DISRUPTIVE AND SUSTAINABLE TECHNOLOGY FOR NITRATE REMOVAL IN SALINE WATERS, WATER RECOVERY, AND VALORIZATION OF OTHER IONIC CONTENTS

PATENTED TECHNOLOGY

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ABSTRACT

The **Applied Electrochemistry and Electrocatalysis Research Group (LEQA)** at the **University of Alicante**, in collaboration with the **University of Valencia** and the company **AVSA**, has developed an innovative technology that efficiently removes nitrates (NO_3^-) from saline streams through an electrochemical denitrification process (REN). This system focuses on optimizing the treatment of reject streams generated by reverse electrodialysis (EDR) plants, effectively integrating pretreatment, denitrification, and post-treatment phases to maximize resource recovery, such as water and hydrogen.

The process is highly efficient in converting nitrates into nitrogen gas (N_2), with minimal formation of toxic by-products. Additionally, the comprehensive resource management allows for the reintegration of demineralized water into the treatment cycle, electricity generation, and the recovery of valuable salts such as calcium and magnesium. Another distinguishing feature is the absence of sludge generation, a common problem in other methods, and its compliance with stringent environmental regulations. The operational flexibility of this technology, which supports both continuous and batch modes, further expands its industrial applicability.

The technology, protected by a patent application, has been developed at a pilot scale and is ready for demonstration. Companies interested in its commercial exploitation are sought.

INTRODUCTION

Groundwater contamination by nitrates (NO_3^-) is a growing global problem, primarily attributed to the intensive use of fertilizers. This excess negatively affects both the environment and human health, being associated with diseases such as methemoglobinemia, cancer, and thyroid dysfunctions. Regulations such as the European Union's Nitrate Directive and the World Health Organization (WHO) recommendations limit the nitrate content in drinking water to 50 mg/L, driving the development of technologies for its removal.

There are two main approaches: separation and transformation techniques. The former, including reverse osmosis, electrodialysis, and anion exchange resins, displace nitrates into concentrated auxiliary streams requiring further management. While effective, these methods generate secondary waste, posing environmental challenges.

Transformation techniques, on the other hand, chemically convert nitrates. Biological denitrification employs bacteria to degrade them but faces limitations such as sludge generation and the risk of bacterial contamination. (Electro)catalytic methods, such as electrocatalytic reduction and heterogeneous catalysis, use reducing agents and electrocatalysts to transform nitrates into less harmful compounds, with nitrogen gas (N_2) being the desired product.

Electrochemical denitrification (REN) is a promising alternative that directly reduces nitrates at the cathode of an electrolytic cell. However, its complex chemistry can generate intermediate products such as NO_2^-, NH_3, or N_2O, whose toxicity must be controlled. Selectivity toward nitrogen gas depends on cell design, operating conditions, and cathode material, which acts as an electrocatalyst.

The REN process faces challenges in energy efficiency, as it competes with water reduction to generate hydrogen (H_2), decreasing system efficacy. Although current technologies achieve selective reduction to N_2, they present industrial limitations, such as difficulties in treating hard water, moderate efficiency at low nitrate concentrations (less than 500 ppm), and managing ammonia (NH_3) as a by-product.

The presented solution addresses these limitations through an integrated system for treating reject water from Reverse Electrodialysis (EDR) plants, characterized by high nitrate levels. It combines a REN process with pre- and post-treatment stages, improving viability and efficiency. Additionally, it incorporates a colorimetric sensor to monitor ammonia release and a design that valorizes the generated hydrogen, optimizing energy efficiency.

This solution offers an effective approach to treating saline streams with high nitrate concentrations, minimizing the drawbacks of previous technologies while meeting regulatory standards, representing an advancement in sustainable water management.

TECHNICAL DESCRIPTION

The **Applied Electrochemistry and Electrocatalysis Research Group** at the **University of Alicante**, in collaboration with the **University of Valencia** and **AVSA**, has developed an innovative procedure based on electrochemical denitrification (REN) for treating saline waters with high nitrate concentrations (NO_3^-). This method, designed for saline aqueous streams from reverse electrodialysis (EDR) desalination plants, integrates pretreatment, denitrification, and post-treatment technologies, achieving water recovery and electricity generation.

The process consists of **three main stages**:

1. PRETREATMENT: In this initial phase, saline aqueous streams are prepared for treatment in the electrochemical reactor, involving:

- **Reduction of water hardness** from the EDR plant's saline stream;
- **Concentration of NO_3^- ions** using reverse osmosis;
- **pH adjustment** of the concentrated stream from the previous osmosis stage before entering the electrochemical reactor.

2. ELECTROCHEMICAL DENITRIFICATION PROCESS: During this stage, NO_3^- ions are efficiently removed through electrochemical reduction at the cathode, converting them into nitrogen gas (N_2). Simultaneously, water reduction at the cathode generates hydrogen gas (H_2) with a purity of ≥ 97%. The reactor output consists of a gaseous hydrogen stream and an aqueous stream containing ammonium (NH_4^+) and residual NO_3^- ions.

