

Powering denitrification: the perspectives of electrocatalytic nitrate reduction

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Received 3rd August 2012, Accepted 24th September 2012

DOI: 10.1039/c2ee23062c

Imbalances in the nitrogen cycle caused by human activities (combustion, fertiliser-intensive agriculture) have resulted in alarmingly increased levels of nitrate in groundwater and other water bodies, with potentially health-threatening consequences. The electrocatalytic removal of nitrate from polluted water is a promising alternative to bacterial denitrification, provided that full selectivity to harmless N₂, which can be returned to the atmosphere, is achieved. This perspective article discusses the state-of-the-art of research on electrocatalytic denitrification, critically evaluating the obstacles still hampering large-scale application of this technique. The milestones of fundamental research focussing on the cathode reaction will first be dealt with, followed by their translation into electrochemical reactors of practical interest. Finally, a short foray into the novel field of bioelectrochemical reactors will close the article. Challenges and opportunities pertaining to these three topics will be analysed.

Introduction

Among the various environmental issues that affect the Earth, the anthropogenic perturbation of the nitrogen cycle poses the most impending threat on the short timescale, both for human health and the biosphere.^{1–3} The very etymology of the name *nitrogen* (“generating nitre”, *i.e.* KNO₃) bears witness to one of the most worrisome consequences of human-driven imbalances in the nitrogen cycle: an increased runoff of nitrate to groundwater, rivers and coastal water.

There is a growing consensus in the scientific community that the nitrogen cycle has suffered the most extensive human “footprint” since the beginning of the Anthropocene,⁴ which has caused this cycle to exceed the safety threshold for a sustainable future (the so-called “tipping point”).^{5,6} The influence of human activities is often quantified in terms of “reactive nitrogen” (Nr) produced within a biogeochemical system over a certain timespan. Nr, defined as “the biologically active, photochemically reactive and radiatively active nitrogen compounds in the atmosphere and the biosphere of the Earth”,² represents an accurate indicator of the human footprint because natural Nr formation has been sluggish and rate-limiting throughout the geologic eras.⁷

The start of the anthropic nitrogen cycle was the discovery and subsequent large-scale implementation of the Haber-Bosch process⁸ (which is now the main contributor to Nr (ref. 3)), on which relies our ability to produce fertilisers and, in turn, to

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Broader context

The Haber-Bosch process represents a milestone in the history of chemistry, providing mankind with a plentiful and inexpensive supply of fertilisers. Yet, growing evidence from environmental science research indicates that the excessive use of fertilisers, along with fossil-fuel combustion, has caused alarming imbalances in the nitrogen cycle, leading to nitrate accumulation in groundwater and coastal areas. This environmental issue calls for efficient denitrification strategies ancillary to the widespread biological denitrification. Electrocatalytic denitrification is a very promising alternative, since it could be fed with “green” electricity from renewable sources and it can target nitrate-laden liquid industrial wastes unsuitable for biological treatment or water for human consumption. However, daunting problems are to be solved for electrocatalytic denitrification to become a large-scale technology, the achievement of 100% selectivity to harmless N₂ being the foremost challenge. Fundamental research has shed light on the elementary underpinnings of N₂ formation, suggesting a few strategies to steer selectivity; some of them, such as bimetallic catalysts combining a “promoter” and a “selector”, have been implemented in electrochemical reactors. The progress of electrocatalytic denitrification will increasingly rely on this relay between fundamental and applied research, along with the alliance of spectroscopy, computation and experimental electrochemistry to unravel reaction mechanisms.

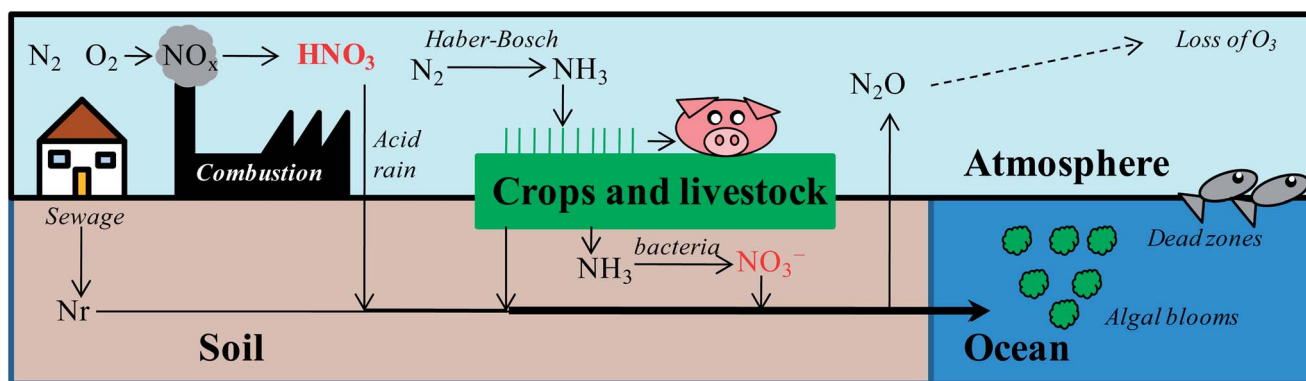


Fig. 1 A schematic view of the contribution to Nr originating from human activities, and ensuing environmental consequences.

ensure food supply for a growing population. However, the inefficient use of fertilisers, along with NO_x formation during combustion,¹ has resulted in a steadily growing runoff of Nr into the environment, not only causing the well-known “acid rain” but also more insidious consequences, such as the development of algal blooms, which transforms coastal and humid areas in “dead-zones”,⁹ creating a breeding ground for disease-carrying insects and parasites, too¹⁰ (Fig. 1).

Nitrate is the most oxidized form of nitrogen and the main nitrogen-containing pollutant of groundwater, rivers and lakes.¹¹ Three sources contribute to the accumulation of nitrate: the above-mentioned acid deposition of airborne NO_x , the oxidation of ammonia (from overfertilisation) by terrestrial communities of

nitrifying microorganisms and, finally, the improper disposal of nitrate-laden domestic sewage, agricultural or industrial wastewater. The accumulation of nitrate has raised widespread concern for the toxicity of nitrite,^{12–14} resulting from *in vivo* reduction of nitrate. Nitrite is an established cause of methaemoglobinemia and a suspected carcinogen. Therefore, strict regulations have been issued, defining a maximum allowed concentration for nitrate and nitrite in drinking water (respectively equal to 50 and 0.5 mg l^{-1} , equivalent to 0.8 mM and 11 μM (ref. 15)). As a result, several analytical techniques have been developed for the accurate determination of nitrite and nitrate in aqueous solutions.¹⁶ In the absence of anthropogenic pollution, nitrate background levels of nitrate concentration are



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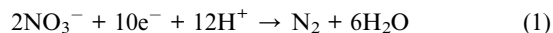


Marc T.M. Koper

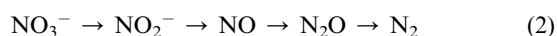
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usually much lower (typically below 10 mg l^{-1} , equivalent to 0.16 mM (ref. 11)), since natural denitrification is performed by waterborne microbial communities according to the overall reaction,



producing harmless N_2 (which is thus released and restored to the atmosphere) but the rate of this reaction is sluggish. Moreover, it is perturbed by the inflow of nitrate from human activities, leading to a harmful nitrate accumulation and persistent imbalances in the nitrogen cycle. The need to remove excess nitrate efficiently has led to the development of artificial denitrification methods. The study of bacterial denitrification allows us to draw some useful lessons: reaction (1) being a multi-electron transfer reaction, nature achieves the selective formation of N_2 by means of a pool of enzymes (or a cooperation of different microbial species dwelling together) performing the stepwise reaction:



Note that most steps in reaction (2) are two-electron transfer steps, which are generally much easier to catalyze than steps involving more than two electrons.¹⁷ It should also be noted that in the ideal case, no intermediate metabolite is lost to the environment. However, certain soil bacteria do release N_2O which is a known contributor to the greenhouse effect and to ozone disruption.¹⁸ Besides this mechanistic complexity, highly varied conditions typical of each ecological niche favour different bacterial communities, exploiting a large variety of metabolic anaerobic pathways (primarily heterotrophic, but also autotrophic). Therefore, it is to be expected that selective formation of N_2 will require functionally complex strategies with little or no space for a *one-size-fits-all* approach applicable to all types of waste- and groundwater.

Three main approaches have emerged in the field of denitrification for wastewater remediation:

- **Biological denitrification:**^{19–24} this is the most widespread and technologically mature approach, in which a bacterial community is used to perform denitrification. A broad variety of reactor designs and process conditions have been implemented, and the interested reader should refer to the cited reviews. This technique is applicable to all water effluents as long as bacterial growth is not impaired. Another drawback is the possible development of pathogenic bacteria, which is a serious issue if water is to be purified for human consumption.

- **Physical removal of nitrate:** reverse osmosis,^{21,25} electro dialysis,²⁶ electrocoagulation^{27,28} and ion exchange²⁹ are typically used for the treatment of drinking water. These methods are all based on the displacement of nitrate from the polluted solution, and not on the destruction of this ion. Therefore, the main drawback is the creation of secondary nitrate-containing wastewater which in turn needs to be treated and disposed of.

