Electrocatalytic Reduction of Nitrate for Water Treatment Applications

Using Platinoid Catalyst Family

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Overview

Nitrate contamination as a non-point source pollution is a common problem throughout the world. The contamination of nitrate in surface and groundwater poses a major engineering challenge in groundwater management. Nutrients export from residential catchments and agricultural sources contribute to water quality impairment in water bodies. Current processes such as ion exchange, membrane separation have disadvantages and poses engineering difficulty. The objective of this study is to evaluate electrocatalytic reduction process for selective removal of nitrate from groundwater associated with agricultural communities and surface runoff in the urban water bodies. The focus is on electrochemical mechanisms and pathways that led to the formation of ammonium, nitrate and more favourably, nitrogen gas. These pathways include Vetter mechanism, Schmid mechanism, Duca-Feliu-Koper mechanism, Vooys-Koper mechanism. (*1*)

Intellectual Merit

Nitrogen is essential to all life-forms but a wrong form at the wrong place can be very detrimental. The synergistic effect that Nitrogen has with other anions and cations can lead to the formation of carcinogens. Nitrate in drinking water can lead to methemoglobinemia which oxidizes haemoglobin's ferrous ions and consequently disabling oxygen transport mechanisms of the RBCs. Other form such as ammonia and nitrite lead to the formation of Disinfection By-Products in the drinking water with reaction with residual chlorine used for disinfection. It is worth noting that Ammonia (NH^{4+}/NH_3; $pKa = 9.25$) is easily transformed via biotic and abiotic processes to nitrate, nitrite and nitrogen gas in the environment. (*2*) However, nitrate pollution due to anthropogenic activities such as fertilizer runoff from agricultural lands, stormwater runoff from urban surfaces and discharge of sewage or treated wastewater have dramatically increased the available nitrogen in the groundwater ecosystem leading to imbalance of the natural nitrogen cycle. This has led the US National Academy of Engineers to identify the efficient management of the nitrogen cycle in water as one of the Grand Challenges for the 21st century. (*1*)

Broader Impacts

Nitrates due to their high mobility and solubility in water can easily combine to give rise to undesirable by-products, some having relatively higher toxicity to the human body. To minimize the adverse health impacts, Environmental Protection Agency (EPA) has promulgated Maximum Contaminant Level of 10 mg/l as $N-NO_3^-$. More than 40 million people in the US don't have access to municipal-treated water. Even in China, India, and Europe, nitrogen contamination of groundwater is widespread. Thus, a need for efficient nitrate removal technology arises. Electrochemical reduction can be an effective and efficient method of water-treatment systems for point-of-use (POU) treatment systems within homes. (*3*)

Further on, we shall be discussing about the catalysts used in the electrochemical denitrification of waste water. Electrochemical nitrate removal is the most efficient removal technique from the ecological point of view as the toxic nitrates can easily get converted into harmless nitrogen gas. The other common technologies used for nitrate removal include physico-chemical, biological and acatalytical processes. However, the physico-chemical technologies only remove the nitrates from water into brine which has to either be treated afterwards or has to be disposed of. Other advantages of electrochemical methods with respect to physico-chemical technologies like Reverse osmosis or ion exchange are lower cost, less space requirement, less sludge production and fewer chemicals required. Biological denitrification, although reduces nitrates to nitrogen, are extremely slow processes, sometimes incomplete and definitely not easy to handle.(*3*)

What are supported catalysts?

Supported catalysts are prepared by deposition of the active metal on the support materials. This is most importantly done to obtain an optimal dispersion of the catalytically active component and to stabilize it against sintering.

Supported catalysts are prepared in two main steps:

1. Deposition of the precursor of the active component on the support.
2. Transformation of this deposited precursors to catalytically active site.

Catalyst Preparation

1. Wet impregnation: A Pd(5%)/Al2O3 catalyst is served as a base for the preparation of the bimetallic impregnation catalyst. The Pd catalyst in suspended in a solution of the second metal nitrate. The water was then evaporated under heat. The catalyst was then activated under hydrogen or nitrogen gas stream. (*4*)

2. Deposition/Precipitation: The alumina support material was calcined. Then, it was suspended in Sodium Carbonate solution for 15 minutes. By dropping a 1.4% Na2PdCl4-solution slowly into the suspension, the Pd was allowed to precipitate and deposit onto the support under vigorous stirring. After that, the second metal was introduced in the desired amount as a metal chloride solution in the same manner. The

catalyst was finally reduced by adding sodium formate at about 80∘C. The catalyst was dried overnight. (*4*)

3. Controlled surface reaction with Sn(n-butyl)4: In this method, the previously prepared Pd/Al2O3-catalyst was saturated with hydrogen in gas phase By dropping a solution of Sn(n-butyl)4 in n-hexane to the catalyst the Sn(n-butyl)4 was led to react with the Pd–H groups at the catalyst surface. Following that, the catalyst was then reduced with hydrogen. (*4*)

4. Controlled surface reaction with Sn(HCOO)2: The preformed Pd/Al2O3-catalyst was suspended in 25 ml of 0.01 mol H2SO4 and 1 ml of 98% HCOOH. The second metal was introduced as a metal sulfate dissolved in sulphuric acid. Sn(HCOO)2 decomposes at the Pd surface thereby generates the bimetallic sites. After this, the catalyst was dried. (*4*)

In this case, two types of bimetallic catalysts were prepared i.e., **Pd-Cu and Pd- Sn**. Here, nitrates are further reduced to nitrites and then ammonium ions. As per the paper, very less amount of nitrites is released when Pd-Sn when compared to Pd-Cu. In addition, the nitrites released are converted to nitrogen with a much higher rate than with the Pd–Cu catalyst, so that the nitrate reduction to nitrogen can be regarded as complete. Therefore, the nitrogen formation activity of the Pd–Sn catalyst is about 10 times higher than for the Pd–Cu catalyst.
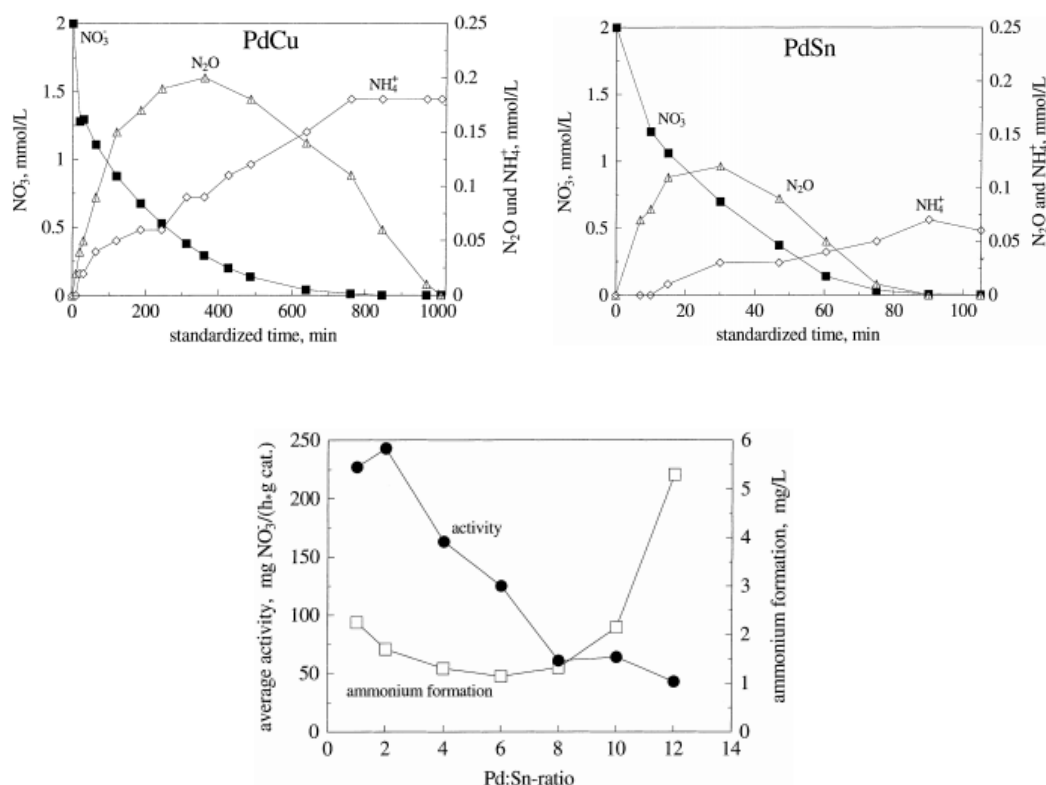

