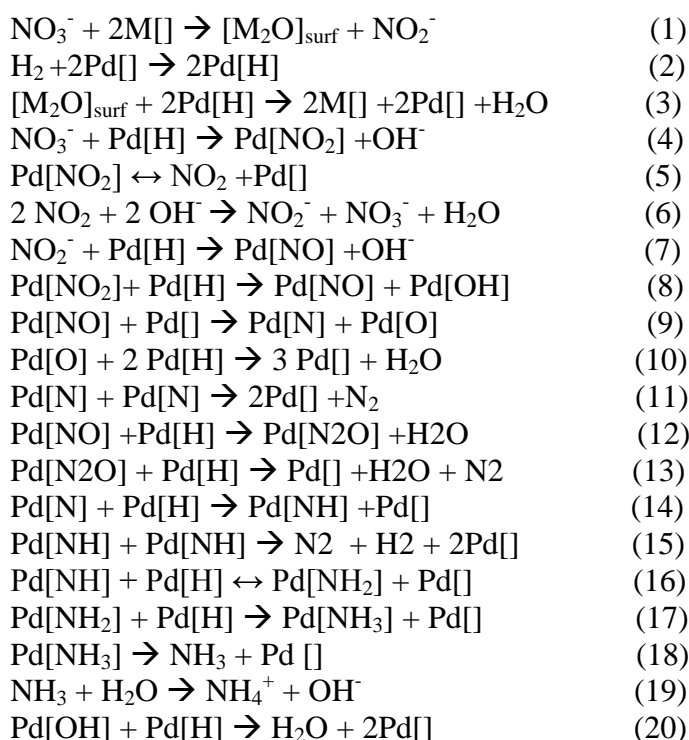
M: Cu, Sn. In

With the exception of steps (1) and (3) the same sequence of equations can be suggested to describe the reaction mechanism over monometallic Pd catalyst.

The reaction occurs when nitrate ions and hydrogen, both adsorbed on the bimetallic catalyst surface (Eq.1 and Eq.2), get in contact (Eq.3). In a first step, bimetallic active sites are required to initiate the reduction of nitrate to nitrite. The transition metal promotes the reduction of nitrate in a redox process in which the promoter metal is

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oxidized. In contrast, the role of the precious metal is to activate hydrogen, allowing the *in situ* reduction of the second metal, as shown in Figure 1 [34, 38]. No activity was found when monometallic Pd or Pt catalyst by themselves were used to reduce nitrates (Eq. 4) in absence of a reducible support or a promoter metal, which plays an active role in the redox mechanism responsible for nitrate reduction.
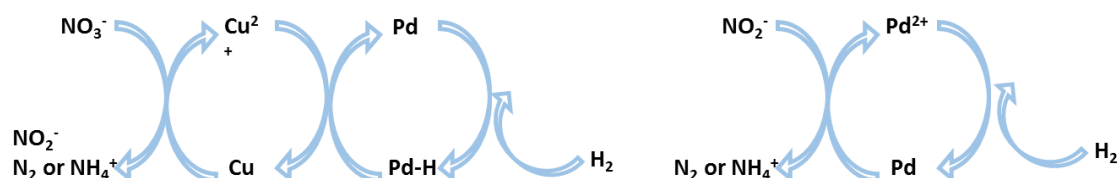

Figure 1. Reaction mechanism of the catalytic reduction of nitrate

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Second, nitrite ions, which have been identified as intermediate products in the nitrate reduction, are reduced on the surface of the noble metal to $NO_{(ads)}$ (Eq.7 and Eq. 8) as the key intermediate in the generation of nitrogen and ammonium [6,29,32,33,39-42]. This time, the noble metal itself can reduce the nitrite ions by activated hydrogen. Hörold *et al.* [3,4] reported a mechanism to generate nitrogen [32,33,39-41] from $NO_{(ads)}$ directly (Eqs.9-11) and through stepwise reactions in which N_2O appears as intermediate in the reduction mechanism (Eqs. 12-13).

Nevertheless, the generation of ammonia, the main drawback of this technology, depends on the NO_2^- reduction path. Wärna et al. [30] proposed a reaction system for nitrate reduction over Pd-Cu/Al_2O_3 in which the generation of ammonia is supposed to occur via the stepwise addition of hydrogen to the adsorbed NO with the formation of successive hydrogenation intermediates: $NH_{(ads)}$ (Eq. 14), $NH_{2(ads)}$ (Eq. 16) and $NH_{3(ads)}$ (Eq. 17). Participation of the $NO_{(ads)}$ species in the pathway of NH_4^+ production has also been illustrated by Zhang et al. [7]. In that work, isotopically labelled nitrogen species were used to follow nitrite hydrogenation over Pd-In/Al_2O_3 catalyst. The observations demonstrated that catalytic $NO_{(ads)}$ reduction can lead to two stable end-products: NH_4^+

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and N_2. More recently, Shin *et al.* analysed the role of NO as an intermediate in NH_4^+ evolution [43]. In this report, two different pathways for the reduction of NO to NH_4^+ are proposed: **NO dissociation,** in agreement with the above-mentioned ammonium pathway, and **NO hydrogenation**, where $HNO_{(ads)}$, $H_2NO_{(ads)}$, $H_2NOH_{(ads)}$, $NH_{2(ads)}$ and $NH_{3(ads)}$ are the successive intermediates.

The study of the influence of Pd-M ratio on the selectivity of the nitrate reduction pathway has been addressed in different works [18, 33]. When catalysts with a low content of the second metal are used, only few bimetallic and large monometallic ensembles are present in the catalyst. In this case the nitrate removal activity is lower, as fewer bimetallic ensembles are present. During the reaction course, the now larger palladium ensembles will be provided with nitrite and therefore N-species with a slower rate, whereas the palladium ensembles will be covered with the reductant species as usual. This leads to a remarkable shift in the N:reductant ratio, which now is smaller with a corresponding low selectivity. If catalysts with a high content of the second metal are used, these catalysts exhibit many and large bimetallic ensembles, whereas monometallic palladium ensembles are few and small, even if the total crystallite size is broadened to some extent in these catalysts. Now the situation is again different. Nitrate now is reduced at a high rate and a corresponding high rate will be obtained for the production of nitrite. As in this case the palladium ensembles are fewer and smaller, not every nitrite molecule which is produced can directly re-adsorb at the palladium surface, which is "overcrowded". Therefore, the intermediate nitrite release is much higher for these catalysts than for catalysts with a lower content of the second metal. The high ammonium formation, which is observed for these catalysts simply results from such palladium ensembles, which are too small to enable the pairing of two N-species, so that in the end ammonium is formed. [8, 33]. Thus, the Pd-M ratio of the bimetallic catalyst

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plays a crucial role in the priority pathways through the reactions that take place as well as in the activity of NO_3^- reduction and selectivity towards N_2.

With all, the most accepted mechanism for the catalytic hydrogenation of nitrates from water is shown in Figure 2. It can be concluded that active bimetallic sites with an optimal Pd-M ratio are required to carry out the reduction of nitrate to nitrite and that monometallic Pd (or Pt) sites are needed to hydrogenate nitrites to the end-products. Nitrogen is produced through reactions (11, 13 and 15) and at the same time, the intermediate NH_2 is achieved via two different pathways, NO dissociation and NO hydrogenation, to give ammonium as the final product at the reaction 19. [7].
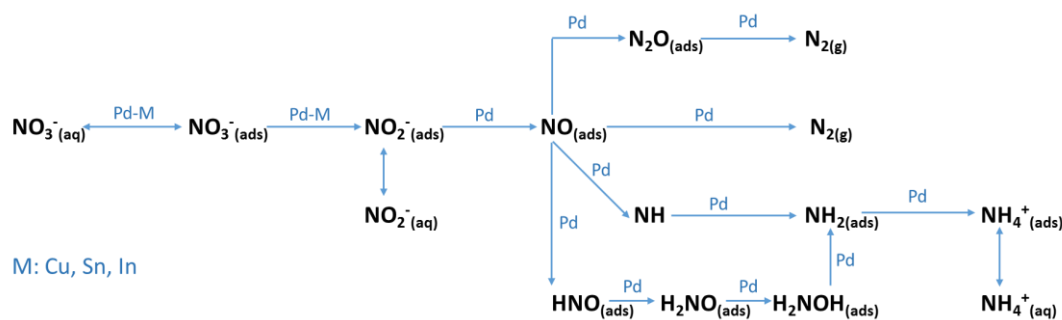

Figure 2. Mechanism of the catalytic nitrate reduction over bimetallic catalysts.

2.2 pH Influence

At different pH values, the metal surface will be covered with different adsorbed species, which are hydrogen species at low pH values and hydroxide or even oxide species at high pH values. Since nitrate needs to be adsorbed prior to its reduction, the repulsion between the negative nitrate ions and the reduced or more negatively charged metal surface at lower pH values leads to the observed drop in the activity at lower pH values. This effect is markedly different for the three promoter metals under consideration (Cu, Sn and In). Indeed, the maximum activity has been observed at about pH 9 for the Pd–Cu catalyst. For high pH values a drop in the activity has been

observed for all the catalysts. As the catalytic reaction proceeds, the increase in OH$^-$ concentration due to reactions (4), (7) and (19) increases the pH. These hydroxide species can competitively be adsorbed on the active sites of the bimetallic catalyst, resulting in the inhibition of nitrate and nitrite adsorption, limiting the nitrate reduction activity and favouring the accumulation of nitrites in the aqueous phase at high pH values [44,45]. Here, the active sites at the catalyst surface are progressively blocked by the strongly adsorbing oxygenated species (e.g. OH, OH$^-$, Ox$^-$), i.e. the bimetallic site is oxidized. Thus, high activity of nitrate reducing catalysts is favoured at pH values, at which the second metal or the bimetallic ensemble, respectively, is positively charged to some extent to facilitate the adsorption of the opposite charged nitrate ion. Obviously, the pH value has some effect on the palladium sites as well. The catalyst surface is increasingly covered with strongly adsorbing oxygenated species (hydroxide ions) whit the increase in the pH value. These hydroxide species may act as blocking barriers disabling the pairing of N-species diffusing on the surface [33]. In a way, this effect resembles the negative effect, which catalysts with a high ratio (M-Pd) of the second metal have on the selectivity, resulting in less palladium active sites available, at which only ammonium can be formed. Again, the formed nitrite ions cannot directly re-adsorb at the palladium ensembles, which are blocked by hydroxide ions. As avoiding NH$_4^+$ formation is still the main challenge in the catalytic hydrogenation of nitrates from polluted waters, the pH value must be controlled during the reduction reaction to improve the activity and selectivity of the process. An interesting application was reported by Pintar et al. [46,47] who found almost stoichiometric transformation of nitrates to nitrites conducting the catalytic nitrate reduction consecutively in separate, single-flow fixed-bed reactors. In the first reactor, that was packed with a Pd–Cu bimetallic catalyst, nitrate ions were transformed to nitrites at pH 12.5 with selectivity

as high as 93%. Liquid-phase nitrite hydrogenation to nitrogen was conducted in the second reactor unit packed with a Pd monometallic catalyst working at low pH values of 3.7 and 4.5, respectively.