- **(Electro)catalytic denitrification:**^{30–32} a reducing agent (either a chemical or electrons) is used in combination with a catalyst which should promote reaction (1) selectively. The energy required for driving NO_3^- reduction³² can be supplied in the form of heat, light (*photocatalysis*) or electrical energy (*electrocatalysis*). Electrocatalytic nitrate reduction is fundamentally

akin to biological denitrification in the sense that enzymes are *redox catalysts*.^{33,34}

Ideally, (electro)catalytic denitrification can sidestep the limitations of the other two alternatives, provided that an efficient and selective conversion of NO_3^- to N_2 is achieved. Low-temperature catalytic denitrification driven by electrical energy is particularly interesting considering that the driving force can in principle be obtained from renewable sources, thus creating a veritable “green” approach to denitrification. Therefore, at this stage it is of paramount interest to understand what still prevents electrocatalytic denitrification from achieving large-scale implementation, evidencing, in particular, the bottlenecks identified by fundamental research. This perspective article will deal with this issue by discussing recent developments in electrocatalytic denitrification, pointing out challenges and perspectives along a range of research topics including fundamental studies focussed on the reduction of half-cells (the cathode), denitrification in practical conditions (electrochemical reactors) and also the more recent bioelectrochemical reactors.^{19,24,35–37}

Fundamental studies of cathode materials and reaction mechanisms

This section will discuss research on nitrate reduction aimed at achieving fundamental insight at a mechanistic level. Whenever possible, we will compare and contrast electrocatalysis with the non-electrochemical catalytic nitrate reduction, covered in two other reviews.^{31,32} Fundamental studies typically involve electrolytes of simple composition (*not* mimicking actual wastewater), stable, controlled conditions (pH, nitrate concentration below 0.1 M , temperature) and relatively short timescales.

State of the art and challenges

Thermodynamically speaking, N_2 should be the most stable product of NO_3^- reduction: under standard conditions, the equilibrium potential of this couple is the highest among all possible couples featuring nitrate and a product of nitrate reduction: $E^0 = 1.246 \text{ V vs. NHE}$. However, kinetic and mechanistic factors come heavily into play when NO_3^- is reduced electrochemically,³⁰ giving rise to three recurrent fundamental issues.

- High overpotential related to sluggish reaction kinetics.
- Preferential formation of NH_3 and N_2O as reaction products.
- Significant influence of the electrolyte composition and pH on the catalytic activity/selectivity.

Detailed mechanistic studies of nitrate reduction on platinum

Pure transition metals have been extensively investigated as electrocatalysts for nitrate reduction in acidic media, and much of our understanding of the mechanism of electrochemical nitrate reduction has been obtained with platinum as a catalyst. As suggested by reaction (2), a stepwise mechanism is operative.

Fig. 2 shows all possible steps and emphasizes two determining steps: the formation of nitrite is the *rate-determining step* for most metal systems:



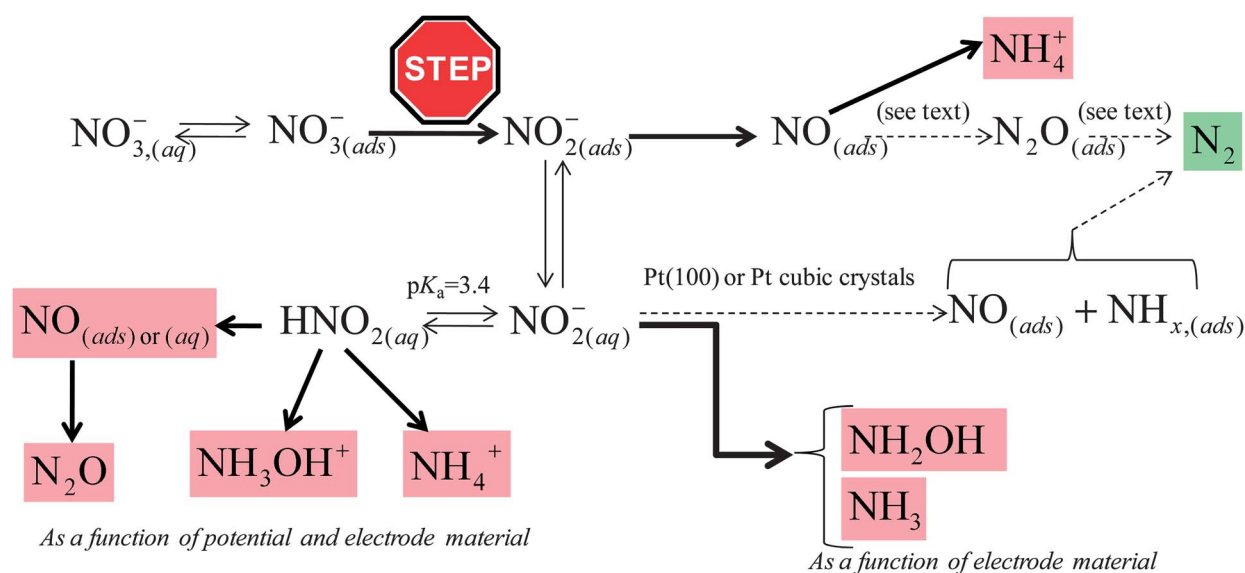
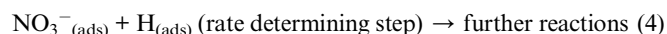


Fig. 2 The major reaction pathways for nitrate and nitrite reduction on noble-metal electrodes. The ideal product, N_2 , is highlighted in green, other products in red. The cartoon of the “STEP” sign highlights the rate-determining step. Thick lines emphasise those pathways that occur most often, while broken lines indicate reactions taking place under more specific conditions.

while the ensuing reduction of intermediate NO_2^- is the *selectivity-determining step*. Fig. 2 shows the general case: NO_2^- is quickly converted to NO ; then, two major pathways can be followed, leading to the two main reaction products, *i.e.* ammonia and nitrous oxide. It should be noted that non-electrochemical catalytic denitrification follows, by and large, an identical pathway.³¹ This mechanistic scheme highlights the most important concepts concerning the electrocatalytic nitrate reduction, and it also shows one of the possible reaction pathways leading to the desired final product (N_2): through the conversion of N_2O . This *stepwise* formation of N_2 is challenging because, as we will see, very few catalysts are able to perform the reduction of N_2O before this intermediate desorbs from the surface and is lost to the electrolyte as a product.

Let us rewind to the beginning: it is assumed that NO_3^- must adsorb at a metal electrode from an aqueous solution of varying composition and pH for NO_3^- reduction to occur. The reaction mechanism sketched above is common to all noble metals, although the catalytic activity is variable, following the order $Rh > Ru > Ir > Pd \approx Pt$.³⁸ A reaction order lower than 1 is commonly observed for nitrate reduction at Pt – and other noble metals – in acidic media, which indicates that adsorption precedes the rate-determining step. Pt is characterised by a relatively weak NO_3^- adsorption, which makes this metal particularly sensitive to the interference of more strongly adsorbed species, such as H_{ads} and anions. Numerous studies in the two acidic electrolytes, $HClO_4$ and H_2SO_4 , demonstrate that in the presence of the non-adsorbing perchlorate anion, NO_3^- reduction happens at 0.15 V vs. RHE (note the high overpotential), while nitrate reduction is largely suppressed in the presence of strongly adsorbed (bi)sulphate. In both acids, NO_3^- reduction is inhibited at lower potentials, as the electrode potential approaches the region of hydrogen evolution and the coverage of hydrogen (θ_H) increases accordingly, suggesting that H_{ads} blocks nitrate adsorption on the metal surface.

Studies on Pt single crystals have suggested that the structure-sensitive adsorption of hydrogen and anions determines the structure-sensitivity of NO_3^- reduction. In perchloric acid, *i.e.* in the absence of interfering anions, Pt(110) was identified as the most active surface. For this surface, *in situ* Fourier Transform Infrared (FTIR) spectroscopy experiments have highlighted a band located at 1550 cm^{-1} , which can be ascribed to $N=O$ stretching modes typical of multifold-coordinated NO .^{39,40} This adsorbate can be observed in a large potential window ($0.25 < E < 0.45\text{ V vs. RHE}$) and its removal (*via* further reduction) overlaps with the electrochemical signal of NO_3^- reduction. So, NO_3^- seems to be converted to NO (with a coverage of $\theta_{NO} \approx 0.1\text{ ML}$) which is then reduced further. Similar conclusions were drawn for polycrystalline Pt.³⁸ However, Pt(110) is peculiar because its rate-determining step appears to be slightly different from other noble metals, involving a surface-confined chemical step,⁴¹



which is a Langmuir–Hinshelwood reaction.⁸ Also steps and defects of (110) orientation play a key role during NO_3^- reduction. Experimental evidence shows that intermediate $NO_{(ads)}$ accumulates at steps;³⁹ in other words, monoatomic steps with (110) geometry are the preferred sites for NO_3^- adsorption and reduction.⁴² In conclusion, NO_3^- reduction falls within the large group of surface-sensitive reactions that are *catalysed by steps*⁴³ although the effect of steps is not as large as for certain oxidation reactions. We stress that such site-selectivity is not peculiar to Pt: for instance, Bae and Gewirth have shown that NO_3^- reduction at Cu(100), the least active Cu surface, is restricted to step-like features.^{44,45}

In contrast to the clear FTIR-based evidence for NO adsorption during nitrate reduction, there still is no solid IR evidence concerning the geometry of *nitrate* adsorption itself on

Pt. NO_3^- can assume two configurations upon adsorption, both characterized by characteristic IR bands:^{46,47} the “unidentate” configuration ($\text{NO}_2\text{-O-Pt}$) and “bidentate” ($\text{NO}(\text{O})_2\text{-Pt}$). The latter is characterized by a $\text{N}=\text{O}$ stretching vibrational mode (like adsorbed NO) located in a broad region ($1480\text{--}1630\text{ cm}^{-1}$). Using the internal reflection configuration, Nakata *et al.*^{48,49} have suggested that, on the basis of a combined kinetic and spectroscopic study, the band observed at $1547\text{--}1568\text{ cm}^{-1}$ ought to be assigned to NO_3^- adsorbed in a bidentate geometry, rather than to adsorbed NO. DFT calculations for a very different metal, Cu(100) in acidic media, indicate that both NO_3^- and NO_2^- preferably adsorb with a bidentate bridge geometry.⁴⁵ Identification of reaction intermediates with IR spectroscopy is also a topic for non-electrochemical catalytic denitrification.^{31,50–52} Experimental evidence of NO_3^- adsorption on the titania support of denitrification catalysts has been obtained,^{31,50} suggesting an interconversion between the bidentate and the unidentate configuration.