Figure 1: Concentration-time-curves of nitrate, nitrous oxide and ammonium for the nitrate reduction with hydrogen using a Pd(5%) Sn(1.25%)/Al2O3 catalyst, Pd(5%)Cu(1.25%)/Al2O3 catalyst prepared by the deposition/precipitation method and the variation with Pd to Sn ratio

From this, it is clearly evident that the activity of Pd-Sn catalyst can be clearly characterized by their nitrate removal activity. But this is not the case in a Pd-Cu catalyst. (*5*)

For the reduction of nitrites to nitrogen gas or ammonium complex, various hydrogenation catalysts were tested. The highest activity was obtained using the Pt catalyst. On iridium and rhodium catalysts, nitrite is completely reduced to ammonia. Only the palladium catalyst is suitable for a selective nitrite reduction to nitrogen. (*5*)
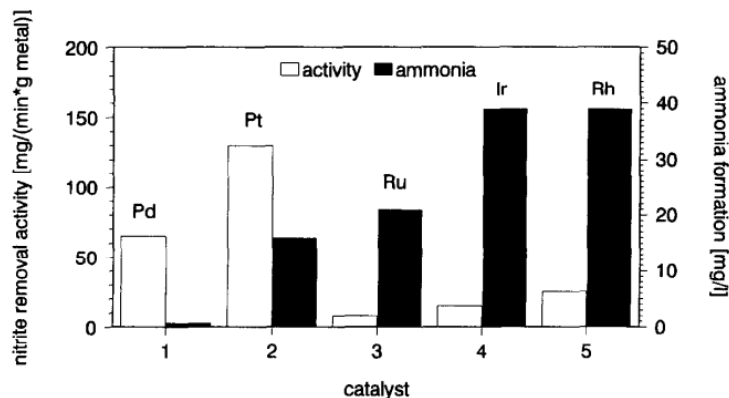

Figure 2: Nitrite removal activity and ammonia formation of various hydrogenation catalysts 1. Pd(5%) on alumina, 2. Pt(5%) on carbon, 3. Ru(.5%) on alumina, 4. Ir(2%) on alumina, 5. Rh(2%) on alumina

Next, an alumina support was impregnated with solutions of different palladium compounds. The commonly used palladium-precursor is palladium chloride. As we can see from the graph, the nitrite removal activity and the selectivity of the catalysts were poor when using palladium chloride. (*2*) We obtained higher activity rates preparing the catalysts with tetraaminopalladiumhydroxide instead of palladiumchloride or –nitrate. This was because of the better adsorption of the cationic tetraaminocomplex compared to the anionic tetrachlorocomplex.
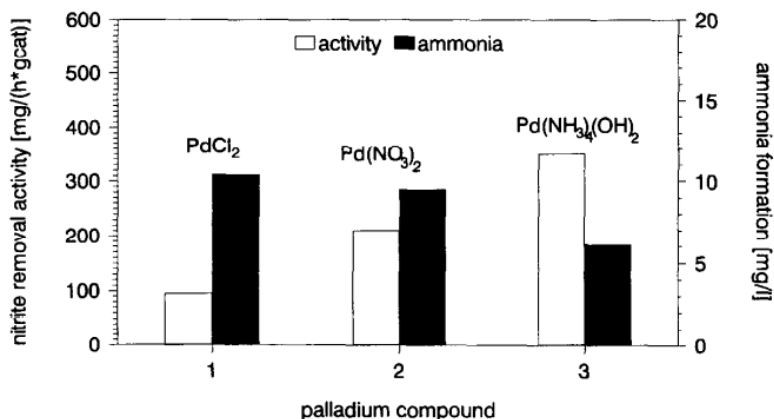

Figure 3: Influence of the palladium compound on the catalyst activity and selectivity. Alumina support was impregnated with solutions of different palladium compounds

The supports with the lower surface area are more favourable due to the higher nitrogen selectivity.
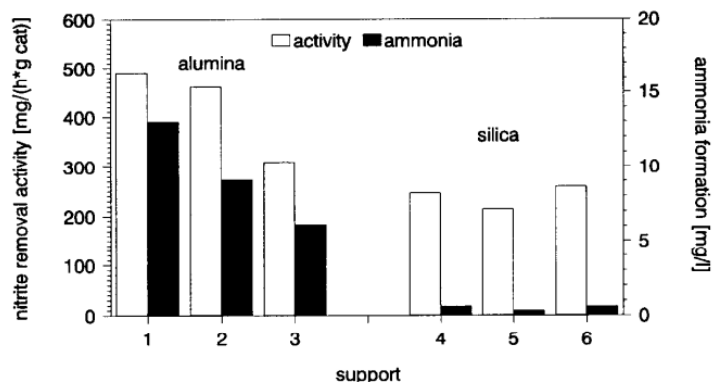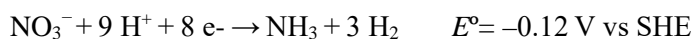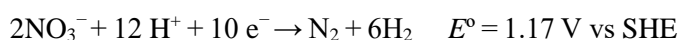

Figure 4: Alumina and silica supports for nitrite reducing palladium catalysts (2% palladium). 1) Al 3972 2)Al 3984. 3)Al 0174 4)300 MP, 5) 500 MP, 6)1000 MP

To conclude, by increasing tin content of the catalyst (decreasing Pd : Sn ratio) the nitrate removal activity increases.. It becomes obvious, that the nitrate reduction takes place at active sites containing tin, which are suspected to be real bimetallic sites. On the other hand, the ammonium formation is increasing significantly with decreasing tin amount, i.e., increasing palladium content of the crystals and also the surface. Therefore, it is clearly evident from the above that the selectivity is determined not by the tin-containing (bimetallic) sites but by monometallic palladium sites known to be also present at the catalyst's surface.