To control de value of pH, different inorganic and organic buffers have been widely tested. For instance, the use of zwitterionic organic buffers such as 2-(N-morpholino)ethanesulfonic acid (MES) or N-Cyclohexyl-2-aminoethanesulfonic acid (CHES) were compared with phosphate and bicarbonate buffers at pH values of 6 and 10, respectively. MES and CHES buffers allowed higher nitrate removal than the phosphate and bicarbonate buffers due to the inhibitory role of the anions of the inorganic buffers on the catalytic nitrate reduction [48,49]. However, carbon dioxide, formic acid [8,11,39,42,43,50-60] or hydrochloric acid [6,36,40,45-47,57,61-64] have been the most used compounds to control the pH and to keep the nitrate solution acidified. These buffers behave differently: pH control with HCl has been shown to be more dependent on the system fluid dynamics, while CO_2 allows better control of the pH inside the pores of the catalyst since it is better distributed in the reaction system [57,63].

$$OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \qquad\qquad (21)$$

$$CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^- \qquad\qquad (22)$$
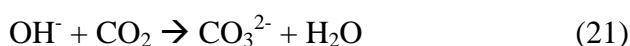
Operating in a continuous reactor, both the activity and selectivity significantly increased with CO_2 buffering instead of HCl buffering [57]. CO_2 bubbling keeps the pH of the aqueous solution between 5 and 6 during the reaction by neutralizing OH^- ions by reactions (21) and (22) [32]. Although the activity and selectivity are enhanced with lower pH, significant dissolution of the bimetallic particles may occur with pH values below 4.0 [41,47]. In addition, in the treatment of drinking water, lowering the pH would require an additional step to return the pH to a neutral value.

2.3 Monometallic catalyst

Reaction rate, activity and selectivity towards the end-products in catalytic nitrate reduction are significantly affected by the support, catalyst composition and structure. On the one hand, it has been reported that Pd or Pt monometallic catalysts are inactive for nitrate reduction when they are supported over non-reducible supports such as Al_2O_3 [36,58,60,63,65], active carbon (AC) [41,66,67], Nb_2O_5 [63], SiO_2 [36], pumice [39], resin [62] or zeolites [68-70]. The reason for the inactivity is the lack of a promoter metal, which plays an active role in the redox mechanism responsible for nitrate reduction. However, monometallic Pd or Pt catalysts deposited on reducible supports and iron-based catalysts have shown sufficient activity in water denitrification, reaching total nitrate conversion [50,71].

The use of SnO_2 as the active support for NO_3^- reduction in the absence of an added promoter was proposed for the first time by Gavagnin et al. [71]. In this case, nitrate reduction occurs due to the presence of tin in a low oxidation state, promoted by the active role of Pd in SnO_2 reduction [50]. Table 1 reports the selectivity and conversion values achieved with active Pd/SnO_2 catalysts, along with other active monometallic catalysts reported in the literature with different buffer systems.

Table 1. Active monometallic catalyst for nitrate reduction

Metal	wt%	Support	Mode	$Co_{[mgNO_3^-/l]}$	X (%)	S_{N2} (%)	S_{NH4} (%)	$[NO_2^-]_{max}$ (ppm)	Initial rates (ppm/min)	Activity (mol/min gcat) x 10-5	pH	Buffer	Red.	Ref.
Pd	5	Al-Pillared Clay	Semi-Batch	100	64	-	42	-	-	0.7	6_f	CO_2	H_2	[56]
Pd	5	SnO_2	Semi-Batch	100	100	-	18.3	0	2.1	-	3.4_o-5_f	CO_2	H_2	[50]
Pd	5	SnO_2	Semi-Batch	100	100	-	17.2	0	2.1	-	4.2_o-4.4_f	Acetate	H_2	[50]
Pd	5	SnO_2	Semi-Batch	100	100	-	48.2	1.9	5.7	-	4.5_o-4.5_f	HCl	H_2	[50]
Pd	5	SnO_2	Semi-Batch	100	100	-	41.7	2.8	5.26	-	4_o-5_f	HCl	H_2	[71]
Pd	5	SnO_2	Semi-Batch	100	100	-	13.8	0.5	1.05	-	4_o-5_f	CO_2	**H_2**	[71]
Pd	5	CeO_2	Semi-Batch	100	100	±52	±48	-	-	-	-	CO_2	H_2	[72]

Pd	1.6	CeO$_2$	Semi-Batch	100	25	-	>50	0	-	-	-	CO$_2$	H$_2$	[51]
Pd	1.6	CeO$_2$	Semi-Batch	100	100	-	80	0	-	-	-	No	H$_2$	[51]
Pt	0.2	CeO$_2$	Continuous	60	93	46.0	54.0	0	-	-	-	No	H$_2$	[37]
Pt	0.5	CeO$_2$	Continuous	60	99	45.0	55.0	0	-	-	-	No	H$_2$	[37]
Pt	0.5	CeO$_2$	Continuous	60	30	76.0	24.0	0	-	-	-	CO$_2$	H$_2$	[37]
Pt	1	CeO$_2$	Continuous	60	99	0.0	100.0	0	-	-	-	No	H$_2$	[37]
Pt	1	F-CeO$_2$	Continuous	60	90	79.0	21.0	0	-	-	-	No	H$_2$	[37]
Pd	5	TiO$_2$	Semi-Batch	100	±55	56	-	0	-	5.1	-	CO$_2$	H$_2$	[73]

Using carbon dioxide or acetate as buffers in a semi-batch reactor, 5 wt% Pd/SnO$_2$ catalyst exhibits rather good activity. Even higher activity was found using HCl [50] despite the larger amount of ammonium that was produced. A more favourable N$_2$ selectivity was found using CO$_2$ buffering with a final NH$_4^+$ concentration of 4 ppm, which still exceeds the established legal limits [50,71].

The use of TiO$_2$ as a partially reducible support with monometallic catalysts has also been investigated for nitrate reduction. A 5 wt% Pd/TiO$_2$ catalyst was tested in a slurry reactor with a constant feed flow-rate of carbon dioxide and hydrogen. Relatively high activity for the removal of nitrates was achieved, which in some cases was higher than the activity of the bimetallic Pd-Cu/Al$_2$O$_3$ catalyst at the same reaction conditions [73]. The reaction is controlled by the generation of Ti^{3+} centres, which seem to result from the generation of Pd β-hydride species [73-75]. This type of catalyst is known for its strong hydrogenation character, a high nitrate reduction rate that favours ammonium evolution and, consequently, a nitrogen gas selectivity of lower than 60% [73].

CeO$_2$ has been tested as a partially reducible support as well. When the catalyst is exposed to hydrogen, cerium is reduced from Ce^{4+} to Ce^{3+}, and oxygen vacancies are generated at the metal-support interface. In this way, the oxygen atoms present in the nitrate ions can interact with the support, leading to their reduction over the Pd/CeO$_2$ catalyst, while the noble metal would maintain the ceria support in its reduced state. The

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activity of monometallic Pd/CeO_2 catalyst was reported for the first time by Epron et al. [51] in 2002. Despite the high activity shown for nitrate reduction, the CeO_2 support is not suitable for water denitrification due to the high selectivity towards ammonium. As shown in Table 1, when CO_2 is used to control the pH, the catalyst is deactivated independently of the noble metal used, decreasing the conversion from 100% to 25% or from 99% to 30% for palladium or platinum, respectively. This is due to the inhibition of the oxygen vacancies caused by the presence of carbonate or bicarbonate species at the cerium surface, resulting in the loss of activity for nitrate reduction [37,51,72].

Fe-based monometallic catalysts have proven to be active for the catalytic reduction of nitrates as well. The Fe^{3+} and Fe^{2+} oxidation states are easily interchangeable. Fe^{3+} present in the surface of the catalyst is reduced to Fe^{2+} when it is in contact with H_2. Iron in its Fe^{2+} oxidation state acts as a reducing agent and can convert nitrate to nitrogen while recovering its initial oxidation state, Fe^{3+}. Figure 3 depicts the redox mechanism. The use of monometallic Fe catalyst supported on activated carbon was investigated by Shukla et al. using batch and continuous reactors [76]. The overall selectivity towards nitrogen was nearly 100% with conversions of approximately 50% in both systems. The capacity of Fe to reduce nitrates in the presence of hydrogen has also been examined using monometallic catalysts supported on Fe-based supports. For instance, monometallic Pd catalysts with pillared clays as a support [77] or green rusts modified with trace metals (Pt, Cu, Zn) [78,79], which enhance the reaction rate of nitrate reduction, showed satisfactory activity, but high ammonium production was observed.
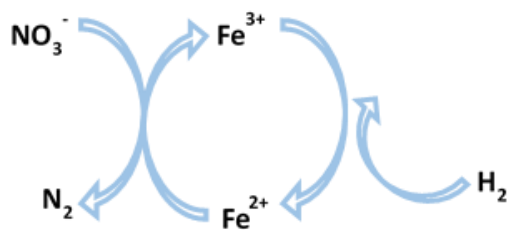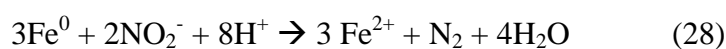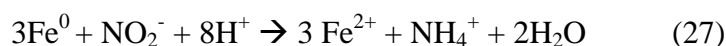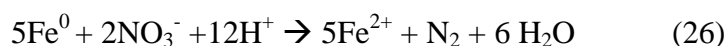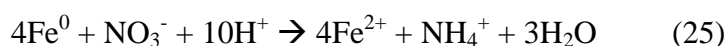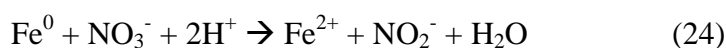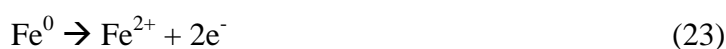
Figure 3. Mechanism of nitrate reduction over monometallic Fe catalyst.[76]

Zero valent iron (ZVI) systems are the most representative catalysts containing iron studied in the literature so far. The general mechanism of ZVI in water denitrification is based on its adsorptive capability towards nitrates in addition to its reductive activity. In the presence of nitrates, Fe^0 is oxidized to form Fe^{2+}/Fe^{3+} in a redox process in which nitrates are reduced to form nitrite, nitrogen and ammonium [80,81]. In the proposed pathways, direct and indirect electron mass transfer processes, which are defined in reactions (23-28), are involved [81-84].

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (23)$$

$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O \qquad (24)$$

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (25)$$

$$5Fe^0 + 2NO_3^- + 12H^+ \rightarrow 5Fe^{2+} + N_2 + 6 H_2O \qquad (26)$$

$$3Fe^0 + NO_2^- + 8H^+ \rightarrow 3 Fe^{2+} + NH_4^+ + 2H_2O \qquad (27)$$

$$3Fe^0 + 2NO_2^- + 8H^+ \rightarrow 3 Fe^{2+} + N_2 + 4H_2O \qquad (28)$$

Low price and low toxicity, which make ZVI suitable for direct injection into aquifers for *in situ* nitrate remediation, are the most remarkable advantages of this catalyst. Furthermore, the use of nano-scale zero valent iron (nZVI) has shown several benefits compared to micro-scale ZVI, such as high reduction capacity, large specific surface area and low required dosage [26,82,83,85]. The need for a reducing agent able to reduce the Fe^{2+}/Fe^{3+} species back to Fe^0 to close the catalytic circle [86] and the fact that ammonium was found to be the main species in the final product are the principal

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disadvantages that make this option still impractical. ZVI modified by noble and transition metals has been determined to enhance the selectivity to nitrogen gas [26,85,87].