The determination of the reaction selectivity is clearly of particular importance to reaction (1) and relies on a variety of techniques including FTIR spectroscopy, rotating ring-disk electrode voltammetry^{53,54} (RRDE), (on-line) electrochemical mass spectrometry^{53,55,56} and ion-chromatography,^{57–63} which all contribute in providing insight into the product distribution. These techniques have provided compelling evidence that during nitrate reduction on most metals, including Pt, no gases are released, NH_4^+ being the only product detected *on a short timescale*.^{30,38} Electrolysis over longer time spans – mimicking the actual conditions of large-scale denitrification – often produces a mixture of products^{30,58–60,62,63} but, in our view, it is less meaningful in terms of fundamental, mechanistic insight. It should be emphasized that intermediate NO_2^- is rapidly converted to $\text{NO}_{(\text{ads})}$, and does not leave the Pt surface. Should this happen to any significant extent, then the selectivity would be altered, as electrochemical HNO_2 reduction yields a much broader range of products.^{64,65} Dissolved HNO_2 decomposes to $\text{NO}_{(\text{aq})}$, which is electrochemically reduced to N_2O at Pt around 0.3 V vs. RHE. At potentials close to hydrogen evolution (below 0.1 V), HNO_2 is converted to NH_3OH^+ in a diffusion-controlled reaction.^{65,66}

As indicated, NO_2^- and NO_3^- feature a rather different electrochemical reactivity. For instance, Pt becomes inactive towards NO_3^- reduction as the pH is raised,^{30,67} whereas it retains a significant catalytic activity towards NO_2^- reduction also at alkaline pH values.⁶⁵ The study of alkaline solutions is of interest in relation to the electrochemical treatment of low-level nuclear wastes,^{68–71} which will be discussed in a later section. Fundamental studies have shown that the most active catalysts under alkaline conditions (Cu (ref. 72) and Rh (ref. 64 and 73)) are unable to select N_2 as the main product, NO_2^- and NH_3 predominating at different potentials.

NO_2^- reduction at Pt deserves a more detailed discussion because of its significant structure sensitivity.^{74–76} The catalytic activity of the three basal planes follows the order $\text{Pt}(111) < \text{Pt}(110) \ll \text{Pt}(100)$. Furthermore, quasi-perfect Pt(100) surfaces are also unique in their selectivity, achieving the direct conversion of NO_2^- to N_2 (ref. 76 and 77) in 0.1 M NaOH . This selectivity is especially remarkable because it is achieved by a single catalyst without the detectable formation of side products. This conversion appears as a sharp voltammetric peak located at

around 0.55 V vs. RHE (Fig. 3), which is a relatively positive potential for NO_2^- reduction: by comparison, Pt(110) reduces NO_2^- at 0.15 V in the same electrolyte. The mechanistic underpinnings of the exceptional selectivity of Pt(100) have been unveiled by spectro-electrochemical FTIR experiments and the use of isotope labelling.⁷⁷ The current model is that Pt(100) represents an ideal surface for the simultaneous – though fleeting – stabilisation of two adsorbates both originating from NO_2^- : $\text{NH}_{x(\text{ads})}$ (in all likelihood $x = 2$, dominant when $E < 0.55\text{ V}$) and $\text{NO}_{(\text{ads})}$ (dominant for $E > 0.55\text{ V}$).^{30,78,79} These two fragments, both present at low coverage, recombine in a Langmuir–Hinshelwood-type reaction to give N_2 :

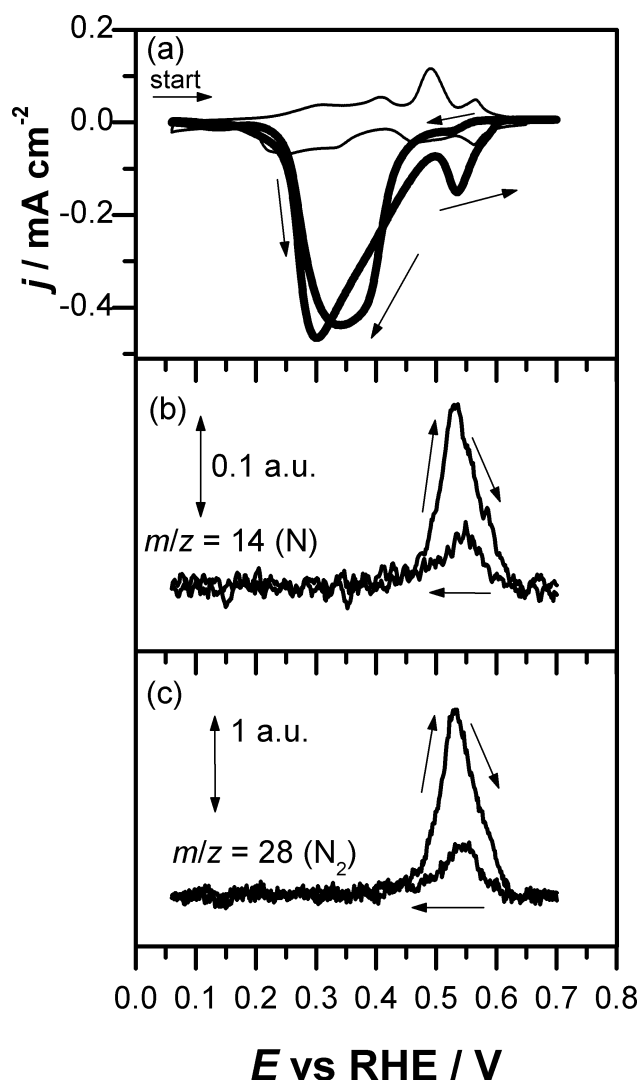
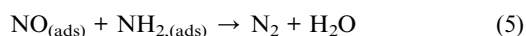


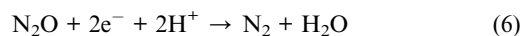
Fig. 3 Cyclic voltammetry combined with on-line mass spectrometry for detecting the formation of volatile products as a function of potential. A Pt(100) crystal is the working electrode, immersed in 0.1 M NaOH containing 2 mM NaNO_2 . Panel (a) shows the voltammetric profile in the nitrite-containing solution, recorded at $v = 1\text{ mV s}^{-1}$, overlapped with the blank voltammogram (thin line, recorded at $v = 50\text{ mV s}^{-1}$). Panels (b) and (c) display the ion current profiles for $m/z = 14$ and $m/z = 28$, respectively (Reprinted with permission from M. Duca, M. O. Cucarella, P. Rodriguez and M. T. M. Koper, *J. Am. Chem. Soc.*, 2010, **132**, 18042–18044, copyright 2010 American Chemical Society).



Thus, selectivity to N_2 is achieved, thanks to a reaction pathway different from the (more common) “stepwise” process. However, reaction (5) is a more widespread process. It is believed to occur under UHV conditions during the recombination between NO and NH_3 at a $\text{Pt}(100)$ surface to give N_2 .^{80–86} Also, it is a proposed metabolic shortcut of the nitrogen cycle exploited by “anammox” bacteria⁸⁷ (which could be used to treat polluted sewage⁸⁸). Moreover, reaction (5) closely resembles the SCR (Selective-Catalytic Reduction) process⁸⁰ which occurs in the removal of NO_x from diesel exhaust gas. Despite being an apparently very selective pathway to N_2 , as it does not involve the weakly ligating N_2O intermediate, reaction (5) is subject to limitations. For instance, the catalytic activity of $\text{Pt}(100)$ drops as the pH decreases and approaches the $\text{p}K_a$ of NH_4^+ .⁷⁵ More importantly, defects of any type, which disrupt the ordered $\text{Pt}(100)$ surface, bring about a simultaneous decrease in selectivity and activity.⁷⁷ In contrast to the step-catalyzed NO_3^- reduction (*vide supra*), NO_2^- reduction in alkaline media belongs to a different class of reactions *requiring well-ordered (100) terraces*.⁴³ Hence, although a comparison between acidic and alkaline pH regions might not stand on solid ground, the activation of NO_3^- and the subsequent control of selectivity to N_2 belong to different structure sensitivity classes. This may be a potential obstacle in designing a catalyst for reaction (1) which would make use of reaction (5).

Fundamental studies of nitrate reduction on bimetallic catalysts

We now turn to a discussion of hierarchically more complex electrocatalysts. Bimetallic catalysts have been widely studied for hydrogen-driven catalytic denitrification:^{31,89–92} selectivity to N_2 (sometimes higher than 90%) has been achieved with bimetallic catalysts containing Pd and a second less noble metal, such as Cu or Sn.^{89,91–93} While these promoters are thought to accelerate the rate-determining formation of NO_2^- , the role of the noble metal is twofold: it stabilises the less noble metal and it steers the reaction selectivity.³¹ A certain degree of surface-selectivity has also been claimed⁹¹ for the reduction of NO_2^- to N_2 , although it is actually challenging to define a “terrace” for a system such as PdCu. Not surprisingly, this bimetallic combination has also shown to be a promising electrocatalyst for nitrate reduction Pd–Cu:^{94–96} for instance, a 40% selectivity to N_2 has been obtained at low (<0.2 ML) Cu coverages on a Pd layer and high overpotentials (0.02 V vs. RHE). Generally speaking, there is no modification in the mechanism: the rate determining step is the first electron transfer^{94,97} and the reaction order is lower than 1.⁹⁷ Pd is crucial for generating N_2 , as this metal is one of the best (and few) catalysts^{98,99} for the reaction†



which, as shown in Fig. 2, is the end of the stepwise pathway leading to N_2 . This is a good example of synergistic catalysis by a bimetallic system, since Pd is a poor catalyst for nitrate reduction in the absence of the promoter.³⁰ Additionally, PdCu retains selectivity to N_2 both at acidic and alkaline pH^{94–97,100} (which is quite unusual) and independently of the preparation route (Cu adlayer on Pd,⁹⁴ co-deposited films,^{95,96} PdCu alloys¹⁰⁰ and Cu adlayer on Pd nanoparticles⁹⁷). The same strategy has been extended to Pt, although this noble metal is not as good a catalyst for reaction (6) as Pd. For Pt, the most promising combination appears to be Pt/Sn.^{58–63} Despite extensive research, the role of Sn still remains elusive, although Pt–Sn bimetallic sites supposedly offer a favourable ensemble for the enhancement of reaction (3).³⁰ Experimental evidence points to the formation of N_2 only as a minor reaction product over a short timescale,⁵⁶ while the product distribution can vary upon prolonged electrolysis. A further improvement in the selectivity to N_2 (up to 37% with long-term electrolysis) has been achieved with a trimetallic combination, Au/Pd/Sn, with the additional advantage of a decrease in the amount of noble metal used.⁶² Other promoters also achieve enhancement of nitrate reduction at Pt, but steer the reaction selectivity towards other products: NH_3OH^+ for Pt–Ge (thanks to third-body effects of $\text{Ge}_{(\text{ads})}$)¹⁰¹ and N_2O for Pt–Bi.^{102,103}