Mechanism

The mechanisms for electrochemical conversion of nitrate to nitrogen gas are complex. It involves numerous reactions, products and stable intermediates (e.g., ammonia, nitrite, hydrazine, hydroxylamine, nitric oxide, nitrous oxide) spanning the many nitrogen oxidation states (from -III up to + V). The graphs given below, i.e., the Frost-Ebsworth diagram and Pourbaix diagram for nitrogen species illustrate that N_2 and NH_3/NH_4^+ are the thermodynamically most stable forms of nitrogen under standard conditions, especially drinking waters which have pH levels between 6–9. Even though both species would be expected as preferred end products following reactions, there are several factors such as electrodic material or crystal planes that can alter the final products of electrochemical reduction. (*1*)
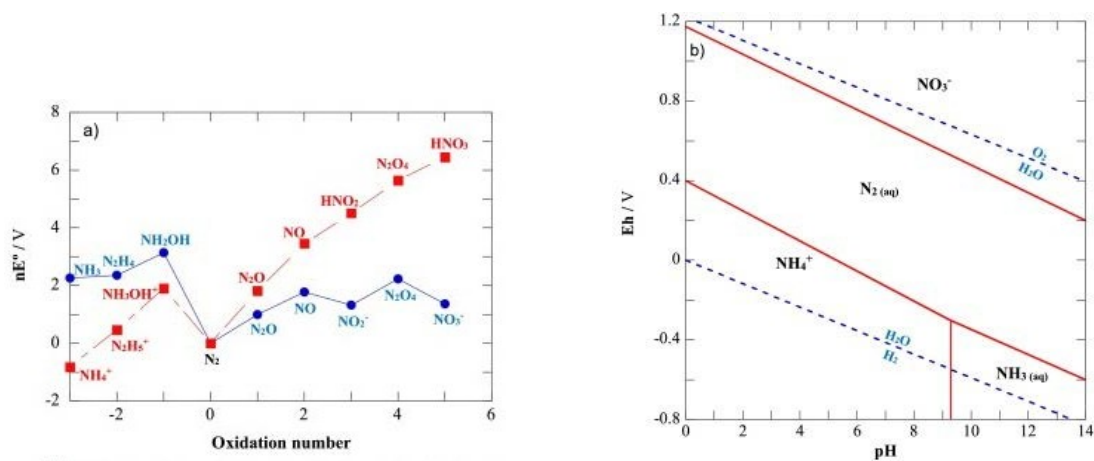
$2NO_3^- + 12\,H^+ + 10\,e^- \rightarrow N_2 + 6H_2$ $E^o = 1.17$ V vs SHE

$NO_3^- + 9\,H^+ + 8\,e- \rightarrow NH_3 + 3\,H_2$ $E^o = -0.12$ V vs SHE

Figure 5: Frost Ebsworth diagram showing the stability of N2 and Fig2: Pourbaix diagram to prove the stability of N2 and NH4+/NH3 (*1*) NH4+/NH3 (*1*)

The mechanistic reduction pathways involving multiple species studies were inculcated into a single flow diagram. The following diagram summarizes groups of these pathways. (*1*)
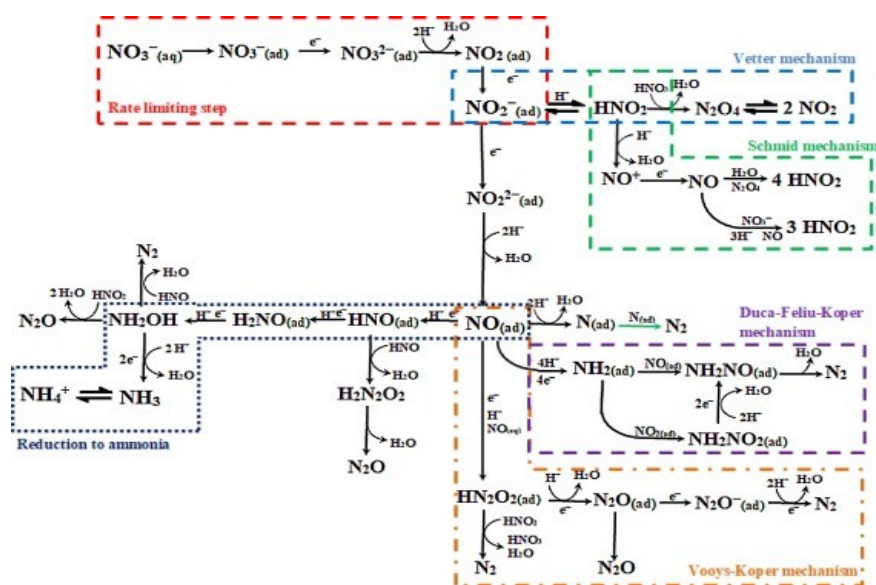

Figure 6: Mechanisms and main processes during electrochemical reduction of nitrite in water. The overall mechanism is divided into different mechanisms to enhance the understanding and facilitate the description as: Rate limiting step, Vetter mechanism, Schmid mechanism, Duca-Feliu-Koper mechanism, Vooys-Koper mechanism and Reduction to ammonia. (*1*)
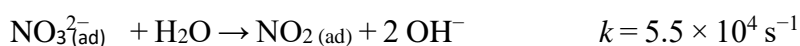
Proposed Mechanism

The reduction of nitrate to nitrite is the main rate determining step and is the main barrier to efficient nitrate removal from water. Nitrite is the main quasi-stable intermediate during electrochemical reduction of nitrate before its complete reduction to ammonia or nitrogen gas. The high activation energy requirement is confirmed by the slow reduction kinetics of nitrate to nitrite. (*1*)
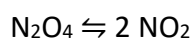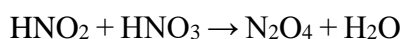
$$NO_3^- + 2\,H^+ + 2\,e^- \rightarrow NO_2^- + H_2O \qquad E^o = 0.01 \text{ V vs SHE}$$
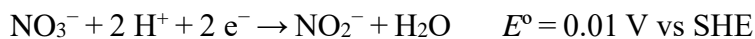
$$K1 = [NO_{2-}]/[NO_{3-}][H_+]^2$$

The elementary charge transfer reactions of one electron per step result in the formation of adsorbed short-lived intermediates. The reduction of nitrate to nitrite counts for a three-step electrochemical-chemical-electrochemical (ECE) mechanism. (*2*)
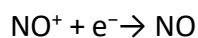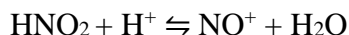
$$NO_3^-{}_{(ad)} + e^- \rightarrow NO_3^{2-}{}_{(ad)} \qquad\qquad E^o = -0.89 \text{ V vs SHE}$$

$$NO_3^{2-}{}_{(ad)} + H_2O \rightarrow NO_{2\,(ad)} + 2\,OH^- \qquad\qquad k = 5.5 \times 10^4\ s^{-1}$$

$$NO_{2\,(ad)} + e^- \rightarrow NO_2^-{}_{(ad)} + H_2O \qquad\qquad E^o = 1.04 \text{ V vs SHE}$$

In the case where electrochemical nitrate reduction is carried out at acidic pH and at really high reactant concentrations of 1.0–$4.0\ M\ NO_3^-$, a secondary pathway for nitrate reduction to nitrite, which simultaneously occurs, may emerge if HNO_2 is present in catalytic concentrations ($> 10^{-6}\ M$).This mechanism is important because it can accelerate the nitrate reduction rates and increase faradaic efficiencies, thus reducing operational costs if strategically used. The autocatalytic reduction of nitrate is considered an indirect reduction mechanism because the nitrate is not the electroactive species, although the overall reaction reduces nitrate to nitrous acid. Therefore, by considering different leading electroactive species in the catalytic cycle leads us to two possible autocatalytic cycle mechanisms are the Vetter mechanism and Schmid mechanism. (*1*)

