



## Cathode potential and anode electron donor evaluation for a suitable treatment of nitrate-contaminated groundwater in bioelectrochemical systems



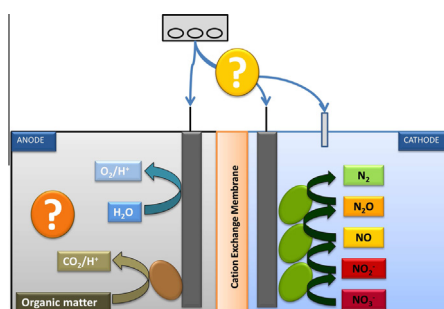
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### HIGHLIGHTS

- Anode feed and cathode potential were evaluated for nitrate treatment in groundwater.
- Cathode potential shifted nitrate removal rate and intermediates accumulation.
- The lowest accumulation of  $\text{NO}_2^-$  and  $\text{N}_2\text{O}$  was observed at  $-123$  mV vs SHE.
- Water, rather than acetate, was the most reasonable anode electron source.
- Carbon-free treatment of nitrate-polluted groundwater at a competitive cost.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Several regions around the world present high levels of nitrate in groundwater. Due to its toxicity, nitrate must be removed before the groundwater is used as drinking-water. This study assessed how a denitrifying bioelectrochemical system could be operated to treat nitrate-polluted groundwater. It evaluated the cathode potential (from +597 to  $-703$  mV vs SHE) and the anode electron donor (acetate and water). Similar trends were found regardless of the anode electron donor. The nitrate removal rate increased from  $1.05$  to  $5.44$   $\text{mg N-NO}_3^- \text{L}_{\text{NCC}}^{-1} \text{h}^{-1}$  when the cathode potential was lowered from +597 to  $-403$  mV vs SHE, where it stabilized. The nitrate reduction end-products (nitrite, nitrous oxide and dinitrogen gas) also changed with the different potentials of the cathode electrode. The World Health Organization nitrates and nitrites standards for drinking-water were reached at cathode potentials between  $-103$  and  $-203$  mV vs SHE. The highest rate of nitrate conversion to  $\text{N}_2$  ( $2.59$   $\text{mg N-NO}_3^- \text{L}_{\text{NCC}}^{-1} \text{h}^{-1}$ , 93.9%) occurred at  $-123$  mV using water as anode electron donor, with an estimated operational cost similar to conventional technologies ( $0.68 \cdot 10^{-2}$   $\text{kW h gN-NO}_3^- \text{removed}^{-1}$ ). The long-term stability of proposed operation was demonstrated during 96 days, and the rate of nitrate conversion to  $\text{N}_2$  even increased to  $4.09$   $\text{mg N-NO}_3^- \text{L}_{\text{NCC}}^{-1} \text{h}^{-1}$ . A carbon-free operation for a bioelectrochemical system has been developed to treat nitrate-polluted groundwater at a competitive cost.

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## 1. Introduction

The presence of nitrate in groundwater has become a worldwide concern because of its toxicity to human health [1–3]. The Environmental Protection Agency (EPA) considers that only removal techniques such as reverse osmosis, electro dialysis and ion exchange are able to reduce nitrate content below its guideline values [4]. However, reverse osmosis, electro dialysis technologies imply high energy costs between 0.69 and 2.09 kW h m<sup>-3</sup> groundwater [5], while ion exchange requires an extra cost for resin regeneration [6]. In all three cases, they also generate waste brine that is difficult to dispose of because nitrate is only separated from groundwater, not treated [7].

Biological denitrification could overcome these drawbacks by allowing a complete treatment of nitrate to produce harmless dinitrogen gas (N<sub>2</sub>). Groundwater is characterized by the absence of organic matter. Therefore, conventional heterotrophic denitrification has to be performed by adding an organic carbon source [8,9]. However, this generates an excess of sludge, and the dose of organic matter increases the treatment cost. Moreover, the presence of organic carbon compounds is forbidden in drinking-water. Therefore, unconventional strategies for biologic denitrification need to be explored. Bioelectrochemical systems (BES) are capable of treating nitrates in an autotrophic denitrifying biocathode [10]. The main challenge of reducing nitrate to N<sub>2</sub> is the accumulation of denitrification intermediates such as nitrite (NO<sub>2</sub><sup>-</sup>) and nitrous oxide (N<sub>2</sub>O). NO<sub>2</sub><sup>-</sup> in drinking-water is more toxic for human health than nitrate (standard value of 0.91 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup>; [11]), and the emission of N<sub>2</sub>O, a high-impact greenhouse gas, should be avoided [12]. Biocathodes used in BESs are able to perform the entire autotrophic denitrificative pathway sequentially from NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and allow N<sub>2</sub>O reduction to N<sub>2</sub> [13]. The single reductions of nitrite and nitrous oxide using a biocathode were also demonstrated by Puig et al. [14] and Desloover et al. [15], respectively.