Molecular catalysts: macrocycles and enzymes

Composites, (supra)molecular or bio-inspired electrocatalysts for denitrification have briefly been reviewed elsewhere.³⁰ Often, they are developed for highly sensitive electrochemical nitrate sensors^{16,104–109} and so mechanistic insight is typically not pursued. The most interesting aspect is that several of such systems are able to reduce NO_3^- in neutral electrolytes, which matches the actual conditions of nitrate-laden water more closely than the acidic (or alkaline) electrolytes usually studied. However, this comes at the cost of a high overpotential, which is not an issue for sensors; on the other hand, a claimed advantage of using a molecular catalyst involves the “caging” of the reactant, which avoids the release of intermediates during multi-electron reactions (such as NO_2^-/NO reduction to NH_3).¹¹⁰

Thus far, all catalytic systems discussed belong to heterogeneous catalysis. A fundamentally different approach to electrochemical denitrification could involve redox-active homogeneous catalysts transferring electrons to the electrode without being attached to it. This research field is still in its infancy and, as far as nitrate reduction is concerned, much progress is still needed.¹¹¹ For example, metal cyclam (1,4,8,11-tetra-azacyclotetradecane) complexes were first used dissolved in the nitrate-containing solution.¹¹² This strategy was abandoned in later works, in which the catalyst was immobilised on the electrode with electropolymerisation.^{113–115} This offers clear advantages as the more intimate contact between the electrode and catalysts allows a more facile electron transfer.

Nitrate reductases, defined as “key enzymes in the nitrogen cycle”,³⁴ are multi-enzymatic complexes belonging to the “molybdenum oxotransferases” as they feature a molybdopterin (molybdenum–sulfur) as an active centre along with electron

† Temperature, as an operational parameter, is not dealt with in this article. However, it is important to mention that, *in the gas phase*, reaction (3) only occurs at high temperature (Kapteijn *et al.* report that a temperature of 900 K is necessary for a sufficient reaction rate to be achieved²⁰⁸). Despite this, the temperature does not seem to be the largest obstacle to the electrochemical reduction of N_2O ; as discussed in the text, desorption of N_2O from the electrode, due to the sluggishness of reaction (3), is the real hurdle for the electrochemical N_2O reduction.

shuttles and cofactors. Nitrate reductases have extensively been studied by direct immobilisation of the enzyme on an electrode,^{30,116} which has provided much insight into the catalytic mechanism of selected nitrate reductases.^{117–121} NO_3^- binds to Mo(IV), which is oxidised to Mo(VI) upon ligation; the cycle is closed by two ensuing one-electron steps (thus involving Mo(V)) leading to NO_2^- and Mo(IV).¹²² Although nitrate reductases could be exploited in electrocatalysis for their high selectivity to a single product in neutral media, they have only been used so far to fabricate electroactive hybrid devices for the electroanalysis of NO_3^- .^{104,105,123}

Perspectives

Future progress in the applicability of electrocatalytic denitrification will entail the need to deploy *electrocatalysts featuring an increased level of complexity*, if we are to meet the simultaneous challenge of achieving selectivity and catalytic activity. We should take heed of enzymatic nitrate reduction: the highly complex machinery set up by nature to perform 2-electron oxygen transfer reactions (such as NO_3^- reduction) lets us suspect that the abstraction of the first oxygen atom from NO_3^- to give NO_2^- must be an intrinsically arduous step, for which evolution has specifically selected molybdenum enzymes.¹²⁴ Moreover, only a set of enzymes achieves final selectivity to N_2 , following reaction (2), and therefore there must be a synergy between (at least) two components: a *rate-enhancer* and a *selectivity-enhancer*.

In addition to the synergy issue, alloying two metals is one of the most immediate strategies that could be pursued. It is known that Pt is inactive towards NO_3^- reduction in H_2SO_4 , while Rh (the most active noble metal towards nitrate reduction³⁸) is unaffected by the presence of (bi)sulphate. We have recently synthesized Pt–Rh alloys of different composition in the form of nanoparticles.¹²⁵ Interestingly, the highest catalytic activity was not achieved with pure Rh, but with a $\text{Pt}_{20}\text{Rh}_{80}$ alloy. As for promoters for Pt, from an evaluation of a broad range of (semi-)metals in acidic media (In, Ga, Tl, Sn, Pb, As, Sb, Bi, Zn and Cd), even in the most promising cases, the increased catalytic activity is accompanied by enhanced N_2O formation and very little (if any) N_2 formation.¹²⁶ In all likelihood, this is ascribable to a loss of intermediate NO_2^- to the acidic solution (*vide supra*)^{56,64,65,127} and its subsequent reduction to N_2O . We have also confirmed that Pt–Sn is the best combination: thus, the next obvious step would be the evaluation of trimetallic combinations.⁶²

Another possible strategy mimics nature in the sense that a combination of catalysts is deployed to perform the entire stepwise pathway leading to N_2 , like a multi-enzymatic complex. Such an approach has been dubbed “rational design of electrocatalytic interfaces” in a recent paper.¹²⁸ Au nanoparticles and hemin (Fe-protoporphyrin IX) were co-deposited on a GC disk electrode. Usually, Au is a poor catalyst for NO_3^- reduction in mildly acidic conditions, unless Cd^{2+} is present in the solution: in this case, underpotentially deposited Cd selectively enhances the formation of NO_2^- .^{129,130} Nitrite is then targeted by hemin leading to NH_3OH^+ , which is by far the major reduction product.¹³¹ Despite failing to achieve 100% selectivity to N_2 , this approach is very promising and should garner more attention. Ideally, a synergy should be sought between bio-(inspired)

moieties (perhaps nitrate reductase itself) and metallic or molecular catalysts. If noble metals are used in this strategy in an acidic solution, the catalyst complex must ideally avoid releasing NO_2^- into the solution; otherwise, the selectivity might be steered too much towards harmful N_2O .^{64,65,127}

Pt(100) single-crystal electrodes in alkaline media have achieved the best selectivity to N_2 . From a practical point-of-view, this translates into an investigation of catalytic activity on cubic (or cuboid) nanocrystals. Using the “cathodic corrosion” method,¹³² we have obtained Pt nanocrystals featuring a high proportion of (100) domains (up to 60%)¹³³ which still selectively convert NO_2^- to N_2 . However, Pt can only target *nitrite*, not *nitrate*, in alkaline media. This remains an important challenge because at present no promoters are known that enhance the reduction of NO_3^- to NO_2^- at the relatively high potentials (0.55 V) at which N_2 is formed in alkaline media. Pt(100) displays a certain catalytic activity towards NO_3^- reduction in a pH 7.2 phosphate buffer, while other Pt basal planes are inactive.¹³⁴ As mentioned, nitrate reduction is inhibited by other co-adsorbed species: the reaction occurs only when the hydrogen coverage at the surface is below a critical value, a limiting factor that also affects NO_3^- reduction at Pt(100) in HClO_4 .^{39,135} The reduction process occurs at 0.4 V and generates NH_4^+ , closely resembling the main reduction peak of the same Pt surface during reduction of NO_2^- in alkaline media. This corroborates the validity of the stepwise mechanism, showing that an NO_{ads} submonolayer is the main surface intermediate. However, no N_2 is formed, although some prerequisites for reaction (5) appear to be satisfied. A speculative explanation could rely on the observation, reported by Ye *et al.*,⁷⁵ that a marked increase in the reactivity of Pt(100) towards nitrite reduction occurs when $\text{pH} > \text{pK}_a$ of the product NH_4^+ . In relation to this issue, more research on NO_3^- reduction in neutral solutions^{96,136–138} would be welcome, as wastewater is often pH-neutral.

Finally, future work should also aim at theoretical studies trying to rationalise reactivity trends for NO_3^- reduction.^{30,139} The prediction of potentially promising catalysts with DFT calculations has recently become common practice in electrocatalysis,^{140–142} leading to “volcano plots” showing the (theoretically) ideal catalyst for HER and ORR. The complexity of the various reaction pathways of NO_3^- reduction makes the interpretation of such calculations somewhat more challenging but a recent study by Peterson and Nørskov¹⁴³ on the related electrocatalytic reduction of CO_2 nicely illustrates the type of insight that can be obtained. Such calculations can subsequently be performed for a variety of bimetallic surfaces, with the aim to tailor activity and selectivity. Elementary considerations on the much higher catalytic activity of Rh with respect to Pt are currently based on the lower $\text{p}z(\text{t})c$ of Rh in acidic media, which would explain the enhanced tendency to adsorb anions in a wider potential range. However, such considerations are hardly applicable to bond-breaking reactions and the influence of promoters on the activation of nitrate. Finally, we stress that *in situ* measurements should routinely become part of any fundamental study as this supplies a complete mechanistic picture, bearing in mind, of course, the limitations of each method (*i.e.* the small Raman cross-section of nitrogen compounds^{144,145} often impairing electrochemical SERS measurements). A combination of multiple techniques will increasingly be required to tackle the

complex behaviour of nitrate reduction at multi-metal systems, as shown by Huang *et al.* in a recent study of Pb–Ag–Au catalysts combining EQCM (electrochemical quartz crystal microbalance) and impedance.¹⁴⁶

Nitrate reduction in electrochemical reactors and under practical conditions

Studies addressing electrochemical denitrification with a view to practical applications will be dealt with in this section. This will include practical electrochemical reactors, the denitrification of (simulated) wastewater or the study of cathode materials under practical conditions (prolonged electrolyses). In contrast to fundamental studies, the anodic reaction(s) simultaneous to nitrate reduction cannot be neglected in electrochemical reactors.