The Vetter mechanism involves NO_2 . as the electroactive species in the autocatalytic cycle. The electrochemical reduction yields a nitrite anion. This nitrite ion further protonates to form nitrous acid. This nitrous acid further reacts with nitric acid to form dinitrogen tetraoxide and that further disproportionates further to form two of the electroactive species. (*1*)
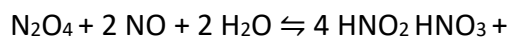
$$NO_2^- + H^+ \leftrightharpoons HNO_2 \qquad\qquad pK_a = 3.4$$

$$HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O$$

$$N_2O_4 \leftrightharpoons 2\,NO_2$$

In contrast, the Schmid mechanism involves nitrosonium cation (NO^+) as the electroactive species in the autocatalytic cycle. The NO^+ initially originates from the protonation of nitrous acid in highly acidic environment. The electrochemical NO^+ reduction yields nitric oxide (NO) in the bulk. Two NO species

react with N_2O_4 in aqueous media to form 4 mols of HNO_2. These NO molecules can also react with HNO_3 in aquaeous media to form 3 mols of HNO_2. (*1*)

$$HNO_2 + H^+ \leftrightharpoons NO^+ + H_2O$$

$$NO^+ + e^- \rightarrow NO \qquad\qquad E^\circ = 1.28 \text{ V vs SCE}$$

$$N_2O_4 + 2\,NO + 2\,H_2O \leftrightharpoons 4\,HNO_2 \; HNO_3 +$$
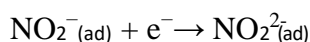
$$2\,NO + H_2O \leftrightharpoons 3\,HNO_2$$

Both mechanisms occur only in highly acidic conditions below nitrate concentrations of 4.0 M where nitric acid usually naturally decomposes. At nitric acid concentrations > 4.0 M, the equations below are further shifted to the right. This leads to the generation of NO and N_2O_4. Even though both NO and N_2O_4 species could lead to HNO_2 formation, this occurs without requiring electrochemical charge transfer reactions. Therefore, these reactions cannot be considered a part of an indirect electrochemical reduction of NO_3^- within an autocatalytic cycle as discussed above.(*2*)

$$2HNO_3 \leftrightharpoons 2\,NO + 3/2\,O_2 + H_2O$$

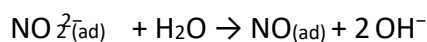$$2HNO_3 \leftrightharpoons N_2O_4 + 1/2\,O_2 + H_2O$$
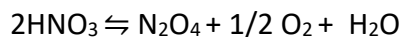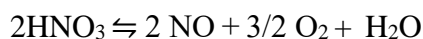
Nitrite is the first stable intermediate produced during nitrate reduction. However, further electrochemical reduction can yield both undesirable (e.g., NH_4^+) or the desired and innocuous (i.e., N_2) products. (*3*)

The electrochemical reduction of NO_2^- leads to the formation of a dianion radical NO_2^2. The dianion radical, NO_2^{2-} quickly hydrolyzes and produces adsorbed $NO_{(ad)}$.

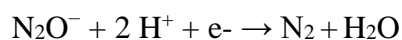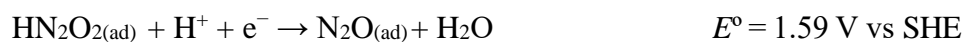$$NO_2^-{}_{(ad)} + e^- \rightarrow NO_2^{2-}{}_{(ad)} \qquad\qquad E^\circ = -0.47 \text{ V vs SHE}$$

$$NO_2^{2-}{}_{(ad)} + H_2O \rightarrow NO_{(ad)} + 2\,OH^-$$

Formation of $NO_{(ad)}$ is central for selective by-product formation. The adsorbed nitrogen reacts with a second nitrogen atom to form nitrogen gas.

$$NO_{(ad)} + 2\,H^+ + 2\,e^- \rightarrow N_{(ad)} + H_2O \qquad N_{(ad)} +$$

$$N_{(ad)} \rightarrow N_2$$
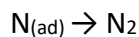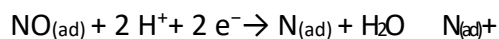
In contrast, the Vooys-Koper mechanism is experimentally based on differential electrochemical mass spectroscopy (DEMS) conducted during NO electrochemical reduction kinetic experiments. The Vooys-Koper mechanism involves an initial elementary electrochemical reaction where adsorbed and dissolved NO forms diazeniumdiolate (HN_2O_2). This is an Eley-Rideal type reaction, where adsorbed NO reacts with a solvated NO species which is further reduced to Nitrogen gas. (*3*)

$$NO_{(ad)} + NO_{(aq)} + H^+ + e^- \rightarrow HN_2O_2 \qquad E^o = 0.0 \text{ V vs SHE}$$

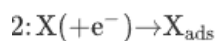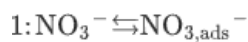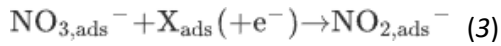$$HN_2O_{2(ad)} + H^+ + e^- \rightarrow N_2O_{(ad)} + H_2O \qquad E^o = 1.59 \text{ V vs SHE}$$

$$N_2O + e^- \rightarrow N_2O^- \qquad E^o = 1.77 \text{ V vs SHE}$$

$$N_2O^- + 2 H^+ + e^- \rightarrow N_2 + H_2O$$
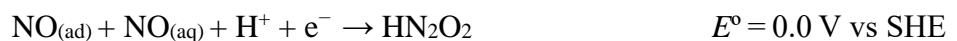
Due to the high solubility of N_2O in water ($K_H = 25$ mmol L^{-1} atm^{-1} at 15 °C), solubilized N_2O would be mostly susceptible to be reduced after re-adsorption. (*4*)

One of the greatest achievements related to nitrite electrochemical reduction mechanisms is the understanding of the Duca-Feliu-Koper mechanism that demonstrates an alternative and highly feasible N_2 formation deduced from the selective catalytic reduction at quasi-perfect Pt(100) domains.

Reaction Conditions

The conversion of nitrate to nitrite is the rate-determining step at low as well as high concentrations. At low concentrations the reaction rate is determined by the amount of adsorbed nitrate, at high concentrations the negative reaction order for potentials higher than 0.1 V combined with the positive reaction order below 0.1 V is highly suggestive of the idea that an adsorbed species reacts with adsorbed nitrate. This adsorbed species could be either water, hydronium, or hydrogen. The negative reaction order for potentials higher than 0.1 V can be explained by the fact that adsorbed nitrate blocks the adsorption of this species ''X'' and therefore impedes the reaction:

$$1: NO_3^- \leftrightarrows NO_{3,ads}^-$$

$$2: X(+e^-) \rightarrow X_{ads}$$

$$NO_{3,ads}^- + X_{ads}(+e^-) \rightarrow NO_{2,ads}^- \quad (3)$$

Both at high and low concentrations the nitrite formed is immediately converted into adsorbed NO,

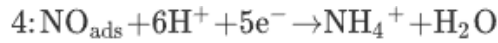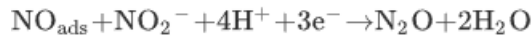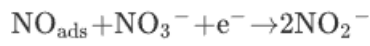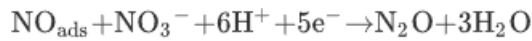$$3: NO_{2,ads} + 2H^+ + e^- \rightarrow NO_{ads} + H_2O$$
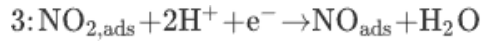
Finally, the nitrate reduction on platinum is mainly selective towards ammonia at both low and high nitrate concentrations.

$$4: NO_{ads} + 6H^+ + 5e^- \rightarrow NH_4^+ + H_2O$$

In solutions with high nitrate concentration and acidity, small amounts of N_2O and N_2 are formed at potentials between 0.4 and 0.2 V. This gas formation can be related to the NO_{ads} coverage, which also has a maximum in the same potential region. The NO_{ads} coverage depends on the supporting electrolyte, the nitrate concentration and the acidity of the solution. For NO_{ads} coverages below 0.2 (based on available hydrogen sites) no gases are observed. (3) This explains why only N_2 and N_2O formation is observed in solutions of high nitrate concentration and acidity.

$$NO_{ads} + NO_3^- + 6H^+ + 5e^- \rightarrow N_2O + 3H_2O$$

$$NO_{ads} + NO_3^- + e^- \rightarrow 2NO_2^-$$

$$NO_{ads} + NO_2^- + 4H^+ + 3e^- \rightarrow N_2O + 2H_2O$$

Finally, in this potential region (0.4–0.2 V) the N_2O produced can react to N_2,

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$$
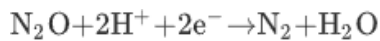
Is the reaction diffusion limited or reaction limited?