Thus, the use of monometallic catalysts (Pd or Pt) deposited on reducible supports (SnO_2, TiO_2, CeO_2, and pillared clays) using appropriate CO_2 buffering favours the increase in the activity of nitrate reduction. However, these systems are not sufficiently selective to the formation of nitrogen due to the strong tendency to hydrogenation of these supports that promotes the generation of ammonium. Fe-based monometallic catalysts and ZVI systems have been reported to reach nearly 100 % N_2 selectivity but poor nitrate conversion rates. These drawbacks have been addressed through the implementation of bimetallic catalysts.

2.4 Bimetallic Catalyst

Since the proposal of Vorlop and Tacke in 1989, the use of bimetallic catalysts to reduce nitrates dissolved in water has been the focus of numerous researchers. Many publications have studied the reaction mechanisms to improve the activity and selectivity of the reaction towards nitrogen gas while avoiding the production of ammonium. For this purpose, laboratory-scale experiments with slurry reactors have been used to study the influence of different variables that can affect the process. The use of different metal pairs and supports has been shown to play a fundamental role in the final performance. For this reason, multiple combinations of noble metals (Pd, Pt, Rh) and promoter metal (Cu, Sn, In, Ag, Au, Ni) deposited on different supports have been examined with the aim of achieving a good compromise between nitrate removal and nitrogen gas production. Pd and Pt have been reported as the most active and selective metals towards nitrogen compared to other precious metals, such as Ir, Rh, Ru

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[3,4,56,67]. When palladium and platinum were compared to each other as the noble metal component in bimetallic catalysts, similar values of N_2 selectivity were found. However, much higher activity for nitrate reduction was achieved using Pd-based catalysts [3,4,88-90].

The pairs Pd:Cu, Pd:Sn and Pd:In, which have provided the best performance in catalytic nitrate reduction, have been compared under the same conditions in different works and clear differences were observed among them. In the results reported by Pintar et al. using synthetic nitrate solutions to carry out the catalytic reduction, Cu-promoted catalysts were more active and more selective to nitrogen than the corresponding Pd:Sn catalyst when both were supported on alumina spheres [91]. However, when nitrate reduction with Pd:Cu and Pd:Sn supported on Al_2O_3 was investigated using natural water from some Spanish aquifers polluted with nitrates, better results were obtained with the Pd:Sn couple because this catalyst was less affected by water hardness and conductivity. In addition, NH_4^+ formation was more pronounced with the catalyst containing Cu [11,53]. It has been reported that In-promoted catalysts are highly active to abate nitrates in water with better effectiveness than Pd:Cu catalysts in terms of selectivity and long-term stability [6,62,92,93]. However, in a different work a slightly lower selectivity towards nitrogen than that obtained with a Pd:Sn catalyst was found [40].

Yoshinaga et al. [41] highlighted the relevance of the structure and geometry of the metal particles in the final mechanism of nitrate reduction. In this sense, although edge and corner sites of Pd microcrystals possess a high ability for hydrogenation, favouring the formation of NH_4^+, nitrogen is favourably formed on the terrace sites of Pd crystals with mild hydrogenation abilities (Figure 4) [94]. If edge and corner sites are occupied by promoter metal particles, the production of nitrogen gas will be enhanced [41]. Thus,

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it is concluded that the nitrate reduction rate and the selectivity for the final products are significantly affected by the dispersion of the particles on the support, the size of the particles and the formation of agglomerates or alloys. These factors, which are strongly dependent on the preparation method, the metal loading and the Pd:Me ratio (Me = Cu, In or Sn), determine the distance between active sites of palladium and noble metal, influencing the interactions between the reactants and the catalyst.
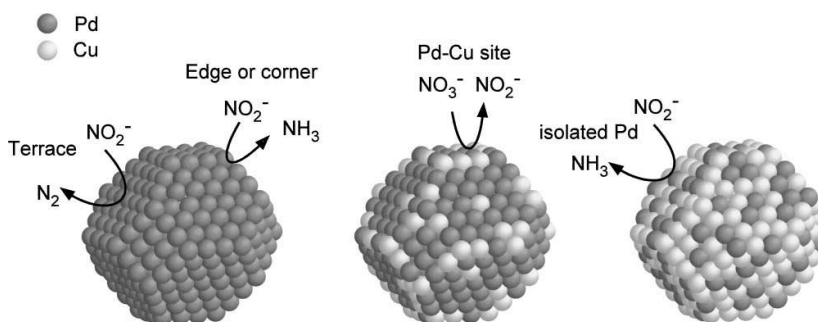

Figure 4. Proposed models of Pd and Pd-Cu particles [41]

This explains why the optimization of the metal loading in the catalysts and the Pd:Me ratio are so important for improving the rate of the catalytic reduction of nitrates.

Therefore, the adequate structural and physico-chemical characterization of the catalysts provides valuable information for a better understanding of the catalysts behaviour in terms of stability, activity and selectivity. Thus, a wide range of characterisation techniques have been used to report useful information, e.g. i) dispersion and composition of metal particles in the catalysts and supports are commonly described by X-ray diffraction techniques (XRD); ii) the specific surface area is calculated applying the BET method (SBET) to N2 adsorption isotherms; iii) the size distribution of the metallic particles is determined by transmission electron microscopy (TEM); iv) the metal content and elemental ratios of the catalysts are measured by X-ray fluorescence; v) X-ray photoelectron spectra (XPS) give information about the evolution of the oxidation and chemical state of the active phases and it is used to determine the binding energy of the different element core levels; vi) the average metal crystallite diameter

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and the metal dispersion in the reduced samples can be estimated from CO chemisorption with the double isotherm method; vii) H_2 pulse chemisorption measurements shows dispersion of palladium based on the hemispherical model and, viii) temperature-programmed reduction of hydrogen (H-TPR) is used to investigate the reducibility of the metals in the catalysts. [53, 65, 106]

The results of many publications with different metal loadings and Pd:Me ratios were collected and are listed in Table 2. Most of the possible combinations have similar trends. Once the maximum conversion is reached with a specific Pd:Me ratio, further addition of the promoter metal does not improve the reaction rate or selectivity [51,52,88,95,96]. This occurs because once the amount of promoter metal is sufficiently large to guarantee the reduction of the total nitrate concentration adsorbed on the palladium sites, larger amounts of the transition metal only decrease the active surface of Pd and thus, the reduction power of the catalyst. When Al_2O_3 particles are used as the support with a metal loading of 5 wt% Pd, optimal Pd:Cu or Pd:In ratios of 4 were reported [3,4,52,97]. Nevertheless, different optimal metallic ratios have been published with different catalytic systems. For instance, Fe-containing supports such as maghemite or pillared clays required a lower Pd:Cu ratio, probably due to the role of Fe in the reaction mechanism [56,95,98]. The influence of the metal loading is also significant. Most authors have worked with Pd or Pt loadings between 0.5 and 5 wt% with no agreement about the optimum composition needed to reach maximum activity or selectivity in water denitrification.

Table 2. Performance of alumina-based catalysts in the catalytic reduction of nitrates

Catalyst	wt%	Support	Co (mg/l)	X (%)	S_{N2} (%)	S_{NH4} (%)	$[NO2-]_{max}$ (ppm	Activity (mol/min gcat) x 10-5	pH	Buffer	Red.	Ref.

Catalyst	Ratio	Support										Ref
Pd:Cu	0.92:0.32	Al_2O_3	360	>90	93.5	3.4	-	-	-	No	H_2 + Air	[99]
Pd:Cu	0.92:0.32	Al_2O_3	100	92.7	95	1.7	-	-	-	No	H_2 + Air	[99]
Pt:Cu	0.75:0.25	Al_2O_3	62	100		5	0	1.1	6.5	H_3PO_4	H_2	[34]
Pd:In	9.03:2.23	Al_2O_3	30	100	72.1	27.9	0	-	4	CO_2	H_2	[52]
Pd:Sn	4.7:1.5	Al_2O_3	100	75	92.8	-	0	2	5	CO_2	H_2	[100]
Pd:Cu	3.9:0.98	Al_2O_3	100	95	78.5	21.3	1.3	-	6	CO_2	H_2	[101]
Pd:Cu	1.6:0.5	Al_2O_3	100	-	<40	60	-	13	11f	No	H_2	[38]
Pd:Cu	5:1.25	Al_2O_3	100	100	82	14	-	4	6	-	H_2	[4]
Pd:Cu	2.4:0.86	Al_2O_3	100	100	87	3.9	-	-	5	CO_2	H_2	[63]
Pd:In	1:0.5	Al_2O_3	100	99.6	93.6	6.4	0	-	5	HCl	H_2	[36]
Pd:In	1:0.25	Al_2O_3	100	100	80.3	19.6	0.1	-	5	HCl	H_2	[36]
Pd:In	1:0.25	Al_2O_3	100	100	75	25	0	78.2	5	HCl	H_2	[93]
Pt:In	1:0.25	Al_2O_3	100	67.7		25.3	0.6	18	5	HCl	H_2	[102]
Pd:In	1:0.25	Al_2O_3	100	±100	±79	±20	-	-	5	CO_2	H_2	[57]
Pd:Cu	5:1.5	Al_2O_3	90	100	±76	±20	-	-	11.2f	CO_2	H_2	[103]
Pd:Cu	4.7:1.7	Al_2O_3	200	100	97	-	-	25	6.5f	No	H_2	[31]
Pd:Cu	5:1.25	Al_2O_3	124	>99.5	93.6	-	12.8	1.6	7	HCl	H_2	[40]
Pd:Cu	5:1.25	Al_2O_3	100	100	93.5	6.5	-	-	5	HCl	HCOOH	[33]
Pd:Cu	5:1.25	Al_2O_3	100	100	97.7	2.3	-	-	5	HCl	H_2	[33]
Pd:Sn	5:1.25	Al_2O_3	124	>99.5	97.1	-	-	-	5	HCl	H_2	[40]
Pd:Sn	5:1.25	Al_2O_3	100	100	93.5	6.5	-	-	9	HCl	H_2	[33]
Pd:In	1:0.25	Al_2O_3:SiO_2 (25:75)	100	82.2	74.4	25.6	0	10.5	5	HCl	H_2	[93]
Pd:In	1:0.25	Al_2O_3:SiO_2 (50:50)	100	99.9	78	22	0	27	5	HCl	H_2	[93]
Pd:In	1:0.25	Al_2O_3:SiO_2 (75:25)	100	99.9	68.7	28	3.3	84	5	HCl	H_2	[93]
Pd:In	1:0.25	Al_2O_3:SiO_2 (75:25)	100	89	89.2	10.8	0	15.8	5	HCl	H_2	[93]
Pd:In	1:0.25	Al_2O_3:SiO_2 (75:25)	100	93.2	94.8	5.2	0	15.8	5	HCl	H_2	[93]
Pd:Cu	5:1.5	Al_2O_3-TiO_2	30	100	70.8	29.2	0	-	6.1	CO_2	H_2	[61]
Pd:Cu	1.5:0.5	Al_2O_3-TiO_2	100	±97	±60	±38	-	-	-	No	H_2	[99]
Pd:Cu	0.75:0.36	CeO_2-Al_2O_3	100	97.1	89.4	8.9	-	-	-	No	H_2 + Air	[104]
Pd:Cu	0.75:0.37	Cr_2O_3-Al_2O_3	100	95.3	89.8	6.6	-	-	-	No	H_2 + Air	[104]
Pd:Cu	0.50:0.34	Mn_2O_3-Al_2O_3	100	92.6	88.6	6.8	-	-	-	No	H_2 + Air	[104]
Pd:Cu	0.64:0.35	SrO-Al_2O_3	100	92.2	82.3	13.5	-	-	-	No	H_2 + Air	[104]
Pd:Cu	0.77:0.37	TiO_2-Al_2O_3	100	68.8	92	1.5	-	-	-	No	H_2 + Air	[104]
Pd:Cu	0.61:0.35	Y_2O_3-Al_2O_3	100	88.8	84.5	10.5	-	-	-	No	H_2 + Air	[104]