State of the art and challenges

The use of electrochemical reactors to treat nitrate-laden (waste) water competes with the widespread and technologically mature biological remediation; both approaches seek to achieve highly efficient nitrate removal at the lowest cost, while avoiding unwanted side-products (formation of NO_2^- is a common problem¹⁹). Generally speaking, the electrocatalytic remediation offers the following advantages:

- No chemical needs to be added (bacteria usually need an extra input of carbon if they are heterotrophic or an electron donor if they are autotrophic^{19,21–24}).
- No formation of sludge (which must be disposed of).
- Avoidance of potentially pathogenic bacteria, this being a central issue for remediation of drinking water; in other words, a final disinfection treatment is not required.
- Use of electrical energy from renewable sources.
- Suitability for the remediation of industrial wastewater in which bacterial growth is unviable.

A high carbon-to-nitrogen ratio is a key for a successful biological denitrification,^{19,21–23} which might be optimal only for those waste streams containing a sufficient organic carbon content (sewage, agricultural runoff).¹⁹ On the other hand, electrocatalysis should be advantageous for targeting water for human consumption or *specific* types of industrial wastewater with a high nitrate content[‡] or a very low carbon content, such as:

- High- and low-level nuclear wastes.
- Spent electroplating baths.
- Liquid wastes from mineral processing, semiconductor manufacturing and synthesis of fertilisers or explosives (ammonia is usually oxidised to nitrate prior to further treatment²⁷).

We shall now discuss selected examples of applied electrocatalytic denitrification.

Product distribution at the cathode: prolonged electrolysis

The study of the selectivity of electrocatalytic denitrification over long timescales is the first step towards its practical application;

‡ “High” roughly corresponds to 200 mg NO_3^- -N per l (0.014 M);²⁴ very high (low-level nuclear wastes) to 50 000 mg NO_3^- -N per l (3.6 M). In the presence of a very high concentration of nitrate, reduction to ammonia could become the desirable process. However, in the majority of cases the process must be steered to the reduction to N_2 .

this does not usually involve a careful control of the anodic reaction.

A wide range of noble metals, pure and modified with Sn as a promoter, have been tested for prolonged electrolysis at constant potential of a nitrate- (or nitrite-) containing acidic electrolyte (usually 0.1 M HClO_4).^{58,59} The product analysis invariably unveils the formation of several molecules (up to five), the major products being NH_4^+ , NH_3OH^+ and N_2O . N_2 is indeed formed at a Pt/Sn electrode⁶¹ (Sn coverage 0.28–0.41 ML, 30% selectivity to N_2).

Long-term denitrification of a nitrate-containing K_2SO_4 solution was studied at a Sn cathode¹⁴⁷ at very negative potentials. NO_3^- was effectively destroyed and converted to N_2 , NH_3 amounting to only 8% of the products. Such selectivity to N_2 is among the highest reported for a monometallic cathode; however, the very negative potential required may impair practical applications of Sn due to energy consumption. Analogously, prolonged electrolysis of slightly alkaline simulated wastewater at a Bi cathode leads to a mixture of NH_3 , N_2O , NO_2^- and N_2 dominated by the latter product (60%). The poorer performance with respect to Sn is counterbalanced by a larger resistance to cathodic corrosion.⁷⁰ In both cases the Faradaic efficiency never exceeds 80%. These studies on prolonged electrolysis of a nitrate-containing electrolyte clearly show that achieving a 100% selectivity to N_2 at a cathode is a daunting task, whatever the reaction conditions.

Reactor designs for electrochemical denitrification

A broad variety of processes and reactor designs has been tested for electrochemical denitrification: schemes of three processes and reactors are shown in Fig. 4. A selection of them will be discussed below; their performance is summarised in Table 1.

A *zero-gap solid polymer electrolyte reactor* is composed of a cation-exchange membrane which supports, on the two opposite faces, the cathode and the anode. Cheng *et al.*¹⁴⁸ demonstrated that such a reactor, run under *flow* conditions (continuous circulation of the electrolyte in the anodic and cathodic compartments) can successfully achieve denitrification of a simulated, slightly alkaline nitrate-containing solution. The cathode material was a Pd–Rh deposit on Ti. Reactor parameters, such as the type of electrolyte used in the anodic compartment and the flow rate, were optimised to enhance nitrate removal and selectivity to N_2 . Unfortunately, no direct analytical evidence of N_2 was presented; NH_3 was always detected as a side product. Incidentally, 100% selectivity to N_2 would be surprising as Rh is known to be a very active nitrate reduction catalyst but selective for NH_3 . Solid polymer electrolyte membranes carrying the anode and cathode material on opposing sides have also been used under stationary conditions (*batch* reactors). Machida *et al.*¹⁴⁹ showed that such a reactor, run under constant current conditions and featuring a Pt–Cu cathode – a variation of the bimetallic combination Pd–Cu discussed in the previous section – converts a 0.05 M NO_3^- solution to N_2 with high selectivity (95%, side-product NH_4^+), provided that the solution pH is buffered with continuous CO_2 bubbling.¹⁴⁹ Pd–Cu performs well also in the absence of buffering, although NO_2^- and NH_4^+ are formed with 17% and 6% selectivity, respectively. Other electrocatalysts used at the cathode of the same zero-gap reactor

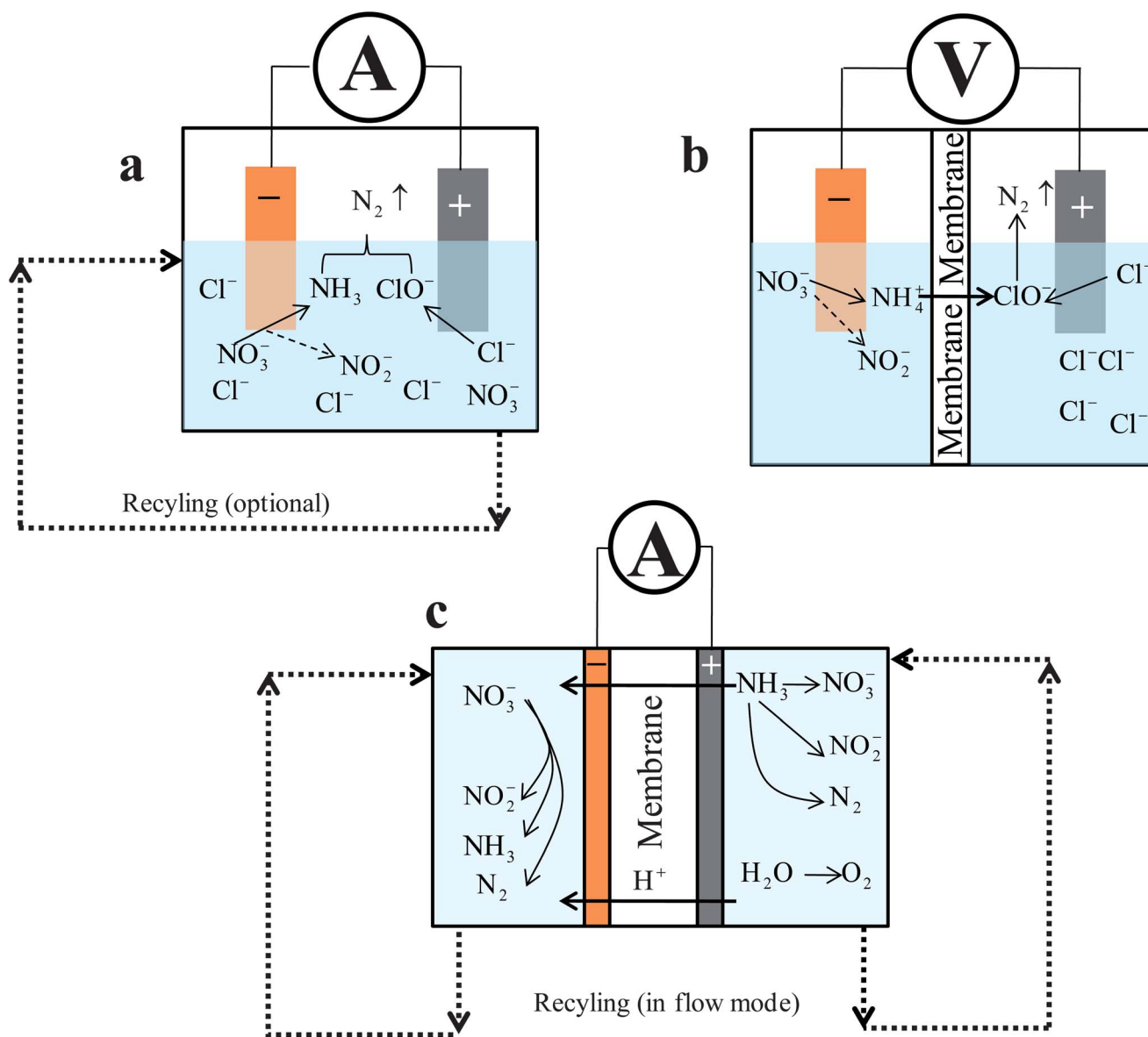


Fig. 4 Schemes of three reactor designs for electrochemical denitrification; (a) constant-current denitrification in undivided cells, batch or flow mode, applied to chloride-containing electrolytes. (b) Constant-potential denitrification in divided cells (ammonium can cross the proton-exchange membrane), applied to chloride-containing electrolytes. (c) Zero-gap solid polymer electrolyte reactor: electrodes are thin films deposited on the proton-exchange membrane separating the anodic and cathodic compartments. The anodic reaction can either be ammonia oxidation, if ammonia is added to the anodic electrolyte, or usually water oxidation. Thin arrows represent the major reaction pathways, while broken arrows represent the pathways to minor products; thick arrows highlight cation movement through the membrane. Dotted arrows connecting the bottom and the top of the reactor compartments stand for recycling, which is usually an optional choice. The drawing is not to scale. For additional information refer to Table 1 and the text.