The initial steps of the electrocatalytic reaction as mentioned before, involves the conversion of nitrates to nitrites. The mass transfer of nitrate from bulk to the electrode surface limits nitrate adsorption, surface-bound nitrate concentrations and ultimately, the overall electrochemical nitrate reduction rate. Electrochemical nitrate reduction is a mass transfer limited process, and consequently the nitrate concentration is relevant because it defines the diffusion rate from solution towards the cathode surface according to Fick's law. During the treatment of high nitrate concentrations, the amount of free surface catalytic sites on the electrodes determines the achievable reaction rate. (6)
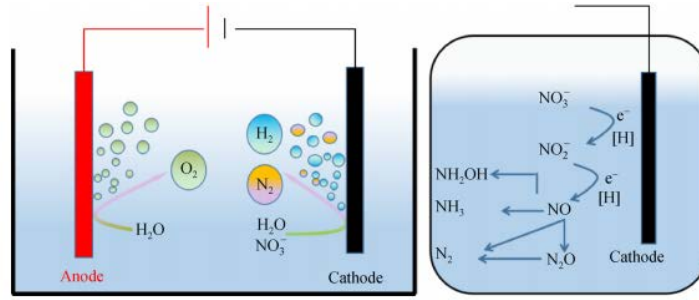
Figure 7: Electrochemical denitrification technology

In the paper that we have used to determine if the reaction is diffusion limited or reaction limited, the catalysts used are copper catalysts. Copper catalysts are better suitable to be used in alkaline medium. This is in contrast to the Platinoid catalysts which are usually used in acidic media. In this case, copper catalysts have higher electrocatalytic activity in a strongly alkaline medium or even in hydrogen carbonate solutions. $NaHCO_3$ is the electrolyte used in this case as bicarbonate ions are much better for water treatment when compared to chlorine or sulphate ions.

As mentioned before, mass transfer to the cathode is the driving force for the electrocatalytic denitrification reaction.

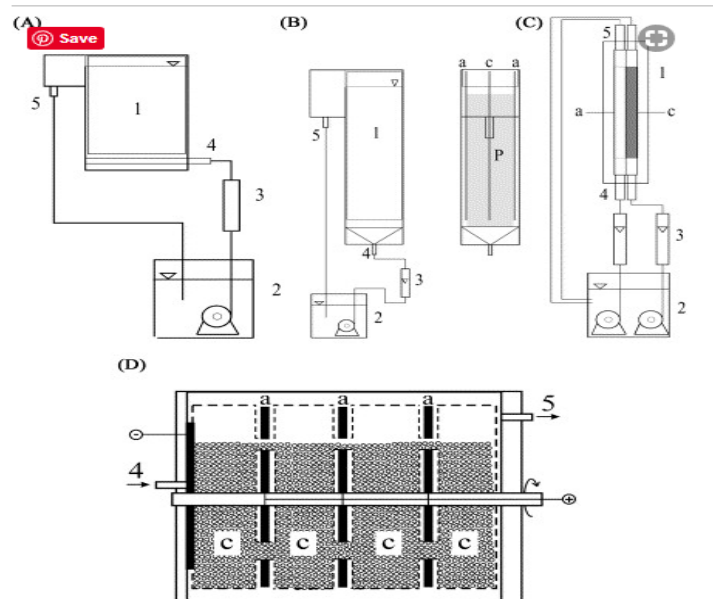Figure 8: (A) Plate-electrodes cell, (B) cell with fluidising bed of inert particles, (C) packed bed cathode cell, and (D) VMPB cathode cell. 1: electrolytic cell; 2, 3: electrolyte reservoir and flow meter; 4, 5: electrolyte inlet and outlet; a—anode; c—cathode; P—inert particles.(7)

The mass transfer coefficient, k for the electrolyte laminar flow between the plate electrodes can be calculated as,

$$Sh = 1.85\left(\frac{d_e}{L} \cdot Re \cdot Sc\right)^{1/3}$$

For the mass transfer coefficient to the plate electrodes immersed in the fluidized bed of inert particles,

$$j_D \varepsilon = 0.28 \cdot \left(\frac{Re_\phi}{1-\varepsilon}\right)^{-0.36}$$

where,

$$j_D = \frac{k}{v} \cdot Sc^{2/3}$$

$$Re_\phi = \frac{d_p v}{v_e}$$

In case of a 3D electrode, the variation of electroactive species along the electrode has to be considered. So, from mass balance we obtain,(6)

$$c_y = c_0 \cdot \exp\left(-\frac{a \cdot k}{v} \cdot y\right)$$

Further on, the current density can be calculated using the above equation;

$$\bar{j}_b = \frac{nFhv}{L} c_0 \cdot \left[1 - \exp\left(-\frac{ak}{v}L\right)\right]$$

The mass transfer coefficient k, can be finally calculated by the culmination of the above equations and thereby,

$$k = 1.875 \cdot v \cdot Re_p^{-0.55} \cdot Sc^{-2/3}$$

Factors Affecting the Electrocatalytic Reaction

1. Electrode material:

 Different electrodes have been used to test the activity and the reduction of nitrates. Electrodes can be of two types: metal electrodes or non-metal electrodes.In some of the papers, Boron doped diamond electrodes, graphite electrodes, Rh-graphite electrodes, etc… But these non-metallic catalysts have been found to possess low nitrogen selectivity and low reduction. Metallic catalysts, on the other hand have been found to have higher Nitrogen selectivity and higher reduction potential. For eg., bimettalic catalysts like Pt-Sn, Pd-Sn are efficient nitrate reduction catalysts. In this case, Pt and Pd protects the Sn from corrosion and enhances the nitrate reduction potential and Nitrogen selectivity. Cu cathode has poor nitrogen generation.(*8*)

2. Potential:

It is clearly evident from the published papers that by enhancing the potential of Cu electrodes from -1.1V to -1.4V increases the nitrate reduction on the electrode. However, lowering the potential can increase the selectivity of the catalysts to generating ammonium ions. This is not acceptable. The different product selectivity was attributed to the different demands for electrons of products. However, when the potential was higher than a certain value, the electroreduction efficiency of nitrate decreased. When the potential was enhanced from -1.8 V to -2.0 V, the electrocatalytic reduction rate of nitrate over graphite cathode decreased. The lower efficiency was because of the strong inhibition by hydrogen evolution limiting the nitrate reduction.(*8*)

3. pH:

Again, it can be seen that the pH conditions of the entire medium depends on the kind of electrode used as a catalyst. This, in turn determines the electrocatalytic reduction of nitrates. For eg., Pt catalysts only work efficiently in acidic medium and copper catalysts work well in alkaline medium.

