Nitrate electro-bioremediation and water disinfection for rural areas

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HIGHLIGHTS

- Treated groundwater meets standards for nitrogen compounds and pathogens.
- Highest reported nitrate reduction rate of 5.0 kg NO_3^- m^{-3} d^{-1} at HRT_{cat} of 0.7 h.
- Water disinfection ensured through in-situ electrochemical chlorine evolution.
- Cost-effective treatment with an estimated competitive operational cost of 1.05 € m^{-3}.

GRAPHICAL ABSTRACT
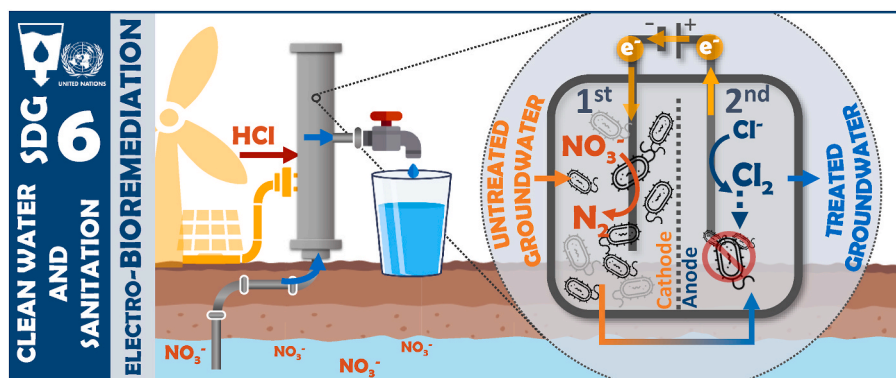
ARTICLE INFO

ABSTRACT

Nitrate-contaminated groundwater is a pressing issue in rural areas, where up to 40 % of the population lacks access to safely managed drinking water services. The high costs and complexity of centralised treatment in these regions exacerbate this problem. To address this challenge, the present study proposes electro-bioremediation as a more accessible decentralised alternative. Specifically, the main focus of this study is developing and evaluating a compact reactor designed to accomplish simultaneous nitrate removal and groundwater disinfection. Significantly, this study has established a new benchmark for nitrate reduction rate within bioelectrochemical reactors, achieving the maximum reported rate of 5.0 ± 0.3 kg NO_3^- m_{NCC}^{-3} d^{-1} at an HRT_{cat} of 0.7 h. Furthermore, the in-situ generation of free chlorine was effective for water disinfection, resulting in a residual concentration of up to 4.4 ± 1.1 mg Cl_2 L^{-1} in the effluent at the same HRT_{cat} of 0.7 h. These achievements enabled the treated water to meet the drinking water standards for nitrogen compounds (nitrate, nitrite, and nitrous oxide) as well as pathogens content (T. coliforms, *E. coli*, and *Enterococcus*). In conclusion, this study demonstrates the potential of the electro-bioremediation of nitrate-contaminated groundwater as a decentralised water treatment system in rural areas with a competitive operational cost of 1.05 ± 0.16 € m^{-3}.

1. Introduction

The United Nations has established the objective of universal access

to safe drinking water through the adoption of the 2030 Agenda (SDG 6, A/RES/70/1). Unfortunately, by 2020, around two billion people will still lack access to safely managed drinking water services. This challenge is particularly prominent in rural areas, where only 60 % of the population has access to safely managed services, compared to 86 % in urban areas (WHO and UNICEF, 2021). This highlights the urgent need for significant efforts to expand access to safe drinking water in rural areas. Therefore, developing and implementing novel treatments and technologies are pivotal in bridging this gap and ensuring universal access to safe drinking water.

Intensive agricultural and livestock production practices in rural areas are a major concern, leading to nitrate contamination of groundwater (Suthar et al., 2009; Yu et al., 2020). Such contamination threatens freshwater quality and safety, making it inappropriate for human consumption. The European Directive 2020/2184 has established a nitrate concentration threshold of 50 mg NO_3^- L^{-1} to ensure the safety of the drinking water. Furthermore, water is a passive carrier for many pathogens, including viruses, bacteria, protozoa and larvae (Ashbolt, 2004; Gerba, 2015). This risk arises in rural areas due to localised contamination, such as faecal and manure leaching, and during water transportation from the source to the point of use due to unhygienic practices (Chique et al., 2021; Peter-Varbanets et al., 2009). The same directive (EU, 2020/2184) sets *Escherichia coli* and intestinal *Enterococcus* guideline values of 0 UFC mL^{-1} for drinking water.

To increase access to treated water in rural areas and drive technological transition in the water sector, compact decentralised water treatment systems have become crucial. These decentralised solutions offer effective and sustainable methods, characterised by low operating costs, sustainability, minimal maintenance, and independence from utilities such as energy sources. Within this context, electro-bioremediation is one of the emerging decentralised treatments for sustainable groundwater remediation. Electro-bioremediation involves the utilisation of electroactive microorganisms to carry out specific oxidation and reduction reactions using solid electron conductors (Wang et al., 2020). This approach addresses the constraints associated with electron donor/acceptor availability in groundwater. It facilitates the efficient removal of various pollutants, including inorganic substances (e.g. metals and nutrients) and organic compounds (e.g. hydrocarbons) (Pous et al., 2018).