(Ag–Pt (ref. 150) or trimetallic combinations Ag–Pd–Pt (ref. 151)) performed well in terms of rate of removal but yielded a mixture of products with a lower selectivity to N_2 . It should be remarked that these experiments targeted unbuffered model solutions (containing a supporting electrolyte and a nitrate salt), which, from the point of view of the pH, are more similar to actual nitrate-laden water.

More traditionally, electrodes can be immersed in the electrolyte in the centre of the anodic or cathodic compartment, the two being separated by a cation-exchange membrane. Usually, these reactors are suitable for *batch* operation. Wang *et al.*¹⁵² applied such a reactor for the electrochemical denitrification of

nitrate-laden tap water. The cathode material, carbon fibres impregnated with a varying ratio of Sn and Pd, is an example of application of the results of fundamental studies. The best balance between activity and selectivity was obtained for a Pd/Sn weight ratio of 4/1, and neutral or slightly acidic pH values (NO_2^- formation was enhanced at higher alkalinity). NH_4^+ and N_2O were always detected as side products, although their concentrations were small; N_2 was assumed as the major product on the basis of the nitrogen mass balance. The anodic reactions observed were oxygen evolution and oxidation of carbon to CO_2 . Even though the performance of this electrochemical reactor is satisfactory, nitrate is reduced to a mixture of various

Table 1 Overview of experimental conditions for electrocatalytic denitrification (selected cases)

Ref.	Anode ^a	Cathode ^a	Electrolyte	Membrane	Reaction conditions ^a	Performance ^a
159	Ti/IrO ₂ (DSA)	Cu, Ni, <i>Cu : Ni 70 : 30,</i> <i>Cu : Ni 90 : 10</i>	0.01 M NaNO ₃ , 0.05 M NaCl, 0.01 M NaOH, deaerated	No	Undivided multi-cell electrolyser, semi-batch mode; constant cathode potential, anode potential uncontrolled	42% < φ < 75%, 10 < SEC < 20 kW h kg ⁻¹ NO ₃ ⁻ , 92% NO ₃ ⁻ removed in 3 h, final product 100% N ₂
160	Ti/IrO ₂ (DSA)	Cu	0.1 M NaNO ₃ , 0.5 M NaCl, 0.01 M NaOH, deaerated	No	Undivided cell, batch mode; constant current (potential controlled by cathode/anode surface area ratio)	SEC = 14.7 kW h kg ⁻¹ NO ₃ ⁻ , final product 100% N ₂
164	IrO ₂ -Ta ₂ O ₅ (DSA) conductive diamond	Stainless steel	ca. 2 mM NaNO ₃ , 0.02 M Na ₂ SO ₄ , pH 2	No	Undivided flow cell; constant current	90% NO ₃ ⁻ removed in 9 h Speculative reaction mechanism, N ₂ formation <i>not directly detected</i> . Several side-products formed
162	Ti/IrO ₂ -Pt	Fe	1 mM NaNO ₃ , 8.5 mM NaCl, 3 < pH < 11	No	Undivided cell, batch mode; constant current. pH uncontrolled during the electrolysis	80% NO ₃ ⁻ removed in 3 h, NH ₃ and NO ₃ ⁻ below detection limit; N ₂ <i>supposed</i> to be only product
173	Ti/Pt, <i>Ti/IrO₂-Pt,</i> <i>Ti/RuO₂-Pt</i>	Cu/Zn (Cu 62 wt%, Zn 38 wt%)	7 mM NO ₃ ⁻ , 3.5 mM Na ₂ SO ₄ , varying amounts of NaCl	No	Undivided cell, batch mode; constant current. pH uncontrolled during the electrolysis	82% NO ₃ ⁻ removed in 2 h (8.5 mM NaCl added), [NH ₃] _{final} = 1 mM. Suppression of NH ₃ formation with increasing [NaCl]. SEC ≈ 183 kW h kg ⁻¹ NO ₃ ⁻
175	Ti/Pt-Ir	Ti/PdO-Co ₃ O ₄ , steel/Pd-Cu, <i>Ti/PdO-Co₃O₄-Cu</i>	3 mM NaNO ₃ , 0.1 M NaCl in anodic chamber	Yes (Nafion 117)	Divided cell, batch mode; constant cathode potential	$\varphi \approx 20\%$, SEC < 50 kW h kg ⁻¹ NO ₃ ⁻ , 80% NO ₃ ⁻ removed in 6 h, kinetics of reaction (9) monitored at open circuit; role of Cl ⁻ shown
152	Carbon plate	Pd/Sn modified activated carbon fibre 4 : 1 <i>weight ratio</i>	Tap water (containing Cl ⁻ and SO ₄ ²⁻) artificially enriched with 0.4 mM NO ₃ ⁻	Yes (Nafion 117)	Divided cell, batch mode; constant current (cell potential also measured). pH controlled at desired value	$\varphi^b \approx 16\%$, SEC ^b ≈ 107 kW h kg ⁻¹ NO ₃ ⁻ , 96.6% NO ₃ ⁻ removed in 4h. NH ₄ ⁺ and N ₂ major products, plus trace N ₂ O. N ₂ formation <i>not directly detected</i>
169	Pt on Ti “mini- mesh”	PdRh _{1.5} on Ti “mini-mesh”	0.1 M NaNO ₃ , 1 M NaHCO ₃ , 6.8 mM NaCl, 2.8 mM Na ₂ SO ₄	Yes (Nafion 117)	Zero-gap solid polymer electrolyte cell; flow reactor; constant current	13.5% < φ < 24.5%, 40 < SEC < 63 kW h kg ⁻¹ NO ₃ ⁻ , 100% NO ₃ ⁻ removed in 150 h, NH ₃ formed as a side product. N ₂ claimed as a major product (N ₂ formation <i>not directly detected</i>)
149	Pt	Pt, Cu, Pd, Pd-Cu, Ni-Pd, <i>Pt-Cu</i>	0.048 M NaNO ₃ (buffered with CO ₂ bubbling)	Yes (Nafion 117)	Zero-gap solid polymer electrolyte cell. Batch mode, constant current. pH kept constant with CO ₂ bubbling	$\varphi \leq 25\%$, 100% NO ₃ ⁻ removed in 1 h, 5% selectivity to NH ₄ ⁺ after 3 h, N ₂ major product

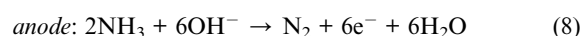
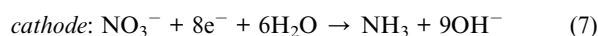
^a If several electrode materials, reactor geometries or electrolyte compositions are evaluated, only the best performances are reported for the sake of brevity. In a list of electrode materials, the best catalyst is *written in italics*. ^b If SEC and φ are not mentioned in the publications, φ is calculated as an overall current efficiency to all products reported and SEC is calculated on the basis of the current efficiency to N₂. These two parameters are reported whenever possible only as an indication, for the sake of comparison.

compounds. A combination of batch and flow conditions has also been suggested, with a single-compartment reactor in which the electrolyte is continuously recycled.¹⁵³

A comparative study of reactor types was carried out by Paudar *et al.*¹⁵⁴ Although restricted to wastewater with particular characteristics (spent liquid phase from a denitrifying ion-exchanger), it demonstrates that a simple undivided cell achieves a rather efficient performance for the electrochemical denitrification. The benign effect of mechanical mixing of the electrolyte, achieved in this study by inert glass particles, was also reported. However, as the authors pointed out, NH₃ is the major product (or an unavoidable side-product).

Paired electrolysis. Compared to the troublesome selective formation of N₂ during NO₃⁻ reduction, the selective oxidation of NH₃ to N₂ is well known.³⁰ Interestingly, N₂ formation from

NH₃ is also peculiar to Pt(100) electrodes in alkaline media.^{79,155–158} Selective ammonia oxidation is the rationale behind another approach to electrocatalytic denitrification, which exploits a combination of anodic and cathodic reactions in a so-called *paired electrolysis*,



in which NH₃ must be allowed to diffuse through the cell and reach the anode. Generally speaking, paired electrolysis targets alkaline solutions. Formation of side-products (primarily NO₂⁻) at the cathode must be avoided, which can be achieved with a careful control of the electrode potential: this is one of the most crucial operation parameters.^{159,160} Pure metals such as Rh

(ref. 64 and 73) and Cu (ref. 72 and 161) can selectively form NH_3 in an alkaline electrolyte but also cheaper materials (Fe,^{162,163} stainless steel¹⁶⁴) can be used. Similarly, there has been much research aimed at identifying the ideal conditions for N_2 formation from NH_3 .^{27,165–168} Generally speaking, two different routes can be followed:

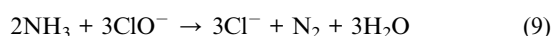
- Electrochemical NH_3 oxidation.^{30,166}

- *Indirect (non-electrochemical) NH_3 oxidation*: the anode generates the species which will in turn oxidise ammonia in a chemical reaction.