The reduction rate of nitrate increases with increase in the proton donating ability of the proton donor. It decreases in the order of $H_2O < NH_4 + < H_3O+$. In acidic condition, where the proton donor is the hydronium cation, the reduction rate of nitrate is expected to be proportional to the concentration of the hydronium cation. This explains why a pH above 5 would be unsuitable for Pt catalysts.(*8*)

4. Distance between the electrodes:

Increasing the distance between electrodes increases electric resistance against the current flowing between anode and cathodes. So, as the electrode gap becomes less, mixing rate of the fluid between electrodes reduces and thereby, cannot provide sufficient concentration polarization layer on electrode

surface. This, in turn, increases electric potential or resistance of electrodes, diminishing the NO3 – removal efficiency subsequently.(*8*)

5. Flow Rate:

The flow rates and the applied high voltages are responsible for occurrence of concentration polarization owing to the existence of boundary layers near the membrane surfaces. In previous papers, it has been found that the electrocatalytic reduction of nitrate increased with increasing the flow rate of feed. This is due to the decrease in the thickness of the boundary layers adjacent to the membrane surfaces (static zones of solutions) with increasing solution velocity. The thickness of the boundary layer gives us an idea about the ion transportation.(*8*)

6. Temperature:

Temperature is an important parameter in the electrolytic reduction of nitrates in water. Many researches have proved that the electrolysis efficiency of nitrate increased with increasing temperature. The increase in the removal efficiency of nitrate with temperature is due to the increase in the ion mobility and thereby enhances the mass transfer of the nitrate ions to the catalyst surface. (*8*)

Poisoning of the Catalyst

Catalyst poisoning refers to the partial or total deactivation of a catalyst by a chemical compound. It is generally undesirable, but could be helpful when it results in improved catalyst selectivity (e.g. Lindlar's catalyst).

Poisoning involves chemisorption of the reactant/product or feed impurities to the active surface sites of a catalyst. In electrocatalysis, if undesirable chemical species compete to be reduced or oxidized at the electrodes, they can be regarded as poison. A poison tends to decrease the number of catalytic sites or the fraction of the total surface area thus decreasing the reaction kinetics. In some cases, poisoning leads to the total deactivation of the catalyst. Poisoning differs from fouling in the sense that the latter involves physical deposition of substance on the active sites of catalysts. Carbon deposition on catalysts for fractional distillation of petroleum is an example. While poisoning can be reversible or irreversible, fouling is most of the cases is partially reversible.

A qualitative way to explain the poisoning processes is Sabatier Principle. It states that in order to have high catalytic activity, the interaction between reactants and catalysts should neither be too strong nor too weak. Catalytic sites must bind the adsorbates strong enough to enable activation of reactants. However, the binding strength of the reaction by-products should be weak enough to favor desorption, thus avoiding catalyst poisoning. The binding of reaction by-products generally involves a 'competing effect' on the electrode by these species. This competing species interaction results in the sluggish

kinetics in the electroreduction of nitrate. The species responsible for poisoning in this case include mainly hydrogen. Sulfates can also interfere with the reaction if the electrolyte used is sulfuric acid.

Understanding Poisoning

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement. where the working electrode potential is ramped linearly versus time. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. These cyclic voltammograms give good idea of activity of the catalyst.
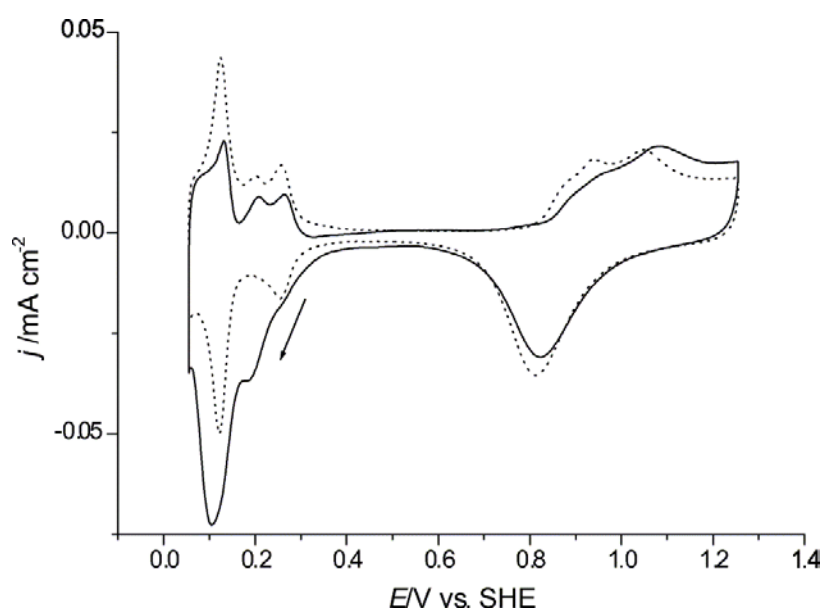

Figure 9: Cyclic voltammograms of 0.5 M H2SO4 (dotted line) and 0.1 M NaNO3 in 0.5 M H2SO4 (solid line) on a Pt flag electrode. Scan rate: 20 mV/s. (*9*)

Figure 9 shows a typical cyclic voltammogram of the direct nitrate reduction at low concentrations (0.1 M NaNO3). The reduction starts at potentials below 0.4 V. The inhibition of the reaction below 0.1 V, which has been ascribed to the increasing surface coverage of H_{ads} and hence the impossibility for NO_3^- to adsorb on the surface. (*3*)

Dependence of Reaction Rate on Nitrate Concentration

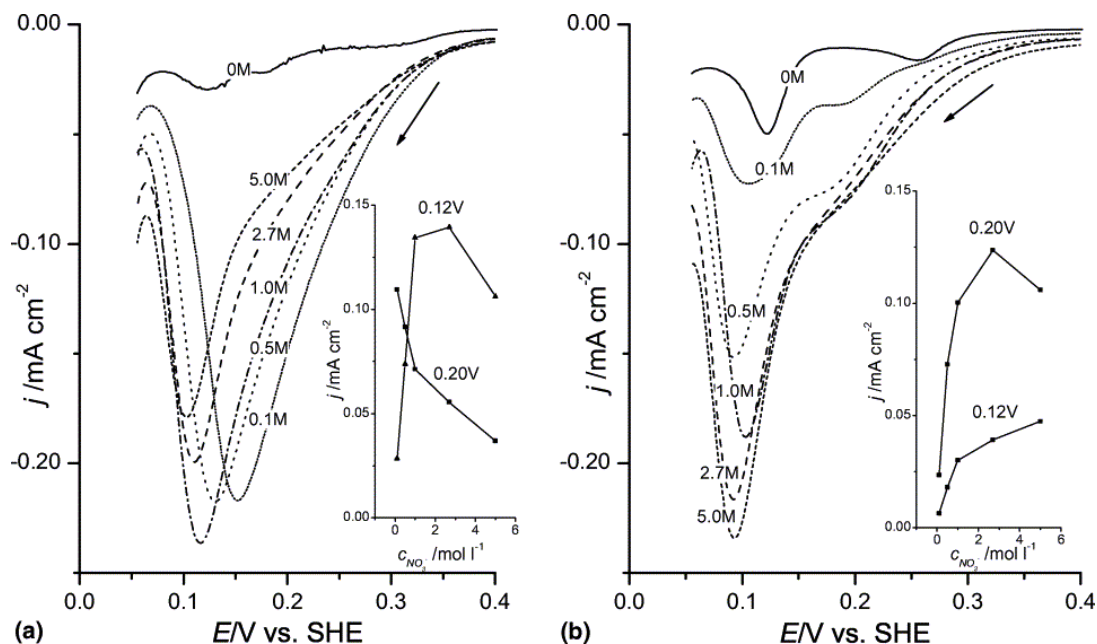*Concentration dependence for nitrate concentrations greater than 0.1 M*