The catalyst preparation protocol and the salt used also have a direct effect on the final size and distribution of the metallic particles over the support surface [60,66,91,96,105,106]. The catalytic behaviour in nitrate reduction experiments was affected by metal-metal and metal-support interactions that can be modified by the temperature of both the reduction and calcination steps [49,89,90,93]. In the same way, the surface area of the support for bimetallic catalysts has been known to determine the dispersion of metal particles, which influences the catalytic activity for nitrate reduction. The higher the surface area of the support is, the higher the catalytic activity for nitrate reduction is [62,107]. In this way, alumina, which is a well-known and suitable support that provides high surface area and good stability of metallic particles, has been extensively used in the literature as the catalyst support for nitrate reduction. Table 2 presents a summary of the conversion values available in the literature for the catalytic hydrogenation of nitrates using alumina-based catalysts. Total nitrate removal with nitrogen selectivity of higher than 90% was reached. The best result achieved was 97% of conversion of the initial 200 mg/l nitrate solution to nitrogen gas using a Pd-Cu/Al_2O_3 catalyst [31]. However, with Pd-In/Al_2O_3 or Pd-Sn/Al_2O_3 catalysts, lower selectivity (but still higher than 90%) was observed [33,36,40,93,100]. Marchesini et al. [99] studied the combination of Al_2O_3 and SiO_2 as the support for a Pd-In catalyst. The catalysts that have their Pd active sites on Al_2O_3 show higher activity to reduce nitrates than those that have them on SiO_2, in good agreement with the results reported by Hörold et al. [2-4]. It was observed that the presence of SiO_2 improves the selectivity to gaseous nitrogen. Al_2O_3 has a pI (isoelectric point) of 8 when the reaction medium has a pH of 5. At this pH, Al_2O_3 has a positive superficial charge that will produce a negative counterion layer (i.e., NO_3^-, NO_2^-), phenomenon that could explain the good catalytic activity. As SiO_2 has a pI of 2, it presents a negative superficial charge producing a

positive counterion layer (i.e., H_3O^+, NH_4^+). In equilibrium, the ammonia present in this layer could prevent the production of more ammonia. This excess positive charge leads to the formation of $N_2(g)$ as a final product instead of ammonia [93].

Both the conversion of NO_3^- and the production of NH_4^+ vary significantly with the support chemical composition. For this reason, Pd-Cu supported on various mixed metal oxides (MO_x = CeO_2, SrO, Mn_2O_3, Y_2O_3 and TiO_2) have been investigated by Constantinou et al. [104]. Metal oxides were coated over the external surface of γ-alumina spheres before incipient wetness impregnation of bimetallic solution. CeO_2, MnO_2, and Cr_2O_3 support coatings appear to be the most active for nitrate conversion, whereas high selectivity towards NH_4^+ and low activity for nitrate reduction were produced with SrO and TiO_2 coatings, respectively (Table 2).

Due to the effect of the support on the performance of catalytic nitrate reduction, many publications have explored the use of different supports to improve the results achieved with alumina-based supports. In Table 3, the performance of different supports in the catalytic nitrate reduction reported by different authors is shown. As shown, the silica support is the most selective towards nitrogen, achieving selectivity values of up to 98% when 90% of the initial nitrates are reduced. The main drawback of silica catalysts is that they have a lower nitrate reduction rate than alumina [57,93,100,108]. In contrast, higher ammonium production was achieved when titania was used as the support despite showing better reduction rates of nitrates [49,109]. Compared with metal oxides, carbon-based supports offer a greater versatility because of their unique surface properties that allow easy recovery of precious metals, the ability to achieve high metal loading and dispersion, stability at low pH, and the ability to control the porosity [96]. The use of carbon materials as catalyst supports for nitrate reduction has been mainly

studied in the literature with active carbon (AC) or carbon nanotubes (CNTs) [13,89,90,92,96,110].

Table 3. Summary of the influences of the support on the catalytic reduction of nitrates

Catalyst	wt%	Support	Co (mg/l)	X (%)	S_{N2} (%)	S_{NH4} (%)	pH	Buffer	Reductor	Ref.
Pd:Cu	1:0.5	Al-Pillared Clay	100	36	-	55.3	6f	CO_2	H_2	[56]
Pd:In	5:2.5	Al-Pillared Clay	100	100	-	16.5	6f	CO_2	H_2	[56]
Pd:Sn	5:2.5	Al-Pillared Clay	100	100	-	25	6f	CO_2	H_2	[56]
Pd:Cu	2:1	CNT	100	100	80	20	5.5	CO_2	H_2	[13]
Pt:Cu	1:0.3	CNT	100	99	29	67	5.5	CO_2	H_2	[89]
Pd:Cu	3.9:0.98	Dower 1x4 (IE resin)	100	83	71	26.8	6	HCl	H_2	[101]
Pd:Cu	1.6:1.6	Hematite	30	96.6	69.1	30.9	6	CO_2	H_2	[98]
Pd:Cu	0.5:0.5	Maghemite	132.8	>95	45	50	5.7	-	H_2	[95]
Pd:Cu	5:1.5	Mg/Al hydrotalcite	90	100	92.2	7.78	11.2_f	CO_2	H_2	[103]
Pd:Cu	1:1	MWCNT	100	64	76	23	5.5	CO_2	H_2	[111]
Pd:Cu	1.9:0.6	Nb_2O_5	100	100	89	3.1	5	CO_2	H_2	[63]
Pd:Cu	0.75:0.25	Pumice	100	100	-	1.2	5.5	CO_2	H_2	[39]
Pd:Cu	5:1.5	ZrO_2	100	100	-	27.9	±5	CO_2	H_2	[71]
Pd:Cu	5:1.5	SnO_2	100	100	-	20.7	±5	CO_2	H_2	[71]
Pd:Cu	0.5:1.2	MOR	200	99.9	51.8	17.9	-	CO_2	H_2	[69]
Pd:Cu	0.5:1.2	FER	200	96.2	14.1	4.9	-	CO_2	H_2	[69]
Pd:Cu	0.5:1.2	ZSM-5	200	95.8	8	12.1	-	CO_2	H_2	[69]
Pd:Cu	0.5:1.2	Y	200	97	41.2	34.1	-	CO_2	H_2	[69]
Pd:Cu	3:1	TiO_2	50	100	50.2	47.7	6	MES	H_2	[49]
Pd:Cu	4:1.5	TiO_2	100	99.9	41.6	50.5	5_o-8_f	No	H_2	[109]
Pd:Cu	4:1.5	TiO_2-2%Nb	100	99.9	45.9	50.1	5_o-8_f	No	H_2	[109]
Pd:Cu	4:1.5	TiO_2-7%Mg	100	99.9	45.6	53.8	5_o-8_f	No	H_2	[109]
Pd:In	1:0.25	SiO_2	100	±15	±20	±66.7	5	CO_2	H_2	[57]
Pd:In	1:0.25	SiO_2	100	90.8	98.6	1.4	5	HCl	H_2	[36]
Pd:In	1:0.25	SiO_2	100	±95	±97.9	±2.1	5	HCl	H_2	[57]
Pd:Sn	4.7:1.5	SiO_2	100	75	93.2	-	5	CO_2	H_2	[108]
Pd:Sn	5:1.5	SiO_2	100	100	-	5.3	$5 - 2.7_f$	HCOOH - CO_2	HCOOH	[100]
Pt:In	1:0.25	SiO_2	100	27	89.3	3.7	5	HCl	H_2	[57]
Pd:Cu	5:0.6	AC	200	100	63	-	5.4	CO_2	H_2	[45]
Pd:Cu	2:0.63	AC	200	86.1	2.4	8.4	10.5_f	No	H_2	[112]
Pd:Cu	1:1	AC	100	95	76	21	5.5	CO_2	H_2	[110]
Pd:Cu	2:1	AC	100	100	52	48	5.5	CO_2	H_2	[13]
Pd:Cu	2:1	AC	100	87.8	47.5	52	$4.5_o-5.5_f$	CO_2	H_2	[96]
Pd:Cu	5:0.6	AC	200	83	21	-	5.4_o-10_f	No	H_2	[45]
Pd:In	**1.8:0.18**	**ACF**	**100**	**80**	**84**	**-**	**5**	**HCl**	**H_2**	**[92]**
Pt:Cu	1:0.3	AC	100	64	33	51	5.5	CO_2	H_2	[89]
Rh:Cu	1:1	AC	100	84	22	77	5.5	CO_2	H_2	[110]

In particular, Sakamoto et al. [112] observed that the activity of nitrate reduction using a Pd:Cu catalyst supported on AC was higher than the activities of the same Pd:Cu

catalyst supported on a metal oxide, such as TiO_2, Al_2O_3 or ZrO_2, at the same operating conditions. Despite the low production of NH_4^+, close to 80% of the initial nitrates were converted into non-desirable nitrite due to the inhibition of nitrite reduction by the formed OH^-. As shown in Table 3, other authors improved on those results by using carbon dioxide or hydrochloric acid as buffers to avoid the effect of increasing pH [92,96]. Soares at al. reported 80% selectivity towards nitrogen with total conversion of nitrates [13] with Pd:Cu/CNT catalyst. However, the concentration of ammonium was 5 ppm, still exceeding the limits established by European legislation for ammonium concentration in drinking water. The use of Pd:Cu/Mg/Al hydrotalcite as the catalyst partially solved the problems associated with the diffusion limitations in the catalytic reduction of nitrates. In this case, the reactant ions and reaction products are captured or released by ionic interactions at the hydrotalcite interlayer space. Nitrate and the produced nitrite ions are kept inside the support, avoiding discharge to the aqueous medium. The selectivity towards nitrogen is increased, yielding values higher than 90% because of the higher concentration of nitrogen compounds on the surface of the catalyst [103]. Nb_2O_5 catalyst supports were tested in the reduction of nitrate and compared with alumina. The performance of 2 wt% Pd:0.5 wt% Cu bimetallic catalyst supported on niobia was similar to the same metallic composition supported on alumina in terms of activity and N_2 selectivity [63]. The effect of Fe-containing supports, such as Al-pillared clays, maghemite or haematite, in the hydrogenation of aqueous nitrate by a bimetallic catalyst was also reported [56,95,98]. A large production of undesirable ammonium was observed for these catalysts because of the involvement of the iron in the reaction according to the mechanism described above for the Fe-supported monometallic catalyst.

After examining the results of the use of different catalysts tested for the catalytic reduction of nitrates in slurry reactors, it can be concluded that monometallic catalyst with partially reducible supports such as Pd/SnO2, Pd/CeO2, Pd/TiO$_2$ or Fe-based catalysts, due to their high formation of NH_4^+, are not competitive when compared to bimetallic catalysts. Regarding bimetallic catalysts, although the Pd-Cu pair has been the most studied catalyst due to its good performance, Pd-Sn and Pd-In have shown promising results in the last few years. Specifically, Pd-Sn catalysts have displayed higher activity and selectivity than Pd-Cu. In addition, the importance of the support composition on the final performance of the catalysts in nitrate reduction has also been investigated. Alumina is the most widely used support due to its high activity and selectivity, high specific area and high stability. Although other supports have been studied, only carbon-based supports are competitive against alumina. However, the production of ammonium with all the tested catalysts is still too high, requiring further study to improve on the current results.