Electrochemical NH_3 oxidation could be an interesting route to eliminate NH_3 produced at the cathode during denitrification. Cheng *et al.*¹⁶⁹ first suggested recycling the ammonia-rich electrolyte from the cathodic to the anodic compartment of a zero-gap solid polymer electrolyte reactor (see above). In principle, if proper electrode materials are chosen, the oxidation of the products of nitrate reduction could simply be achieved at a single electrode by quickly reversing the electrode polarity. This approach was investigated by Polatides *et al.*¹⁷⁰ in a batch reactor featuring a brass ($\text{Cu}_{60}\text{Zn}_{40}$) working electrode. A square-wave potential profile was shown to enhance N_2 formation up to a 70% selectivity in simulated neutral wastewater. Some authors¹⁶⁴ have speculated that the actual processes occurring at some anode materials (conductive diamond and $\text{IrO}_2\text{-Ta}_2\text{O}_5$) during denitrification of a sulphate-containing wastewater involves formation of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ instead of NH_3 oxidation.

Direct NH_3 oxidation is however not predominant in the literature on paired electrolysis. The reason is probably that, generally speaking, 100% selectivity to N_2 at the anode during NH_3 oxidation is not easily achievable under practical conditions. In addition, a very selective chemical oxidation is already available.

The non-electrochemical NH_3 oxidation is a viable route in the presence of hypochlorite, the time-honoured “breakpoint chlorination”,¹⁷¹ summarised in the following equation:



with hypochlorite being formed at the anode in a chloride-containing electrolyte according to the following reactions.



which occur in undivided chlor-alkali electrolysis too. The anodic side-reaction leading to O_2 evolution must be avoided; this can be achieved by choosing an appropriate anode material (for example the well-known “dimensionally stable anodes” (DSAs)¹⁷²) and by keeping the potential at a value where reaction (10) predominates. An enhancement of the overall rate of denitrification is usually observed, thanks to reaction (9), and a significant reduction of noxious side-products can be achieved in the presence of chloride.¹⁷³ Breakpoint chlorination is not totally exempt from safety issues and practical problems which should be borne in mind.¹⁶⁶ In brief, the release of toxic chloramines (which are reaction intermediates) might take place for $\text{pH} < 9$,¹⁷⁴ while the optimum for breakpoint chlorination is reported at $\text{pH} = 8.5$. Additionally, hypochlorite might be further oxidised to

toxic chlorate and perchlorate, although reaction (9) should rapidly take place *in situ* at the anode once hypochlorite is formed, thus preventing bulk accumulation of this ion. For some anode materials, experimental evidence points to direct ammonia oxidation by Cl^- or Cl_2 , with no actual formation of ClO^- .¹⁶⁶

Table 1 summarises the experimental parameters of the cited studies. The following formulae¹⁷⁵ are often used to compute the current efficiency ϕ .

$$\phi = \frac{nF\Delta\nu}{Q} \quad (12)$$

where n is the number of electrons exchanged, F is the Faraday constant ($96\,485\text{ C mol}^{-1}$), $\Delta\nu$ is the number of moles of reactant consumed and Q is the measured charge; the *specific energy consumption* (SEC) (expressed as $\text{kW h kg}^{-1}\text{ NO}_3^-$).

$$\text{SEC} = \frac{nFE_{\text{cell}}}{\phi M \times 3.6 \times 10^6} \quad (13)$$

where n has the usual meaning, E_{cell} is the cell voltage and M is the molar mass.

As Table 1 shows, a comparison of different process conditions is hampered by the diversity of the simulated wastewater types used and because not all parameters have been determined in all cases. In particular, selectivity to N_2 and SEC would be particularly informative and should always be computed. However, it clearly appears that paired electrolysis exploiting breakpoint chlorination stands out as the most energy-efficient process, ensuring an almost 100% selectivity to N_2 . Additional parameters should also be mentioned, such as the resistance to corrosion of cathode materials. A systematic comparison of this parameter for Cu, Ni and Cu_xNi_y , has been carried out by Reyter *et al.*¹⁵⁹ showing that Ni and Ni-rich cupro-nickel electrodes feature a greater corrosion resistance in the chloride-containing working electrolyte. Resistance to corrosion is usually not an issue for anodes, considering that DSAs are generally employed. Among the different anode materials tested (Table 1), Ti-supported IrO_2 stands out as one of the most reliable anodes for denitrification in undivided cells in the presence of chloride.

Nuclear wastes

Two factors warrant a separate discussion of the electrochemical denitrification of nuclear wastes: these liquid solutions are unsuitable for bacterial growth and feature a complex composition giving rise to so-called “matrix interferences”. Usually a difference is made between “high-level” (*i.e.* with high radioactivity) and “low-level” (low radioactivity) wastes.^{68,69,71,176–178} Typically, the latter are highly alkaline and contain high (*ca.* 1 M) concentrations of NO_2^- and NO_3^- along with SO_4^{2-} , halides, $[\text{Al}(\text{OH})_4]^-$, Cr(vi) (at a millimolar level) and traces of Ru(III) and Hg(II). Chromate is the most troublesome species because it can be electrochemically reduced to create a $\text{Cr}(\text{OH})_3$ film poisoning the cathode.⁷¹ Thus, “simulated” nuclear wastes ($\text{NaOH} + \text{NaNO}_2 + \text{NaNO}_3$) are often used in preliminary experiments, for which both divided or undivided cells can be used.^{68,69,71,176,177} In a recent publication, Bi and Sn cathodes have shown to be promising cathode materials, in which a proof-of-concept remediation of simulated low-level nuclear wastes has been

achieved.⁶⁹ A two-compartment cell equipped with a proton-exchange membrane (Nafion 117) is used; under galvanostatic conditions NO_2^- and NO_3^- can be reduced to N_2 in a chromium-free electrolyte with good selectivity (80% for Sn and 60% for Bi) and an acceptable energy consumption (though always higher than for the best electrode combinations for paired electrolysis: 20–100 kW h kg^{-1} NO_3^- as a function of the current used).⁶⁹ In the presence of Cr(VI), deposition of the Cr metal at the electrode occurs with no observable decrease in catalytic activity; unfortunately, no data on the product selectivity in the presence of Cr(VI) are available in the abovementioned publication.⁶⁹

The latter observation merits a final comment: articles dealing with “applied” denitrification often lack accurate product analysis. It is strongly recommended that direct evidence of N_2 formation *be always obtained* with the appropriate analytical techniques (usually gas chromatographic or mass spectrometric analysis of the gases evolved during electrolysis in a sealed cell^{69,159,160}) to corroborate the kinetic measurements of nitrate removal. From this point of view, simple analysis of total nitrogen content and subtraction of nitrogen ascribable to nitrate, nitrite and ammonia^{152,162,163,169,179} should be deemed unconvincing, to say the least. Although N_2 might be the only gaseous product by chance, the complex chemistry of nitrogen-containing molecules³⁰ necessitates a rigorous identification of reaction products.

Perspectives

Despite the potential advantages of electrochemical denitrification, biological remediation remains the economically favourable option for sewage and wastewater from the agro-food industry;^{19,180} arguably, biological denitrification represents a growingly viable alternative also in the presence of an unfavourable carbon-to-nitrogen ratio or toxic chemicals, such as in wastewater from metal refineries.^{19,181,182} Thus, electrochemistry faces a fierce competition and, in our opinion, should focus on niche applications dedicated to specific types of industrial wastewater, optimising *ad hoc* “customised” processes.

Additionally, the model electrolytes (Table 1) are often extremely different from the actual composition of wastewater; for instance, domestic wastewater contains organic matter, fats, oils, suspended solids, CaCO_3 , soluble phosphorus and ammonium nitrogen.¹⁷⁴ Many of these species will pose problematic interferences with the desired electrochemical nitrate removal. This is a veritable limiting factor if electrochemical denitrification is to demonstrate proof-of-concept viability. Fortunately, “more realistic” simulated wastewater has been studied in some cases, for example, the municipal tap water artificially enriched with nitrate,¹⁵² or the carefully simulated nuclear wastes mentioned above. More recent studies have targeted the remediation of nitrite-laden wastewater from aquaculture farms.¹⁸³

High selectivity to N_2 has mainly been achieved with chloride-containing electrolytes which raise, as mentioned above, safety and health concerns. Alternative processes exploiting chloride-free electrolytes should be investigated. In turn, this implies that a renewed attention will have to be paid to the anode material because an optimum has been reached only for denitrification in the presence of chloride (Table 1). Finally, research should also

seek to develop energy-efficient catalysts, aiming at the decrease of energy consumption (SEC).

Bioelectrochemical reactors (BERs): the best of both worlds?

The use of microorganisms for the electrochemical synthesis of high-added value products is attracting growing attention³⁶ in the framework of novel “chemical plants” dubbed *bio-electrochemical refineries*. Similarly, microbes are being investigated for their application in fuel cells.^{37,184,185} Catalysis by a microbial biofilm attached to the electrode has several advantages:³⁶

- Versatility.
- Specificity of enzymatic reactions coupled to enhanced stability.
- Self-regeneration of “living” catalytic materials.

The study of the mechanisms of electron transfer is central to current fundamental investigations in microbial bio-electrochemistry;^{35,36,184,186,187} four major electron transfer routes can be mentioned:

- Direct electron-microbe transfer.
- H_2 mediated electron transfer, in which electrochemically generated H_2 carries “reduction equivalents” to the microbe.
- Electron transfer via mediators, in which a reversible electrochemical couple shuttles electrons from the electrode to the biofilm.
- Electron transfer mediated by a metabolic intermediate, which is generated and transferred to the microbe (this route has been demonstrated only for single enzymes).

Ideally, wastewater remediation *via* microbial electrocatalysis could combine the selectivity unique to microbial metabolism with the advantages of electrocatalysis, and the safer use of immobilised bacteria (for example for remediation of drinking water). We now make a brief foray into the state of the art of bioelectrochemical denitrification.

