



Review

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



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ABSTRACT

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

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Contents

1. Introduction	43
2. Catalytic reduction of nitrates	43
2.1. Mechanism of catalytic nitrate reduction	43
2.2. pH influence	44
2.3. Monometallic catalyst	45
2.4. Bimetallic catalyst	46
2.5. Continuous reactors	50
2.6. Catalytic membrane systems for nitrate reduction	51
3. Electrocatalytic reduction	52
3.1. Mechanism of nitrate electrocatalytic reduction	52
3.2. Configurations of electrocatalytic reduction cells	53
3.3. Electrode materials	54
4. Conclusions	55
Acknowledgement	56
References	56

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1. Introduction

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

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

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

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

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

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

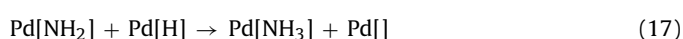
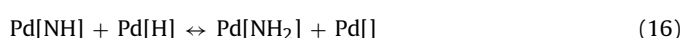
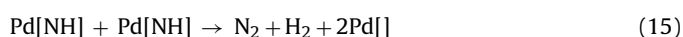
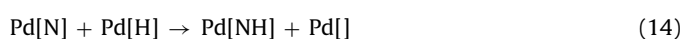
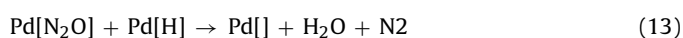
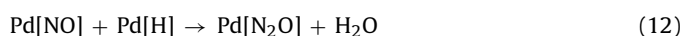
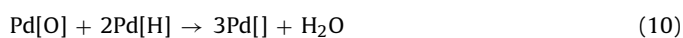
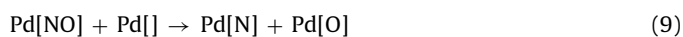
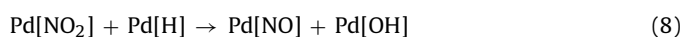
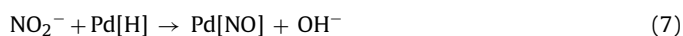
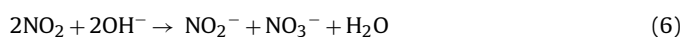
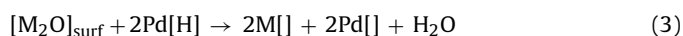
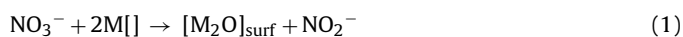
This work aims to give an overview of the state-of-the-art of the most promising nitrate reduction strategies. In particular, this paper focuses on the study of the catalytic reduction and the electroreduction processes due to their high potential to achieve more sustainable nitrate removal. Fundamentals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

2. Catalytic reduction of nitrates

2.1. Mechanism of catalytic nitrate reduction

The reaction mechanism of nitrate removal through chemical reduction over bimetallic catalysts has been widely studied by different authors since the nineties [6,7,29–37]. Nitrate reduction is carried out in the presence of hydrogen as a reducing agent over the surface of a catalyst consisting of both a noble metal and a transition metal deposited on a support. Palladium and platinum have been mainly used as the noble metals for nitrate reduction due to their favourable hydrogen adsorption abilities. In addition, the best activity and selectivity have been achieved with Cu, Sn or In as the promoter metal, Fig. 1.

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



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