The loss of catalyst activity or deactivation is still one of the main drawbacks in the application of catalytic processes entailing many research efforts focused on the responsible phenomena and their control. Factors such as the deposition method, size and distribution of the bimetallic particles on the catalyst surface are responsible of the gradual deactivation and leaching of the metal from the support. [5] Deactivation of the catalyst can also be explained by the non-reversible oxidation of the M–Pd couple. Redox cycles of the Pd and Sn (or Cu) species explain this behaviour, that is, the active sites are re-oxidized and reduced repeatedly; this non-reversible oxidation of some Pd–Sn species has been reported as one reason for the slow deactivation observed for these catalysts after some hours of reaction. [53] Additionally, the competitive adsorption of different species present in water on the active sites [23–25] is another likely cause of

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the catalyst deactivation. The catalyst exposed to organic matter, or high calcium content, will suffer partial deactivation hiding the active metallic sites of the catalyst; high sulfate content in the aqueous solution and the reducing ambient of the reaction are probably responsible for the formation of some sulphur reduced species that slowly deactivate the palladium sites. Thus, sulfide quickly fouled the catalyst resulting in increased NH3 production and ultimately no activity for NO_3^- reduction. Besides, Pd/CeO_2 catalysts can be poisoned by bicarbonates and carbonates. [11]

2.5 Continuous Reactors

The analysis and results of the catalytic activity and selectivity in the reduction of aqueous nitrates previously shown have been obtained with batch or semi-batch reactors. However, further implementation of the process will require the analysis of continuous operation and process scale-up. Fixed bed [9,41,48,57,66] and trickle-bed [55,67] continuous reactors have been successfully tested in catalytic experiments to remove nitrates from water. For instance, the behaviour of Pd-In bimetallic alumina catalyst in a fixed bed reactor to carry out water denitrification was studied by Mendow et al. [57]. Continuous flow experiments were performed in a glass tubular reactor with a 10 mm inner diameter with three grams of catalyst. During the experiment, 200 ml min^{-1} of the initial solution (100 mg/l KNO_3) was continuously fed. Carbon dioxide was compared to hydrochloric acid as the buffer system, and the best conversion and selectivity results, 93% and 78%, respectively, were obtained when the feed solution was acidified with CO_2, which neutralized the OH^- ions, avoiding the generation of a pH gradient inside the reactor, when HCl was used. Moreover, in this reactor, the conversion of nitrates depended on the hydrogen flow rate. This fact is explained by the higher turbulence generated by the higher flow rate, which decreased the mass transfer limitations. However, as may be expected, it was found that the selectivity to N_2

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decreased with increasing hydrogen flow rate. On the other hand, Chaplin et al. [9] developed a packed bed reactor with a Pd-In/γ-Al$_2$O$_3$ catalyst where gases were delivered to the liquid upstream of the reactor using a membrane module gas exchanger (see Figure 5). It was similarly observed that the production of NH$_4^+$ is highly dependent on the inlet solution conditions.
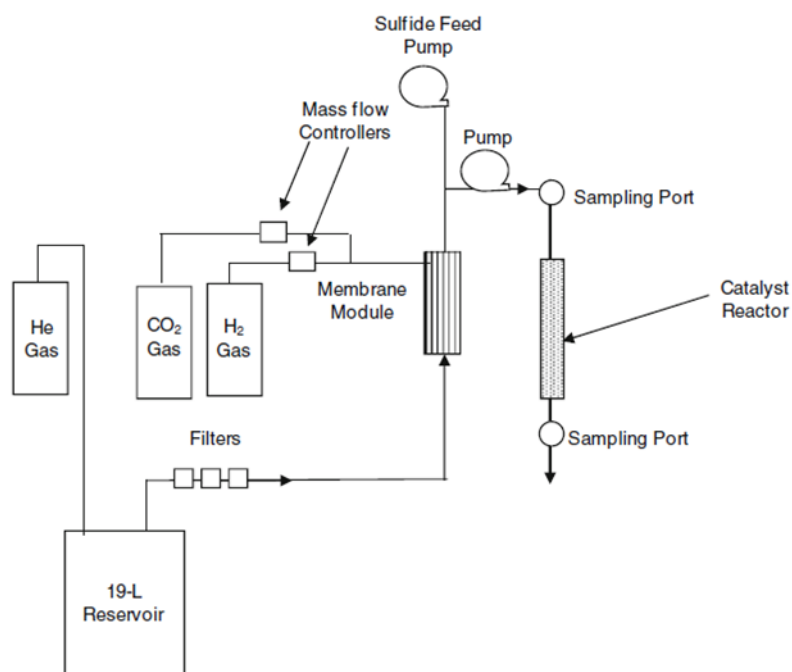

Figure 5. Catalytic reduction of nitrate process using a packed bed reactor [9]

The effect of dissolved oxygen on the catalytic NO$_3^-$ reduction in continuous reactors was investigated for the first time by Constantinou et al. [104]. Dissolved oxygen hinders NH$_4^+$ production, thus changing the ratio of N:H species on the catalyst surface. This fact was later confirmed by Theologides et al. [48,113], who concluded that the production of ammonium could be decreased by up to three times when 20 vol% of air is added to the gas fed to the fixed bed catalytic reactor.

To implement the technology for the treatment of real polluted waters, the influence of natural ions present in groundwater must be considered. The effect of typical groundwater ions was investigated working with a three-phase continuous flow stirred

tank reactor with liquid phase volume of 180 ml, a liquid flow rate of 4 ml/min and an initial nitrate concentration of 75 mg/l [48]. It was concluded that the presence of HCO_3^- and Na^+ ions in the liquid stream can lead to a significant decrease of both the catalyst activity and selectivity, whereas the presence of CO_4^{2-} and PO_4^{3-} does not significantly affect the catalyst behaviour in catalytic water denitrification. In contrast, the presence of Cl^- slightly increases the catalysts activity. These results are not in agreement with other authors who have reported the negative effect of Cl^- ions in the catalytic reduction of nitrates where the reduction was almost completely inhibited [61].

Other interesting work has been reported on the effect of the natural water composition on the catalytic reduction of nitrates in continuous reactors. The results obtained by Pintar et al. [55] show that when drinking water is used instead of synthetic solutions made with distilled water, the nitrate disappearance rate and the reaction selectivity decrease appreciably due to the presence of dissolved ionic species. More recently, it has also been reported that lower selectivity towards nitrogen is always obtained when using natural water than when using distilled water containing nitrates [11,53], while a low concentration of dissolved organic compounds did not exhibit any appreciable influence on the reaction. To the best of our knowledge, the lowest selectivity towards NH_4^+ achieved in catalytic nitrate reduction in continuous reactors using natural water has been 30% with 90% nitrate conversion using Pd-Sn/Al_2O_3 with a total metal loading of 5 wt% and 2.5 wt% for palladium and tin, respectively [32,53].

The use of packed bed or trickle-bed reactors at large scale presents some drawbacks, one of the most important being the loss of catalyst particles due to the sweep effect of the liquid stream. For this reason, Hähnlein et al. proposed the use of a hollow fibre dialyser module for the retention of the small catalyst particles in the intracapillary volume [114]. The schematic of the hollow fibre dialyser, filled with catalytic particles,

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is shown in Figure 6. The nitrate-polluted stream, bubbled with hydrogen, is pumped

through the extracapillary volume of the hollow fibre module. The reaction occurs when

the liquid phase contacts the catalyst located inside the hollow fibre. The catalyst was

completely retained. However, an active layer is considered to reduce the diffusional

limitations in the membrane system. Best results were reported using the 5%Pd-

l.25%Sn/A1203 catalyst, hydrogen as reductant agent and HCO_3^- for buffering effect

that provided 19.3 mg NO_3^-/ (g cat. *h) activity and 88% selectivity to N_2.
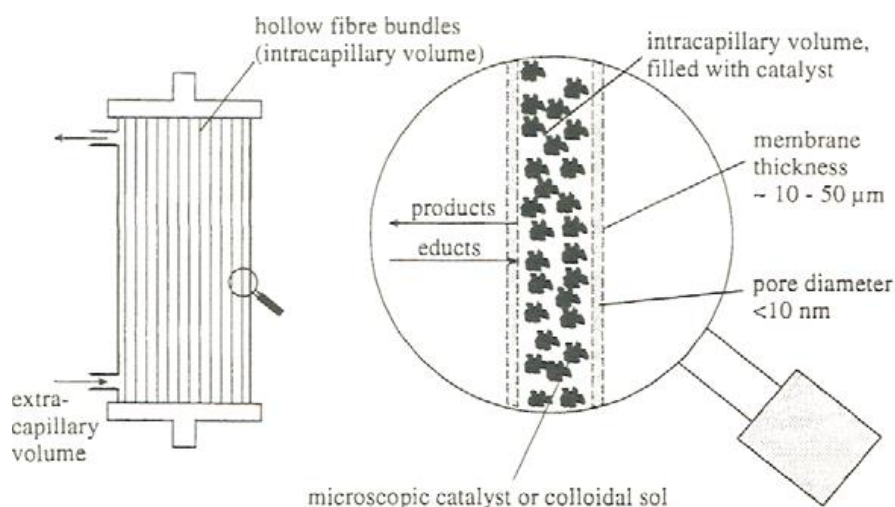
Figure 6. Schematic of a hollow fibre dialyser filled with microscopic catalysts [114].

2.6 Catalytic membrane systems for nitrate reduction

Catalytic membrane reactors, CMRs, which have been developed in the last several

decades, combine reaction and separation in a single step where one (or more) reactant

or product species is removed and separated selectively. CMRs are especially

recommended for industrial processes in which the performance is limited by the

reaction equilibrium. The selective removal of one of the reaction products through the

membrane shifts the chemical equilibrium to product formation and thus increases the

process performance. Therefore, CMRs are intensified reactors that allow for easier

catalyst optimization, smaller reactor sizes and lower energy consumption [115].