State of the art and challenges

Bioelectrochemical denitrification dates back to the 1990s, when an approach was proposed which involved immobilisation of three enzymes of the nitrogen cycle (nitrate, nitrite and N_2O reductases) and electron-mediating dyes in a polymer matrix attached to a cathode. The electron mediators reacted with atomic H generated at the cathode and transferred it to the enzymes, driving denitrification in a flow reactor.¹⁸⁸

A similar idea underlies the first studies on films of denitrifying bacteria grown on an electrode, which, regardless of their metabolic pathways, can all be “fed” by H_2 which provides the reduction equivalents for the reaction:



The *in situ* generation of H_2 from water electrolysis has several advantages, such as the avoidance of the safety issues related to large volumes of gaseous hydrogen and, ideally, a direct control on the denitrification rate. A first proof-of-concept study was published by Sakakibara and Kuroda,¹⁸⁹ who demonstrated that a microbial film grown on a carbon cathode could be activated

for denitrification of a 0.7 mM nitrate solution by electrical current. The rate of nitrate removal was a function of the amount of current delivered to the electrochemical cell, and dropped to zero once the circuit was opened.

Since this first study, the field of bioelectrochemical denitrification has expanded.^{19,24} In particular, the *in situ* generation of an electron donor (H_2) simplifies the use of *autotrophic* bacteria (otherwise, chemical electron donors such as elemental sulphur or hydrogen sulphide should be added to the reactor), which in principle can tackle a broader range of wastewater types with respect to *heterotrophic* denitrifiers because autotrophic bacteria do not need an artificial enrichment of (industrial) wastewater with an external carbon source. Thus, the use of autotrophic bacteria becomes viable provided that enough CO_2 is available for the bacterial metabolism.¹⁹ The oxidation of graphitic anode materials has been proposed as a possible local source of CO_2 ,^{19,190} otherwise, external supply of this gas would increase the operating costs of the process.

BERs exploiting *in situ* H_2 evolution run with a constant current are by far the most studied. Several reactor designs and electrode materials have been screened and the interested reader is referred to specialised reviews.^{19,24} Here, we will briefly mention that proof-of-concept evidence of constant denitrification performance over more than a year has already been shown.^{191,192} Islam and Suidan demonstrated that a flow reactor, featuring a cylindrical graphite anode surrounded by a cylindrical graphite cathode, could effectively remove nitrate from a diluted (*ca.* 1.4 mM NO_3^-) buffered solution, with no accumulation of by-products. A similar type of simulated wastewater was successfully treated in a multi-electrode flow reactor;¹⁹² every individual cathode is a titanium gauze on which polyurethane foam supports the biofilm. This reactor achieved a constant performance over 500 days, provided that CO_2 was added to buffer the pH around neutrality. Reactors using multiple carbon cathodes have also been proposed.¹⁹³ Overall, carbon might be advantageous because of a more facile adhesion of the biofilm, although consumption (“erosion”) of the cathode is a limiting factor for long-term operation.^{19,191} Generally, these reactors target simple wastewater simulating drinking water or groundwater,¹⁹³ although nitrate-laden wastewater rich in organic matter can also be treated with bioelectrochemical reactors.^{194,195}

Another approach involves the development of a biofilm able to exchange electrons with the cathode (usually *via* a redox mediator).^{196–198} In a typical example, “permeabilised” (*i.e.* dead) cells and a redox mediator attached to a carbon support are enveloped in a calcium alginate matrix to enhance stability.¹⁹⁸ In contrast to other BERs, denitrification is driven by a constant potential. Dead cells are endowed with an intrinsic advantage, as they are mere “containers” for enzymes which do no longer need a carbon source. Recently, it has been demonstrated that Cu powder can directly exchange electrons with cells, thus driving denitrification.¹⁹⁹

Perspectives

BERs have been shown to be suitable for water containing a small excess of nitrate, such as drinking water being treated to meet the legally acceptable nitrate concentration for human consumption²⁰⁰ or slightly polluted groundwater. Their

applicability to actual wastewater, as already noted,¹⁹ is still unproven and few studies target aqueous solution with more concentrated (above 1 mM) nitrate solutions. More attention should be paid to simulated industrial wastewater which, as mentioned above, represents one of the niche applications for which (bio)electrocatalytic denitrification could outperform state-of-the-art biological methods.

Fortunately, there are some exceptions. For example, Watanabe *et al.*^{201,202} have addressed the suitability of a BER for the remediation of copper or lead metal pickling wastewater (0.014 M NO_3^- and a maximum copper concentration of 0.4 mM), acetate being added as an external carbon source. The metal ions are mainly removed through electrochemical deposition at the cathode. Indeed, dead cells could be the best choice in the presence of toxic heavy metals.

There are several other disadvantages and technological challenges concerning bioelectrochemical reactors which thwart their practical application:^{19,203} the scale-up of bioelectrochemical reactors has not been tested, more advanced modelling²⁰⁴ of the processes occurring in the reactor is needed, and the start-up is usually long, unless dead cells are used.

Finally, we mention a novel approach, which involves the combination of energy production and denitrification in so-called microbial fuel cells.^{37,205–207} In its earliest version,³⁷ proposed by Clauwaert *et al.* in 2007, this fuel cell featured “anodic microorganisms” which oxidised CH_3COO^- to CO_2 (acetate being a model for organic carbon), and the electrons delivered to special “cathodic” microorganisms (*Geobacter*), driving NO_3^- reduction. Carbonate was the carbon source for denitrifying microbes. Ideally, this fuel cell would combine the remediation of two types of wastewater, for example, agricultural or domestic wastewater rich in organic carbon in the anodic compartment and nitrate-laden aqueous effluents in the cathodic compartment. Energy production would not be the main aim of this fuel cell; rather, it would represent a compact “wastewater remediation plant” characterised by simpler operation parameters.³⁷ Moreover, the C/N ratio required for operation (which, as we have seen, is a limiting factor for heterotrophic biological denitrification) is usually halved.²⁰⁶

Conclusions

The ever-increasing concerns for nitrate accumulation represent a potent driving force for research on nitrate reduction. As this perspective article has shown, there is no silver bullet for electrocatalytic denitrification: the broad variety of wastewater types or operating conditions requires a large array of *ad-hoc* electrocatalysts or processes. Recently, it has been maintained elsewhere³¹ (with respect to *catalytic* denitrification) that “denitrification process research reached an impasse due to the lack of major contribution in terms of novel catalytic systems”. Broadly speaking, this statement could be extended to electrocatalytic denitrification which, to a certain extent, ostensibly seems to have reached a stage characterized by continuous progress but no “eureka moment” unlocking the full-fledged implementation of this technique.

However, we hope that this perspective article will prove that there can be justified optimism for the future of the field of electrocatalytic denitrification. Indeed, much progress has been

achieved with respect to the fundamental understanding of nitrate reduction, and the foundations for novel findings have been laid out. The *selective* formation of N₂ must be the cornerstone of future research on nitrate reduction; when it comes to achieving 100% selectivity to N₂, electrocatalysis can exploit one of the following routes:

(1) Stepwise NO₃⁻ reduction to N₂ via N₂O (e.g. PdCu).

(2) NO₃⁻ reduction to NO₂⁻ and its ensuing conversion to N₂ (e.g. on a Pt(100) surface, arguably restricted to alkaline pH values).

(3) NO₃⁻ reduction to NH₃ in chloride-containing media, followed by reaction with ClO⁻ to give N₂ (e.g. electrolysis in undivided cells).

(4) Coaxing the bacterial metabolism into NO₃⁻ reduction to N₂, either with electrolytically generated H₂ or with direct electron transfer to bacteria (e.g. bioelectrochemical reactors).

The first three options, which need to bypass the unachievable one-step conversion of NO₃⁻ to N₂, all entail the challenge of steering the reaction selectivity to obtain a molecule more reduced than nitrate, which can efficiently be converted into N₂. This points to the well-known strategy of breaking a lengthy, arduous path into easier, more manageable stages. We note that at least one of these three options (strategy 1) can be operative in the entire pH range.⁹⁴ In some instances, this piecemeal strategy requires securing a weakly bound or labile intermediate to the electrode surface: this is the case of N₂O_{ads} (strategy 1) or NH_{ads} (strategy 2). Otherwise, an oxidising agent may be necessary, as shown by the role of NO_{ads} (strategy 2) or ClO⁻ (strategy 3). Possibly, other oxidisers could be exploited to achieve shortcuts of nitrate reduction leading to N₂. In any case, electrocatalysts featuring multifarious properties will have to be tailored to meet the requirements of strategies 1–3 and to enhance the catalytic conversion of nitrate: examples like PdCu, PtSn, or PtRh alloys are suitable candidates for future investigation. Not only the composition but also the shape (as in the case of Pt(100)) must be kept in mind when designing electrocatalysts. Future research should exploit the opportunity to fan out in several directions, including combinations of “the best of both worlds”, such as the integration of solid and/or molecular catalysts with bioelectrochemical reactors (strategy 4).

As a final remark, the translation of laboratory-scale electrochemical denitrification into viable, efficient large-scale remediation plants remains a crucial issue. For electrocatalysis to become advantageous, these major challenges still must be solved:

- High selectivity to N₂ and low energy consumption under practical conditions (*i.e.* in the presence of reducible metal ions, organic matter, and sulphate ions).

- Long-term operational stability of traditional electrochemical reactors and shorter start-up time of bioelectrochemical reactors.

In the light of the competition from biological denitrification, applied research should probably focus on the development and improvement of *ad-hoc* electrocatalytic remediation reactors specifically targeting wastewater unsuitable for bacterial growth. Industrial liquid wastes, from low-level nuclear wastes to spent plating baths, represent both an opportunity and a challenge for electrocatalytic denitrification.

Acknowledgements

We acknowledge the financial support of the European Commission (through FP7 Initial Training Network “ELCAT”, Grant Agreement no. 214936-2). MD would like to thank Dr Bernardini for proofreading the manuscript, for fruitful discussions and invaluable advice.

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