Figure 10: Cyclic voltammograms of NO3− reduction in 0.5 M HClO$_4$ (a) and 0.5 M H$_2$SO$_4$ (b) at different NO$_3^-$ concentrations: 0 M (solid), 0.1 M (short dot), 0.5 M (dot), 1.0 M (dot-dash), 2.7 M (dash), 5.0 M (short-dash). Scan rate: 20 mV/s. Insets: stationary currents, measured after 200 s at 0.2 V (■) and 0.12 V (▲) (*9*)

Figure 10 shows the concentration dependence for higher nitrate concentrations (>0.1 M) in perchloric acid and in sulfuric acid. Perchloric acid is used to avoid co-adsorption of anions from the electrolyte on the surface. Figure 10(a) shows that there is a negative correlation between the current and the nitrate concentration for potentials between 0.35 and 0.15 V and a shift in the maximum of the current to lower potentials with increasing nitrate concentration. However, for potentials below 0.08 V there is again a positive correlation between the current and the nitrate concentration. The negative correlation between the current and the nitrate concentration implies a negative reaction order in nitrate which is caused by the fact that nitrate adsorbates (NO$_3^-$$_{ads}$ and NO$_{ads}$) block the surface for the adsorption of hydrogen or water. The maximum indicates the potential where the hydrogen adsorption becomes strong enough to prevent nitrate adsorption. Below this potential the nitrate adsorbates are no longer the dominant species on the surface and the increasing hydrogen coverage reduces the number of surface sites available for the reduction leading to the drop-in reaction rates.
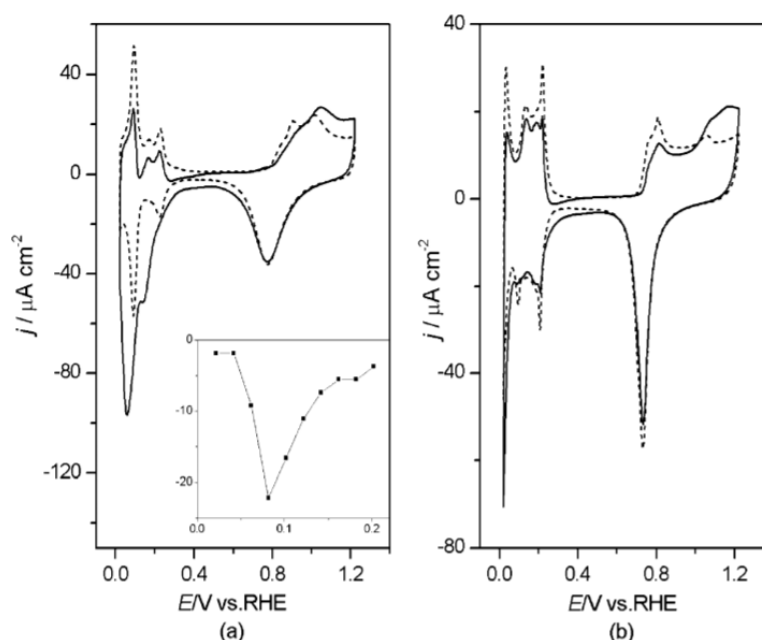
Figure 11: Cyclic voltammograms at 20 mV s1 of Pt (a) and Pd (b) in 0.5 M H2SO4 (dashed line) and 0.5 M H2SO4/0.1 M NaNO3 (solid line). Inset in figure (a) is the steady-state nitrate reduction current as a function of potential. (*10*)

At concentration less than 0.1 M for nitrate, the voltammogram follows a similar trend. The nitrate reduction is inhibited at low potentials, by hydrogen co-adsorption, as is suggested by the inset in Fig. 11(a). On the other hand, Fig. 11(b) shows cyclic voltammograms for a palladized Pt electrode. The solid curve represents the nitrate reduction. Because of the height of peak is less than that in the Fig 3(a), this electrode shows very little activity towards NO_3^- reduction. (*11*)

Influence of Anions

Figure 10(b) shows the effect of an increasing nitrate concentration in sulfuric acid. As mentioned before, Perchloric acid is used to avoid co-adsorption of anions. On the other hand, sulfuric acid interferes with the nitrate adsorption and as a result the concentration dependence is markedly different from perchloric acid. (*9*)

At low nitrate concentrations, the reaction rate is much lower in sulfuric acid than in perchloric acid. This can be explained by the fact that sulfate occupies many active sites on the catalysts and only a limited number of free sites is available for nitrate to adsorb. At high nitrate concentrations, nitrate is much better able to compete with sulfate and reaction rates in sulfuric and perchloric acid are similar. Figure 12 demonstrates this. (*9*)
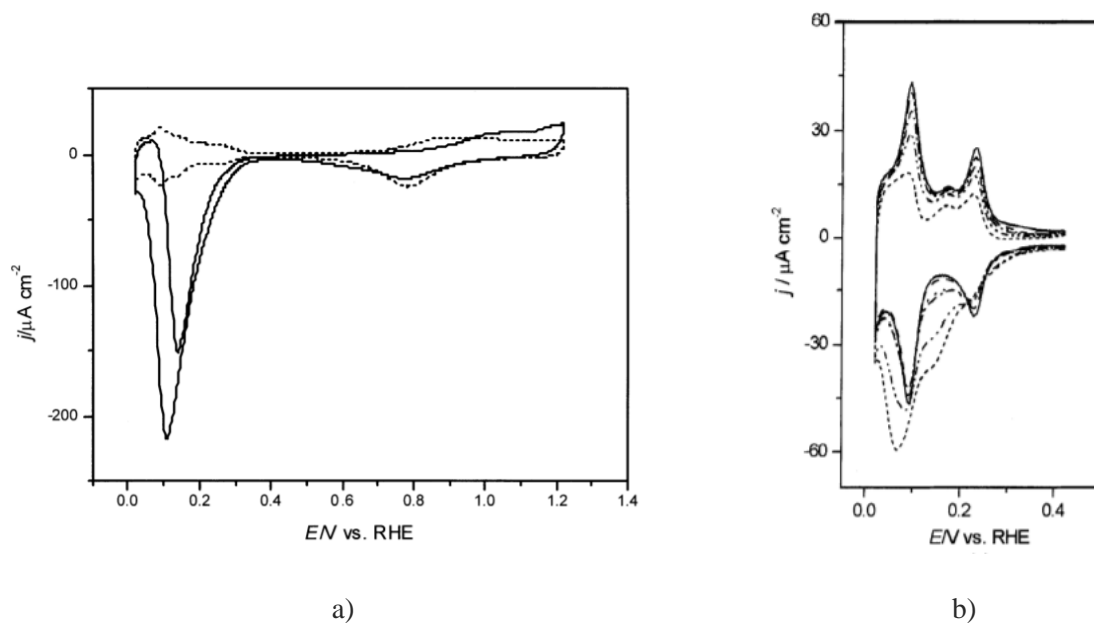
a)

b)

Figure 12: a) Cyclic voltammograms at 20 mV/s for a Pt electrode in 0.5 M HClO$_4$ (dashed line) and 0.5 M HClO$_4$/0.1 M NaNO$_3$ b) Cyclic voltammograms of the NO$_3^-$ reduction on a Pt electrode at different concentrations (0.001, 0.005, 0.01, 0.05, and 0.1M) in 0.5 M H$_2$SO$_4$ (*9*)