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Conventional reactors reviewed in the preceding sections, i.e., slurry or fixed bed reactors that operate in either batch or semi-batch mode, suffer strong diffusional limitations due to the low solubility of hydrogen in water and the limited accessibility of H_2 to the catalyst surface. CMRs have been proposed as an alternative to overcome previous drawbacks and to enhance the performance of the catalytic reduction of nitrates. In this way, the membrane acts as a support for the metal catalyst and as a gas/liquid/solid contactor, promoting the contact between reactants and catalyst. In this sense, two configurations have been reported in the literature: (a) the interfacial configuration, in which the gas/liquid interface is located inside the catalytic zone and (b) the flow-through configuration, in which the gas phase is first dissolved in the liquid phase pumped through the catalytic membrane, as shown in Figure 7.
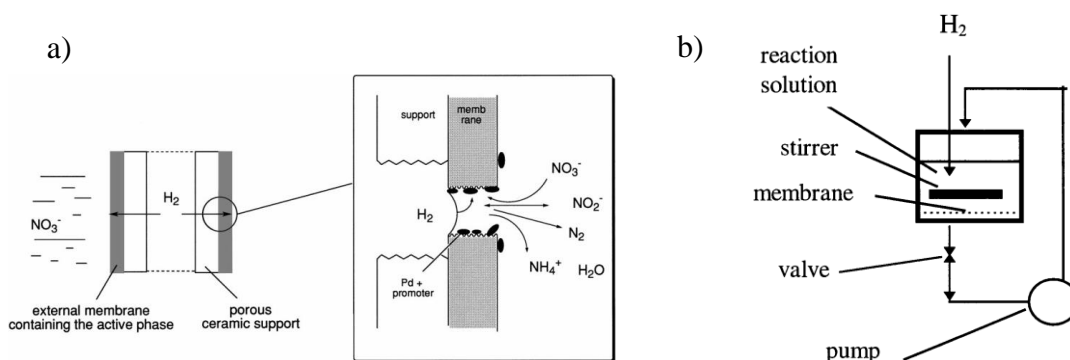
Figure 7. (a) CMR interfacial configuration and (b) CMR flow-through configuration [115]

Nitrate hydrogenation in CMRs has been mainly studied with the catalyst supported on commercial ceramic membranes, typically alpha and gamma alumina tubes with pore sizes between 60 and 400 nm. Ilinitich et al. compared the results obtained in the reduction of nitrates using Pd-Cu deposited on alumina powder and a catalytic membrane made of alumina with a pore size of 1 μm [20]. In this study, pronounced diffusional limitations on alumina powder were observed, with the flow-through

catalytic membrane reactors achieving the best nitrate reduction rate. These results agree with those reported by different authors [16,22].

Strukul et al. [23] reported a lower activity of CMRs based on the addition of Pd-Cu and Pd-Sn catalysts to an alumina support with an external thin layer coating of sol-gel deposited zirconia or titania compared to the activity obtained with powder catalysts. The results were attributed to the lack of control of the pore size of the membranes that showed cracks after being used. Regardless, high nitrate conversions (99%) were achieved when working with a high partial pressure of hydrogen that promoted ammonium formation.

Catalytic reactors with tubular multilayer membranes were investigated by different authors [15-17,25] as hydrogen diffusors with the goal of creating an efficient contact between the different phases (hydrogen, aqueous nitrate solution and catalyst), thus improving the catalytic nitrate reduction. For instance, Daub et al. [17] proposed a catalytic reactor with a tubular membrane with internal and external diameters of 7 and 10 mm, respectively. These membranes were formed by different layers of α-Al$_2$O$_3$ with a graded pore size and an external layer (20 µm) formed by α-Al$_2$O$_3$ (60 -100 nm), ZrO$_2$ (65 nm), TiO$_2$ (5 nm) or γ-Al$_2$O$_3$ (5 nm). The authors analysed the influence of the metal incorporation method and compared the performance of catalytic membranes made with the metal organic chemical vapor deposition (MOCVD) and impregnation methods using palladium and tin as promoter metals. They concluded that this configuration facilitates the change and adjustment of the hydrogen pressure, which influences the activity and selectivity. Therefore, this configuration offers a great potential to adapt the process to the varying needs of an industrial plant with variable water flowrate and nitrate content.

In the studies of water denitrification reported by Chen et al. [15,16], Pd and Cu were deposited using the co-impregnation method on a ceramic membrane made from 95% of α-alumina, with a diameter, thickness and pore size of 10 mm, 1 mm and 2 μm, respectively.
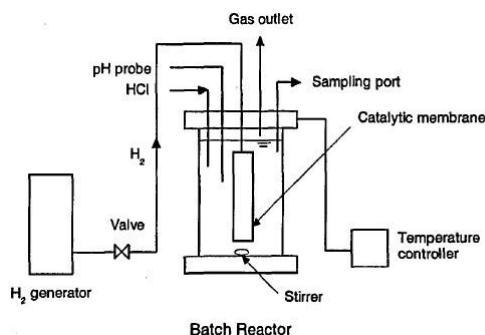

Figure 8. Schematic of the CMR setup used by Chen et al. [16].

The schematic of the experimental system used in this case is shown in Figure 8. Nitrate solution (50 mg/l) is contacted with hydrogen with a partial pressure equal to 0.15 MPa for 2 hours. A nitrate conversion of 70% and a selectivity higher than 90% were reached [15,16]. Similar results were obtained by Whebe et al. [25] more recently using a tubular multilayer membrane of alumina where the influence of the pore size in the outermost external layer was studied. Membranes with a smaller pore size (5 nm) displayed better results than those with higher pore sizes (10 and 25 nm), reaching 92% nitrate conversion and a selectivity towards nitrogen of approximately 80% [25].
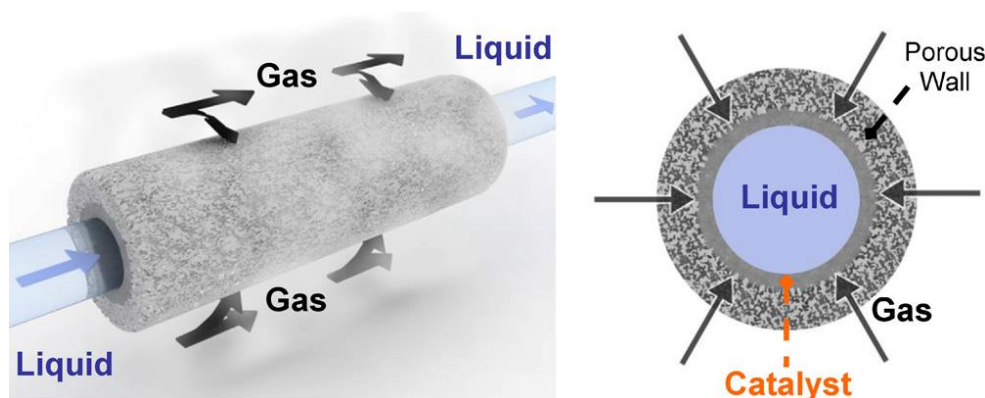
Figure 9. Gas–liquid–solid contact in the porous ceramic reactor [116].

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In the above-described tubular membrane reactors, the active layer was located on the external surface of the membranes. However, the possibility of incorporating this active layer in the lumen side of tubular membranes made of porous alumina has been reported. In this way, direct contact is allowed between the nitrate polluted aqueous streams, fed to the lumen side, and the gaseous phase, fed through the shell side of the reactor, as shown in Figure 9. This configuration attempts to increase the nitrate reduction rate by decreasing the diffusional mass transfer resistance in the aqueous phase. This procedure was used by Aran et al. to carry out nitrite reduction experiments, showing comparable results to those obtained with other tubular membrane reactors in terms of the reduction rate [116,117].

While CMRs for nitrate reduction mostly use ceramic membranes, a few references to polymeric supports have also been reported. Ludkte et al. employed Pd-Cu/Al$_2$O$_3$ catalysts (2.5 µm) supported on a microporous polyetherimide (PEI) membrane [21]. The catalyst powder was dispersed in the precursor solution, which was used to prepare the hollow fibre membranes following the dry-wet spinning technique. Figure 10 shows an SEM photograph of the cross section of these catalytic membranes that contain 27 wt% of catalyst.
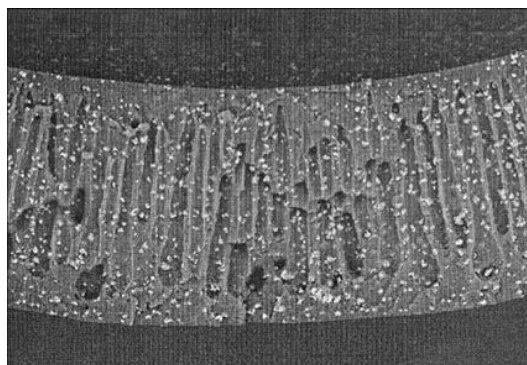
Figure 10. SEM image of the polymeric hollow fibre with 27 wt% of catalyst particles Pd:Cu/Al$_2$O$_3$ [21].

The experiments carried out with this membrane reported a nitrogen selectivity close to 80% with no variation in pH or temperature. In addition, this study showed that

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ammonium production could be minimized by decreasing the contact time of the nitrate solution with the catalytic phase. In addition, this membrane configuration showed good stability of the metallic particles on the membrane, which is one of the most important challenges in polymeric membranes [21].

Table 4. Summary of the results of nitrate catalytic reduction using CMR

Membrane	Pore Size	Catalyst	Method	Feed [NO_3^-]	S_{N2} (%)	X_{NO3-} (%)	Ref.
Sheet α-Al_2O_3	1 μm	Pd:Cu (1:0,8)	Co-impregnation	200 ppm	70.2	95	[18]
Tubular multilayer α-Al_2O_3 + {ZrO_2, TiO_2 or ɣ-Al_2O_3}	0,1 μm	Pd:Sn (1,67:1)	MOCVD	100 ppm	91	50	[17]
Tubular multilayer α-Al_2O_3 {ZrO_2, TiO_2 or ɣ-Al_2O_3}	0,1 μm	Pd:Cu (2,5:1)	Sol-Gel	50 ppm	58	100	[23]
Sheet α-Al_2O_3	1,5-2 μm	Pd:Cu (4:1)	Co-impregnation	100 ppm	91.6	57	[16]
Tubular multilayer 3x α-Al_2O_3 + ɣ-Al_2O_3	5-25 nm	Pd:Cu (2,5:1)	Evaporation - Crystallization	50 ppm	60-70*	92	[25]
Pd/Cu- Al_2O_3 particles in PEI Hollow Fibre		Pd:Cu (4,7:1)	Dry-wet spinning	100 ppm	75-80*		[21]
Sheet - Polyamide	0,4 μm	Pd:Cu (3,67:1)		200 ppm	84*	45-50*	[19]

* Approximate values obtained from graphical results

Ilinich et al. [19] reported the use of mono- and bimetallic catalytic membranes prepared via deposition of Pd and Cu on a flat sheet polyamide microfiltration membrane. These membranes were employed, similar to in the previous cases, to hydrogenate the aqueous solution of nitrates in a flow-through reactor (Figure 7b). It was concluded that the activity of the process is controlled by the mass transfer rate of hydrogen to the liquid phase by diffusion. This conclusion, which is in good agreement with previous studies, shows the importance of improving the contact between the three phases (G/L/S) while at the same time decreasing the mass transfer limitations. Table 4 collects and compares the results obtained with membrane systems in the literature to perform the catalytic reduction of nitrates.

Despite the improved mass transfer rate produced with CMRs, the results achieved with CMRs are comparable with those achieved with the catalyst particles shown in tables 2 and 3. However, the selectivity values of the membrane systems are too low because of the high partial pressures of hydrogen that promote NH_4^+ formation used in the experiments. The challenge in the design and performance of CMRs, as well as in other continuous reactor configurations, is to optimize the operation variables to avoid ammonium formation in a way that a higher selectivity of the process towards nitrogen gas is obtained.

3. ELECTROCATALYTIC REDUCTION

Electrochemical processes offer advantages such as eliminating the requirement for chemicals before and after the treatment, a small area occupied by the plant, not producing sludge and relatively low investment costs [118]. The high-energy efficiency and environmental compatibility of electrochemical processes makes them a promising technology for different applications. Electrodialysis, electrocoagulation and catalytic electroreduction have been considered as possible electrochemical alternatives for aqueous nitrate remediation. Neither electrodialysis nor electrocoagulation are capable of reducing nitrate into harmless N_2; they only separate it from the polluted water, producing highly concentrated nitrate-containing wastewater, which, as consequence, needs additional treatment at an additional cost. Electroreduction of nitrates has been widely investigated as an alternative for the treatment of drinking water and wastewater. Nitrates are mainly converted to nitrogen, nitrite and ammonia in an electrolysis cell.