3. POST-TREATMENT: This stage processes the aqueous and gaseous streams to maximize resource recovery and minimize environmental impact:

- **Aqueous stream**: An oxidizing agent converts NH_4^+ and NO_2^- into N_2 and NO_3^-, respectively. Ion exchange desalinates the treated water, allowing its reintegration into the EDR process as feed water. The ion exchange resins are regenerated, producing sodium (Na^+) and chloride (Cl^-) rich saline solutions, facilitating the recovery of insoluble calcium (Ca) and magnesium (Mg) salts and resin regeneration.
- **Gaseous stream**: Hydrogen purification removes ammonia traces. The gas is then dried and deoxygenated, conditioning it for storage. Stored hydrogen can be used in fuel cells to generate electricity, enhancing process sustainability.

This procedure stands out by incorporating an oxidation system that transforms toxic by-products such as ammonium and nitrite into less harmful compounds, ensuring efficient treatment while complying with environmental regulations. Moreover, the technology integrates a demineralization and water reuse approach, allowing reintegration into industrial processes.

Additionally, the system supports both continuous and batch operations, providing flexibility to adapt to various operational needs. The process includes high-purity hydrogen recovery (≥ 97%), which can serve as a renewable energy source through fuel cells.

ADVANTAGES AND INNOVATIVE ASPECTS

ADVANTAGES OF THE TECHNOLOGY

The developed technology presents multiple advantages, standing out both technically and environmentally:

- **High efficiency in nitrate removal**: The electrochemical denitrification process is designed to maximize the conversion of nitrates into nitrogen gas (N_2), preventing the generation of contaminating residual streams. The pretreatment stage increases treatment capacity and reduces energy consumption, improving industrial feasibility.
- **Advanced by-product management**: The pretreatment and post-treatment stages ensure efficient handling of high-hardness waters and minimize undesirable by-products, such as ammonia, while facilitating the regeneration and reuse of ion exchange resins, reducing operational costs.
- **Energetic use**: The valorization of the hydrogen generated during the process enables its use as a renewable energy source in fuel cells, contributing to a reduction in global electricity consumption.
- **Compliance with environmental regulations**: The technology transforms pollutants into less harmful products, meeting regulatory requirements and eliminating the need to manage solid waste such as sludge.
- **Operational flexibility**: The system supports both continuous and batch operation modes, adapting to different industrial needs.
- **Resource recovery and diversification**: Allows for the reintegration of treated and demineralized water at the beginning of the process, minimizing new water use. Additionally, it enables the valorization of salts such as calcium and magnesium for commercial applications, adding a strategic economic component.
- **Sustainability**: This process destroys contaminants instead of transferring them to other streams, significantly reducing environmental impact. The energy generation from the obtained hydrogen maximizes the sustainability of the process.

INNOVATIVE ASPECTS

On one hand, the technology combines a highly selective electrochemical process for nitrate (NO_3^-) removal with the generation of high-purity hydrogen (≥ 97%) as a recoverable by-product. This approach not only efficiently eliminates contaminants but also transforms a waste material into a renewable energy source usable in fuel cells, representing a significant advancement in energy sustainability and operational efficiency.

On the other hand, the system incorporates an integrated design that allows the reintegration of demineralized water into the reverse electrodialysis (EDR) cycle, maximizing resource reuse. Additionally, the recovery of valuable resins and salts, such as calcium and magnesium, reinforces the circular economy approach, distinguishing it from other technologies that generate difficult-to-manage waste, such as sludge or contaminant-laden streams.

These two aspects position this technology as an advanced and disruptive solution, standing out for its focus on sustainability, energy efficiency, and the circular economy.

CURRENT STATE OF DEVELOPMENT

The system has been developed at a pilot scale and is ready for demonstration.

A stationary pilot system is available at AVSA's facilities in Gandía, developed under the framework of the ELEKTRA project, funded by IVACE+i. Currently, a transportable containerized pilot is being built within the ELEKTRA LIFE project.

MARKET APPLICATIONS

This technology is particularly advantageous for **treating water** from reverse electrodialysis (EDR) desalination plant reject streams contaminated with nitrates. However, it can also be applied to any stream with a high nitrate concentration, such as those from the chemical, food, or textile industries. Additionally, its nitrate removal capability makes it particularly useful in regions where intensive fertilizer use has contaminated aquifers and water sources.

COLLABORATION SOUGHT

Companies interested in acquiring this technology for **commercial exploitation** are sought through:

- Patent licensing agreements.
- R&D collaboration agreements to develop the technology according to company needs.
- Scientific-technical advisory services.
- Etc.

Types of companies sought:

- Manufacturers of water treatment equipment and systems.

- Companies integrating turnkey solutions for treatment plants.
- Desalination and EDR plants.
- Industrial wastewater management companies.

INTELLECTUAL PROPERTY RIGHTS

This technology is protected by **patent application**.

- *Title of the patent: "Procedimiento para la recuperación de agua y eliminación de iones nitrato en corrientes acuosas salinas y equipo para llevar a cabo dicho procedimiento"*
- *Application number: P202330547*
- *Application date: June 29, 2023*

MARKET APPLICATION (4)

Agri-food and Fisheries
Footwear and Textile
Pollution and Environmental Impact
Chemical Technology