Effect of Different Cathodic Catalyst Materials
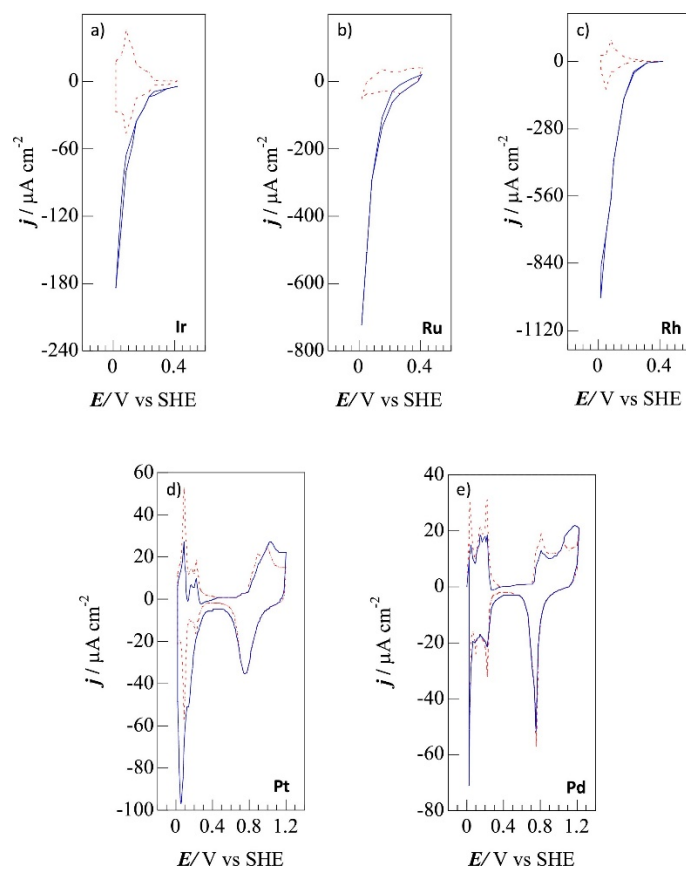

Figure 13: (a) Iridium, (b) ruthenium, (c) rhodium, (d) platinum and (e) palladium cyclic voltammograms recorded at scan rate 20 mV s−1 in 0.5 M H$_2$SO$_4$ (dashed red line) and 0.5 M H$_2$SO$_4$ in presence of 0.1 M NaNO$_3$ (solid blue line). (*10*)

As deduced from the decreasing current densities observed under identical experimental conditions from the cyclic voltammogram for platinoid metals recorded in absence and presence of NO_3^-, the electrocatalytic activity for nitrate reduction decreases in the order Rh > Ru > Ir > Pd-Pt. Although Osmium belongs to the platinoid metal group, it is extreme toxic thus cannot be used for water treatment applications.

Pt and Pd are the most studied platinoid metals for electrochemical reduction because their catalytic performance is not reduced by the poisoning caused by strong and irreversible adsorption of competitive hydrogen evolution and other reaction intermediates. The main limitation for Pt and Pd electrodes, however, is associated with the sluggish kinetics of the first charge transfer reaction. This can be avoided by the use of Bimetallic catalyst: secondary metal catalyst impregnated on the primary electrode to increase the kinetics. (*10*)

Conclusion

Studies of electrochemical nitrate reduction in drinking waters have been increasingly reported, yet there appears no consensus on the optimal electrode material for continuous flow reactors. (*1*) Pilot-scale studies have demonstrated complete nitrate removal (1.8 M NO_3^- or 25.2 g N/L) in a nuclear waste with >70% selectivity towards N_2 using Bi and Sn cathodes after 7 h of treatment. Similarly, Ho Chi Minh City in Vietnam, achieved electrochemical reduction with copper and polypirrole/Cu cathodes under potentiostatic conditions achieved ~10% nitrate removal and ~50% of nitrite formation after five hours of operation. The potentiostatic working conditions employed did not accelerate the electrokinetics. This is related to the inherent nature of Cu electrodes.

The electrochemical reduction process involves various intermediates and products (NO_2^-/HNO_2, NH_3/NH_4^+, N_2O and N_2). For water treatment, the desired end product is N_2 because NO_2^- and NH_4^+ pose health, aesthetic and operational problems. The key rate-limiting step is nitrate reduction to nitrite, which is influenced by mass transfer from the bulk water to the electrode surface, the adsorption of nitrate on the electrode surface, and electron transfer.

Electrode material affects both the kinetics and product selectivity during electrochemical nitrate reduction. Metals with highly occupied d-orbitals (e.g., Cu, Ag, Pt) and unclosed d-orbital shells are ideal for electrochemical nitrate reduction because they have an energy level similar to nitrate's LUMO π* that allows for facilitated first electron transfer.

Hydrogen production during electrochemical nitrate reduction occurs and can compete for cathodic reduction of the electrochemical cell leading to the inhibition of nitrate reduction. This aspect of competing effect of hydrogen needs to be studies in more detail as hydrogen leads to the decrease in the reaction kinetics. Reliable experiments are needed to clearly state the involvement of the

hydrogenation on the reduction of nitrate, which could become a research nexus between electrochemical and hydrogen catalytic technologies. (*1*)

References

1. S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski, P. Westerhoff, Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. *Applied Catalysis B: Environmental* **236**, 546-568 (2018).
2. L. Szpyrkowicz, S. Daniele, M. Radaelli, S. Specchia, Removal of NO3− from water by electrochemical reduction in different reactor configurations. *Applied Catalysis B: Environmental* **66**, 40-50 (2006).
3. B. P. Dash, S. Chaudhari, Electrochemical denitrificaton of simulated ground water. *Water Research* **39**, 4065-4072 (2005).
4. U. Prüsse, M. Hähnlein, J. Daum, K.-D. Vorlop, Improving the catalytic nitrate reduction. *Catalysis Today* **55**, 79-90 (2000).
5. S. Hörold, T. Tacke, K. D. Vorlop, Catalytical removal of nitrate and nitrite from drinking water: 1. Screening for hydrogenation catalysts and influence of reaction conditions on activity and selectivity. *Environmental Technology* **14**, 931-939 (1993).
6. M. D. C. Comnelellis, J. Winnick, Energy and electrochemical processes for a cleaner environment.
7. M. Paidar, K. Bouzek, H. Bergmann, Influence of cell construction on the electrochemical reduction of nitrate. *Chemical Engineering Journal* **85**, 99-109 (2002).
8. D. Xu *et al.*, Electrochemical removal of nitrate in industrial wastewater. *Frontiers of Environmental Science & Engineering* **12**, 9 (2018).
9. M. T. de Groot, M. T. M. Koper, The influence of nitrate concentration and acidity on the electrocatalytic reduction of nitrate on platinum. *Journal of Electroanalytical Chemistry* **562**, 81-94 (2004).
10. G. E. Dima, A. C. A. de Vooys, M. T. M. Koper, Electrocatalytic reduction of nitrate at low concentration on coinage and transition-metal electrodes in acid solutions. *Journal of Electroanalytical Chemistry* **554-555**, 15-23 (2003).
11. O. A. Petrii, T. Y. Safonova, Electroreduction of nitrate and nitrite anions on platinum metals: A model process for elucidating the nature of the passivation by hydrogen adsorption. *Journal of Electroanalytical Chemistry* **331**, 897-912 (1992).