Previous studies [16,17] have demonstrated that nitrate could also be removed from low ionic strength waters. In these studies the BES was operated as a microbial fuel cell (MFC). In a MFC anode and cathode reactions are thermodynamically spontaneous, and no power input is required. Although nitrate could be removed, full denitrification was not reached, with N<sub>2</sub>O emissions accounting the 50% of nitrate removed. The accumulation of denitrification intermediates can be caused by a limitation of the electrons necessary for denitrifying bacteria to completely reduce nitrate to N<sub>2</sub> [18]. In a denitrifying MFC, the electron availability depends on the electron transport from the anode electron donor to the cathode denitrifying bacteria. The overall electron transport is hindered by MFC overpotentials that are mainly caused by electrode materials, bacterial metabolic losses, membrane characteristics and ionic strength [19]. When water with low ionic strength such as groundwater is treated, the overpotentials related to ion-transport (membrane transport, ohmic and pH gradient losses) increase. Puig et al. [16] observed that overpotentials related to ion-transport could be increased up to 80% by reducing water conductivity from 4000 to 1000 μS s<sup>-1</sup>. For groundwater treatment, if conductivity is artificially increased through added chemicals such as NaCl, they must be discarded so that they do not impair water quality. To remove the nitrate from groundwater at higher rates and produce fewer intermediates, other strategies should be followed. If an external power is applied to the BES, the cell is known as a microbial electrolysis cell (MEC). To promote denitrification in BES, the cell can be operated as an MEC instead of an MFC.

This study aimed to improve BES performance in treating nitrate-polluted groundwater and overcome its main drawbacks (low conductivity and accumulation of intermediates). This study focused on the influence of the cathode potential and examined the use of organic matter and water as anode electron donors.

The metrics for the operation and process assessments were: (i) nitrate removal rates; (ii) complete denitrification achieved and (iii) energy requirements. At the end of the study, the long-term stability of the proposed operation was tested.

## 2. Experimental section

### 2.1. Experimental set-up

The BES consisted of an anode and a cathode placed on opposite sides of a single methacrylate rectangular chamber [16]. The anode and cathode chambers were filled with granular graphite (diameter 1.5–5 mm, EnViro-cell, Germany), which decreased the compartment volumes to 450 and 600 mL (net anode and cathode compartments NAC and NCC volumes), respectively. Two thinner graphite electrodes (130 × 6 mm, Sofacel, Spain) were used as anode and cathode current collectors. A cation exchange membrane (CEM, Nafion<sup>®</sup> 117, Dupont, USA) was placed between the anode and cathode frames. At the steady state, influents were continuously fed at a flow rate of 1.12 ± 0.07 and 1.28 ± 0.16 L d<sup>-1</sup> in the anode and cathode compartments, respectively. An internal recirculation loop (105 L d<sup>-1</sup>) was placed in each compartment. The system was thermostatically controlled at 22.5 ± 0.5 °C.

### 2.2. Influent characteristics

Nitrate contaminated groundwater from the village of Ordís (42°13'13"N, 2°54'31"E, Girona, N.E. Spain) was treated in the cathode of the BES. The groundwater was purged with dinitrogen gas prior to being fed into the cathode to ensure anoxic conditions. The groundwater contained 33.11 ± 2.55 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> and 0.11 ± 0.22 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup>. These values were higher than the limits given by the World Health Organization (WHO): 11.29 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> (50 mg NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>) and 0.91 mg N-NO<sub>2</sub><sup>-</sup> L<sup>-1</sup> (3 mg NO<sub>2</sub><sup>-</sup> L<sup>-1</sup>) [11]. The inorganic carbon content of the groundwater was 56.4 ± 2.4 mg C-IC L<sup>-1</sup>. The average pH was 7.8 ± 0.2, with a conductivity of 918 ± 31 μS cm<sup>-1</sup>. Neither ammonium (N-NH<sub>4</sub><sup>+</sup>) nor organic matter (TOC) were detected in the groundwater.

Two different electron donors were evaluated at the anode: acetate, as an example of an organic carbon source, and water. Firstly, the anode compartment was fed with acetate-enriched water with a chemical oxygen demand (COD) concentration of 297 ± 60 mg COD L<sup>-1</sup>, a pH of 7.7 ± 0.1 and a conductivity of 984 ± 119 μS cm<sup>-1</sup>.

In the second round of tests, the anode was fed with tap water without added organic matter. In consequence, the organic matter content was found below the detection limit in both COD (<30 mg COD L<sup>-1</sup>) and TOC (<0.01 mg C L<sup>-1</sup>) analyses. The conductivity was of 817 ± 145 μS cm<sup>-1</sup> with a pH of 8.0 ± 0.4. The inorganic carbon content was 48.7 ± 2.4 mg C-IC L<sup>-1</sup>.

### 2.3. BES operation

In a previous study [17], a BES was operated during 97 days to treat 1.21 L d<sup>-1</sup> of nitrate-polluted groundwater (28.32 ± 6.15 mg N-NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>) at the biocathode. The microbial community established in the biocathode was dominated by *Betaproteobacteria*, *Candidatus Nitrotoga arctica* and *Thauera* sp. species. That work used acetate-enriched water as an electron donor with an anode that was fed at 1.23 L d<sup>-1</sup> and operated at a chemical oxygen demand concentration of 283 ± 75 mg COD L<sup>-1</sup>. Once the BES reached the steady state, the experiments for the present study started.

The nitrate removal and the end-products obtained were evaluated at different fixed cathode potentials (Table 1). Firstly, the

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