### 3.1 Mechanism of nitrate electrocatalytic reduction.

The reduction reaction occurs at and is catalysed by the cathodic surface where in addition to N_2, NO_2^-, and NH_4^+, other cathodic products can be involved, such as NO_2,

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NO, N_2O, NH_2OH or NH_2NH_2. While ammonium may constitute the desired final product of the reaction when the nitrate concentration is high, as it may be further recovered and reutilized, the challenge of the electrocatalytic denitrification of groundwater is the same as the catalytic reduction of nitrates, which is to achieve a 100% selectivity towards N_2.

The main cathodic reactions that can occur in the electroreduction of nitrates were reported by Paidar et al. [28]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-, \qquad E^0 = 0.01 \text{ V} \qquad (29)$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow 1/2N_2^- + 6OH^-, \qquad E^0 = 0.26 \text{ V} \qquad (30)$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-, \qquad E^0 = -0.12 \text{ V} \qquad (31)$$

$$NO_2^- + 2H_2O + 3e^- \rightarrow 1/2N_2^- + 4OH^-, \qquad E^0 = 0.406 \text{ V} \qquad (32)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^-, \qquad E^0 = -0.165 \text{ V} \qquad (33)$$

$$NO_2^- + 4H_2O + 4e^- \rightarrow NH_2OH + 5OH^-, \qquad E^0 = -0.45 \text{ V} \qquad (34)$$
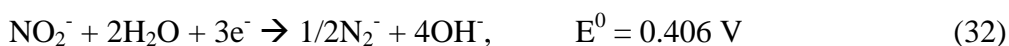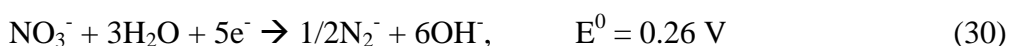
Hydrogen evolution is the main side reaction at the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (35)$$
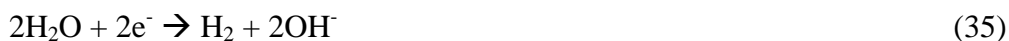
The desired cathodic process is the reduction of nitrate to nitrogen by reaction (30), but the reaction mechanism in the electroreduction of nitrates principally depends on the cathode material, the applied cathodic potential, the cell configuration, the pH of the aqueous solution and the presence of other anions.

The main anodic reaction, when no other ions are present, is oxygen evolution:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (36)$$

If chloride ions, which are common in wastewater or drinking water, are present in the aqueous solution of nitrates, hypochlorite ions can be formed due to the anodic oxidation of Cl^- by reactions (37-39) [119]. Hypochlorite ions are responsible for two anodic reactions that influence the process in different ways. First, ammonium ions

produced at the cathode because of the nitrate reduction are oxidized and transformed to nitrogen gas by reaction (40) [119,120], improving the selectivity towards nitrogen. On the other hand, nitrite ions are oxidized back to nitrate by reaction (41), decreasing the efficiency of the process.

$2Cl^- \rightarrow Cl_2 + 2e^-$ (37)

$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$ (38)

$HClO \rightarrow OCl^- + H^+$ (39)

$2NH_3 + 2OCl^- \rightarrow N_2 + 2HCl + 2H_2O + 2e^-$ (40)

$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^-$ (41)
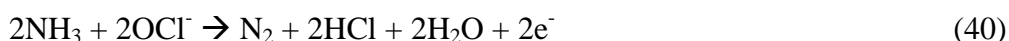
The influence of chloride ions on the electroreduction of nitrates using different cathodic materials has been reported [121-125]., Li et al. [122] studied the influence of Cl^- in the overall performance of the process using Fe, Cu and Ti cathodes. In all cases, increasing the chloride concentration decreased the nitrate reduction rate. Szpyrkowicz et al. reported no improvement with chloride ions when Pd-Cu, Pd-Co or Pd-Cu-Co sprayed on stainless steel (SS) or titania were used as cathodic materials [120]. Nevertheless, a positive effect of the chloride concentration on nitrate electroreduction was reported with tin [126], boron doped diamond (BDD) [119] and graphite (GF) electrodes [124]. It can be concluded that depending on the electrode materials, the presence of chloride ions can lead to different phenomena that influence the electrochemical nitrate reduction rate [122,123,127-129].

3.2 Configurations of electrocatalytic reduction cells

The single chamber cell (SCC) and dual-chamber cell (DCC) have been the most used electrocatalytic cell configurations for the electroreduction of aqueous nitrates. The SCC reactor has a unique compartment in which both electrodes are in contact with the

electrolyte; in the DCC reactor, the cathodic chamber is separated from the anodic one by a cation exchange membrane (CEM), as depicted in Figure 11.
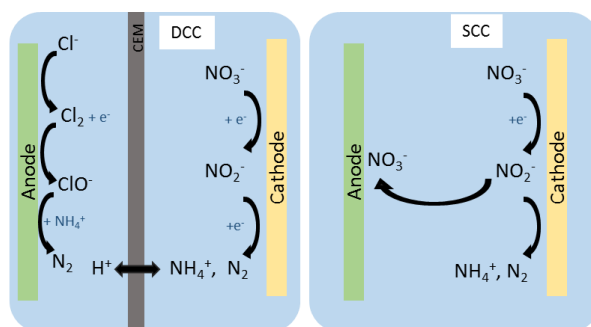

Figure 11. Mechanism of SCC and DCC in the presence of chloride ions. Adapted from [124]

Ammonium ions, which are present in the cathodic chamber in equilibrium with free ammonia, are transported through the CEM into the anodic compartment due to the concentration gradient. Here, ammonium ions can be converted to nitrogen gas by reaction (40), that is, by reacting with hypochlorite ions that were formed from chloride oxidation, as indicated by reactions (37-39) [120]. However, nitrite ions cannot reach the anodic chamber because of the CEM, avoiding the oxidation of nitrite to nitrate. Thus, the anodic compartment works as a "sink" for NH_4^+ ions [120]. The reaction mechanisms in both single chamber and dual chamber cells are depicted in Figure 11. The improvement of the electroreduction performance using DCC compared to SCC has been demonstrated by Ding et al. [124] with different cathodic materials (GF, $Cu_{90}Ni_{10}$, and Ti); graphite achieved the best nitrate removal performance (70%). These results are consistent with the observations published by Szpyrkowicz et al. [120] with the sprayed Pd-Cu/SS, Pd-Co/Ti and Pd-Co-Cu/Ti cathodes.

The electrochemical nitrate reduction using conventional electrochemical cells needs a high conductivity medium that adds to the difficulty of separating the supporting electrolyte from the treated water. In this context, a new reactor configuration with no supporting electrolyte was presented by Hasnat et al. [130]. In this reactor, H_2O molecules are split into O_2 and H^+ on the anode surface. The protons migrate through

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the H^+-conducting Nafion membrane to the cathode surface to be converted into atomic hydrogen under the applied potential. The produced hydrogen is responsible for the chemical reduction of nitrates and nitrites at the cathode surface. The anode and cathode are supported over the external surfaces of the Nafion-117 film. The electrodes are prepared via the deposition of Pt on the both sides of the membrane. Cu is also deposited on the cathode to fabricate an asymmetric reactor (Pt|Nafion|Pt-Cu, Figure 12). The distance between the electrodes corresponds to the membrane thickness, which is 180 μm. The main drawback of this configuration is that ammonia was produced on the Cu surface [130]; when other cathodic materials (Pd, Pt-Pd, Pd-Cu, Pd-Ag) were tested [131], even higher ammonia production was achieved. To increase the selectivity to inert N_2, new reaction conditions and cathodic materials must be explored.
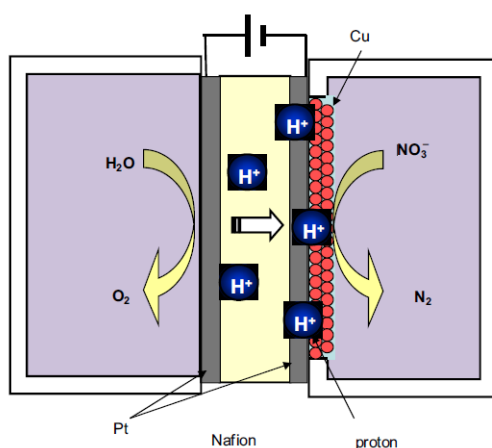
Figure 12. Schematic of the electrochemical reactor with Nafion-117 membrane as electrolyte [130].

A novel reactor configuration in which catalyst particles are introduced into the cathodic chamber of a dual compartment cell was recently proposed to combine the advantages of catalytic and electrocatalytic reduction of nitrate [132,133]. As shown in Figure 13, the protons generated in the anode migrate to the cathodic chamber through the proton exchange membrane that acts as a reducing agent. The beneficial effects of introducing Pd-Cu/Al_2O_3 catalysts in the cathodic compartment of an SCC with graphite electrodes were reported by Zhang et al. Both the nitrate reduction rate and the selectivity of the

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process towards nitrogen were increased, reaching 80% N_2 selectivity when nitrates were completely removed. The enhancement in the performance of the process is due to the presence of the coupled catalytic reduction of nitrate with the appropriate amount of *in situ* generated hydrogen by electrolysis as a reducing agent. In the study reported by Lan et al. [133], in which Pd-Sn/AC particles were introduced in a DCC with DSA electrodes, 90% of the nitrates were converted to nitrogen gas when the initial concentration was 24.6 mg NO_3^-/l.
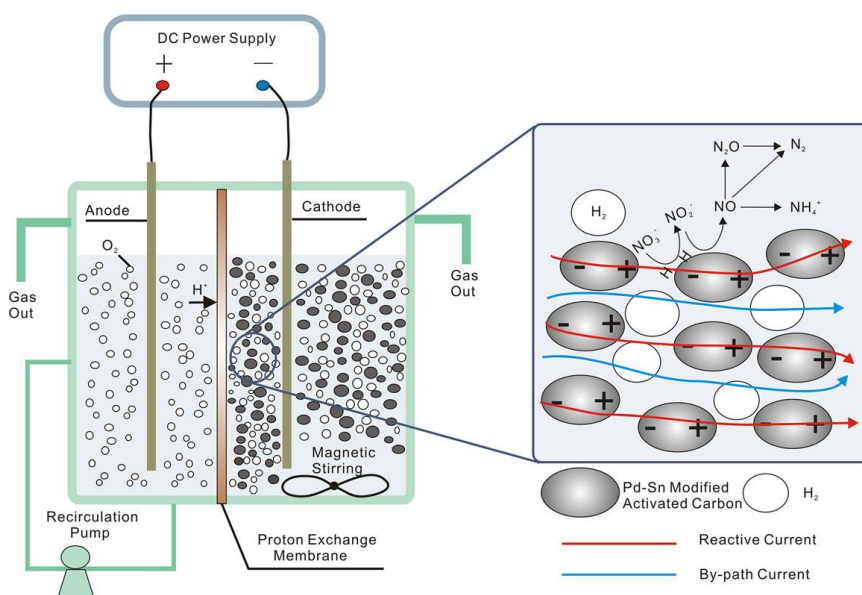
Figure 13. Schematic diagram of an electrocatalytic reactor based on Pd–Sn/AC particles [133].

3.3 Electrode materials

The performance of the electrocatalytic reduction of nitrates in terms of selectivity towards nitrogen and nitrate reduction rate is strongly dependent on the electrode materials, supporting electrolyte, applied potential and pH of the medium. The challenge remains to find suitable operating conditions and electrode materials to reduce nitrate and simultaneously oxidize the unfavourable ammonia formed during the

process, obtaining inert nitrogen as the main product. The reaction pathway in the catalytic electroreduction has been investigated for many electrode materials.

For instance, both the reaction pathways and the nitrate electroreduction performance using a Sn cathode in a dual chamber cell have been reported by Katsounaros et al. [126,134-136]. The ammonium production path, in which hydroxylamine appears as intermediate, was clarified, and the main reaction that leads to N_2 was discussed in terms of two possible reduction routes from NO. In the first route, the identification of the reaction intermediates was not possible; in the second route, N_2O appears as the main intermediate [136]. Therefore, it has been proved that reduction on Sn is more efficient at very negative potentials because both the reduction rate and the selectivity towards nitrogen are higher at that condition. Nitrogen selectivity of 70% was achieved with a Sn cathode in DCC when 95% of the nitrates were reduced from an initial concentration of 100 mg/l. The corrosion of tin appears as the most serious drawback of these electrodes since the presence of tin in the bulk water is non-acceptable [134]. Bismuth cathodes for the electrochemical reduction of nitrates were also studied by the same research group [137-139]. In this case, the rate of cathodic corrosion of Bi was significantly lower than the tin corrosion rate, and its presence in the final solution was not a problem. In addition, the electrocatalytic activity of Bi had the best performance when compared with other metals such as Sn, Al, In or Pb [138]. This is due to the electrochemical reduction of nitrate on bismuth proceeding through an autocatalytic reaction, the rate of which is significantly higher than that of the electrochemical reaction. Moreover, the main products were nitrogen gas and nitrous oxide with selectivities of 65% and 22%, respectively, working with 0.4 M $NaHCO_3$/0.4 M Na_2CO_3 as the electrolyte, an initial nitrate concentration of 0.05 M $NaNO_3$ and very negative potentials (-2.6 V).

Different electrode materials, such as graphite (GF) [124,140,141], SiC [140], SS [140,142], Ni [141], Cu [141,143-146], Pt [141,147,148], Pd [149], Pb [139,140], Ti [122,129], Rh [149] conductive diamond electrode (CDE) and boron-doped diamond (BDD) [119], have been studied in the literature to improve the performance of the electroreduction of nitrates. Graphite and copper showed the highest catalytic activity compared with the other materials [124,129,140,141]. Nevertheless, when Cu or GF electrodes were used, harmful ammonium and nitrite appear as the main products of the process in alkaline media [124] as well as in acidic media [141]. Furthermore, several studies have investigated the nitrate electroreduction on different bimetallic, ternary metallic or alloy electrodes to improve the activity and the gaseous nitrogen selectivity due to the likely synergic effect between the different materials. For instance, significant improvement in the nitrate electroreduction was obtained with Cu-Ni [150-153], Cu-Sn [144], Cu-Rh [152,154], Cu-Zn [123,143,155] Cu-Pd [156-159], and Sn-Pd [160-163] cathodes, all of which have improved corrosion resistance and stability relative to monometallic Cu or Sn electrodes. In the case of the Cu-Zn cathode, ammonia was found as the main product by Mattarozzi et al. [155]. This agrees with the results reported by Macova et al. [143]. Even though Cu-Ni cathodes with high copper content showed high selectivity to ammonium and lower activity than Cu-Rh cathodes, Cu-Ni alloy is considered a promising and suitable cathode due to its good stability under most conditions [152]. On the other hand, although Pd cathodes have displayed practically no activity in nitrate electroreduction [159,160], they might enhance the electrocatalytic activity of Cu or Sn cathodes. In the case of Pd-Cu electrodes, the role of Cu is to promote the reduction of NO_3^- to NO_2^-, and the role of Pd is to reduce nitrite to N_2 with high selectivity [156]. The use of higher amounts of Pd in the electrode composition has been shown to be beneficial towards N_2 selectivity. A maximum N_2 selectivity of 70%

has been reported using Pd-Cu modified graphite cathodes (95 at% Pd, 5 at% Cu) in an alkaline medium with 1 M NaOH as the electrolyte. When neutral pH was used, nitrite and ammonia production was higher [158]. Reyter et al. reported that the higher the Pd at% in the electrode is, the higher the nitrogen selectivity is, and the lower the overall reduction activity is [159]. Similar results were reported by Anastasopoulos et al. with nitrate electroreduction activity as high as 84% using Cu [157]. The role of Pd on the electroreduction of nitrates with tin-modified Pd electrodes was found to be similar to the explanation presented above for Pd-Cu electrodes. N_2O was formed as the main product in the reduction of nitrate ions with 84% selectivity (92% of nitrates reduced) when the reduction proceeded in an electrolysis cell with 0.1 M $HClO_4$ as the electrolyte and Sn-Pd on Au electrodes. In addition, hydroxylamine was formed as the main non-volatile product, whereas low amounts of ammonia were found (<2%) [161,162]. More recently, a similar product distribution was found with Pd-Sn film electrodes by Birdja et al. [160].

Acceptable values of nitrogen selectivity during nitrate electroreduction are very difficult to achieve. The selective anodic oxidation of ammonia, as explained above in reactions (39-43), has appeared as a promising approach in combination with the electrocatalytic reduction of nitrates. If suitable electrode materials and operation conditions are chosen, the oxidation of NH_4^+ (and NO_2^- if no CEM is included in the electrolysis cell) can occur in a selective way towards nitrogen gas. In this way, it has been reported that ammonia oxidation into nitrogen can be enhanced by using BDD or Ti/PtOx-IrO$_2$ anodes in a single compartment cell (Table 5), increasing the nitrate electroreduction rate and the selectivity towards gaseous nitrogen [151,164].

Table 5. Overview of the results published in the literature for the electrocatalytic denitrification with selective ammonium oxidation towards nitrogen. Adapted from [163]

Anode	Cathode	Electrolyte	Cell	pH	Performance	Ref.
Ti/IrO2-Pt	Fe	100 mg/L $NaNO_3$, 0.5 g/L Na_2SO_4, different amounts of NaCl	Undivided	3 < pH < 11 Uncontrolled	X_{NO_3-} = 80%, NH_3 and NO_2- below detection limit	[166]
IrO_2-Ta_2O_5, CDE	SS	21 mM $NaNO_3$, 0.02 M Na_2SO_4	Undivided	pH = 2 Uncontrolled	X_{NO_3-} = 90%. NO_2-, NH_3 by products formed	[167]
Ti/IrO_2-Pt	Fe, Cu, Ti	100 mg/L $NaNO_3$, 0.5 g/L Na_2SO_4, different amounts of NaCl	Undivided	Uncontrolled	Without NaCl: Fe (X_{NO_3-} = 93%) With 0.5 g/L NaCl:(X_{NO_3-} = 93% and S_{N2}=100%)	[122]
Ti/IrO_2-TiO_2-RuO_2	Cu/Zn	60 mg/L $NaNO_3$, 0.5 g/L NaCl	Undivided	pH = 7.8 PBS buffer	X_{NO_3-} = 94.41%, suppression of NH_3 (0.5 g/L NaCl added)	[168]
BDD, DSA	SS	1.76 mM NaNO3, different amounts of NaCl	Undivided	pH controlled	X_{NO_3-} = 100%, NH_3, NO_2^- and ClO_3^- by products formed	[142]
Ti/IrO2-Pt	Cu/Zn	100 mg/L $NaNO_3$, 0.5 g/L Na_2SO_4, different amounts of NaCl	Undivided	Uncontrolled	X_{NO_3-} = 90%. With 0.5 g/L NaCl, Neither NO_2-, NH_3 were detected	[128]
Ti/IrO2		0.1 M $NaNO_3$, 0.5 M NaCl and 0.01 M NaOH	Undivided	pH = 12	X_{NO_3-} < 50% ; S_{N2} = 100%	[146]

High pH and the presence of chloride permit the production of hypochlorite, enhancing the oxidation of ammonia to nitrogen and the production of ammonium in the cathode as a nitrate reduction product. Thus, selectivity of 100% to N_2 was also reached by oxidizing all the ammonia produced with a Ti/IrO_2 anode in an undivided cell with alkaline conditions (pH = 12) and an energy consumption of 14.7 kWh kg^{-1} by Reyter et al. [151]. In the research carried out by Li et al., the selectivity of the process towards nitrogen increased to 100% (87% of nitrate conversion) by using a Ti/IrO_2-Pt anode with a high oxidation rate of ammonium to N_2 [122]. In a similar study carried out by the same author [128], almost complete nitrate conversion to nitrogen gas was reached using a Cu-Zn cathode and a Ti/IrO_2-Pt anode in the presence of sodium chloride as the supporting electrolyte with no pH control. The discovery of the conditions that are

needed to achieve high nitrate removal and high nitrogen selectivity (a basic pH, the addition of electrolyte or the use of chloride ions to oxidize ammonium to nitrogen in the anode) makes electrocatalytic reduction a real alternative for wastewater treatment. However, in the case of drinking water treatment, the use of high pH or chemicals is not a valid option because of the additional treatment needed to adjust the pH or to reduce the concentration of the different species used in the electrolysis, electrolyte or the chloride ions down to acceptable limits.

4. CONCLUSIONS

A comprehensive review of the current state-of-the-art of both catalytic and electrocatalytic reduction of nitrates is presented. These emerging and promising technologies for nitrate removal from groundwater and wastewater have been extensively studied because of their capacity to convert nitrates to nitrogen in a selective way. However, co-production of ammonium is still the main drawback of these processes despite the nitrogen selectivity reaching greater than 90%.

Monometallic catalysts prepared by using partially reducible supports have shown lower performance in terms of activity and N_2 selectivity than bimetallic catalysts. Although the Pd-Cu catalyst was the most active and selective when synthetic water was used, it was more strongly affected by the ions present in natural waters than other bimetallic catalysts, such as Pd-Sn or Pd-In. Although Pd-In catalyst was the most active, Pd-Sn showed a similar reduction rate of nitrates but lower ammonium production. Despite the good results achieved with batch reactors in laboratory conditions, when more realistic continuous reactor and natural water conditions were tested, the performance of the catalytic nitrate reduction showed an ammonium

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selectivity of 30% in the best reported case. The main disadvantages of packed bed or trickle-bed reactors, which are the most commonly used configurations to carry out catalytic reduction are the loss of catalyst particles and the diffusional limitations. Therefore, catalytic membrane reactors have been identified as a sound alternative to perform this process. Nevertheless, more research is required to propose a competitive reactor configuration that improves the performance of the continuous reactors reported so far.

In the electrocatalytic reduction processes, total selectivity towards inert nitrogen gas and high nitrate reduction were achieved when Ti/IrO_2 anodes were used in a single chamber cell in which ammonium was homogeneously oxidized due to the presence of chloride ions. However, high pH values and the addition of electrolyte and chloride ions are required to achieve high efficacy in the process. These needs imply additional steps to neutralize the pH and to reduce the concentrations of the ionic species to the levels allowed for drinking water, making the process less competitive for drinking water production. For this reason, the electroreduction of nitrates in water seems to be a more realistic alternative for the treatment of wastewater.

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List of figure captions

Figure 22. Schematic of the electrochemical reactor with Nafion-117 membrane as electrolyte [130]

Figure 13. Schematic diagram of an electrocatalytic reactor based on Pd–Sn/AC particles [133]