Electro-bioremediation of nitrate has emerged as a promising approach. When nitrate is the target contaminant, autotrophic denitrification is performed using the cathode as an electron donor and inorganic carbon as a carbon source. This overcomes the lack of electron donors in groundwater, avoiding chemical dosing. In particular, nitrate electro-bioremediation offers competitive advantages over conventional treatments by minimising environmental impacts such as brine formation and the accumulation of undesirable by-products such as nitrite. It also has a competitive energy consumption (0.25 kWh m^{-3}, Cecconet et al., 2018a) compared to methods such as reverse osmosis, which typically consumes 0.9–2.2 kWh m^{-3} (Twomey et al., 2010). Nevertheless, conventional treatments still have higher treatment capacities with shorter hydraulic retention times (HRT) in the range of seconds to minutes (Xu et al., 2018). In contrast, studies on electro-bioremediation

typically reported higher HRTs of some hours (e.g., 15.6 h Cecconet et al., 2018b, 2.4 h Puggioni et al., 2022 or 3.3 h Wang et al., 2021). Only one study in this field reported a minimum HRT in the cathode compartment of 0.5 h, although without reaching the nitrate threshold of 50 mg NO_3^- L^{-1} in the effluent (Pous et al., 2017). Therefore, reducing HRT, which would significantly increase the nitrate reduction rate and reduce the number of reactor units, is necessary to achieve a more competitive treatment.

Simultaneously, electro-bioremediation is a versatile treatment option, offering potential water disinfection through diverse anodic evolution reactions, including chlorine, hydrogen peroxide, ozone, or radical formations (Bergmann, 2021). Recent research has explored the fusion of electro-bioremediation with anodic disinfection through chloride oxidation to chlorine to address various challenges, such as wastewater treatment in secondary settlers (Botti et al., 2023) and nitrate-contaminated saline groundwater (Puggioni et al., 2021). Hence, integrating water disinfection and nitrate reduction via electro-bioremediation simplifies the treatment process. This approach can significantly improve the cost-effectiveness of nitrate-contaminated groundwater potabilisation through a single-step treatment.

This study presents an innovative electro-bioremediation system that combines water disinfection with nitrate reduction to nitrogen gas in a compact reactor to treat nitrate-contaminated groundwater. The nitrate reduction rate was significantly enhanced by controlling the cathodic pH to 6.8 ± 0.2. This cathodic pH is decisive for the performance due to its strong influence on the denitrification process in terms of both rate and selectivity to nitrogen gas, as mentioned by other authors (Clauwaert et al., 2009; Puggioni et al., 2021; Zhao et al., 2022). In addition, the hydrochloric acid used for pH control was recovered by oxidising chloride to chlorine in the anodic compartment, serving as an effective *in-situ* water disinfectant. In parallel, there is an increasing need to assess future implementation. This study evaluated treatment performance in terms of nitrate reduction and disinfection capacity. For the first time, this study prioritised achieving standard drinking water quality using electro-bioremediation, focusing on addressing nitrate risks and pathogen presence. Finally, the techno-economic implications were critically evaluated in terms of its benefits and associated operating costs.

2. Materials and methods

2.1. Reactor setup

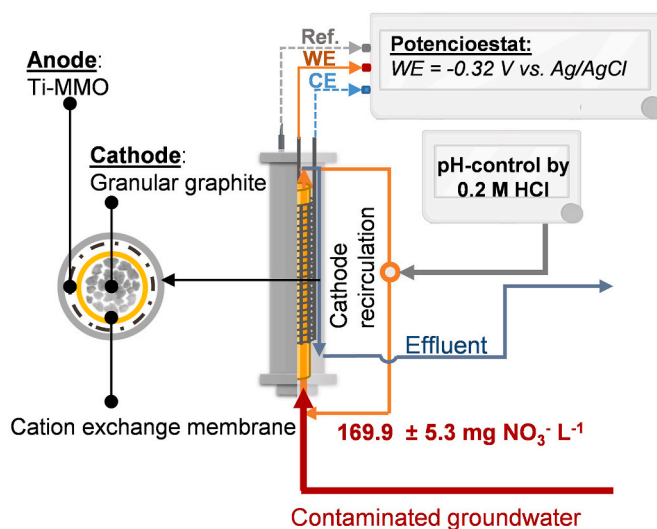A compact tubular bioelectrochemical fixed-bed reactor (Fig. 1) was

Fig. 1. Illustration of the reactor (right) and perpendicular section scheme (left).1.5 -column fitting image.

built with PVC (55 mm diameter and 350 mm length). The cathode and anode compartments were separated with a tubular cation-exchange membrane (40 mm diameter, 1 mm thickness and 300 mm length; CEM, CMI-7000, Membranes Int., USA). The cathode (inner compartment) was filled with granular graphite (average diameter of 3.25 mm, enViro-cell, Germany) with a bed porosity of 50 %, resulting in an estimated electrode surface area of 0.4 m^2 and a net cathode volume (NCC) of 0.22 L. The cathode was initially inoculated with a denitrifying community mainly composed of *Sideroxydans* sp. from another running denitrifying bioelectrochemical reactor, which was characterised previous studies (Ceballos-Escalera et al., 2021, 2024). The anode (outer compartment) was a cylindrical titanium mesh covered with mixed metals oxide (Ti-MMO, 45 mm diameter, 0.5 mm thickness and 200 mm length, Special Metals and Products, SL, Spain), which is a stable material to promote chlorine formation. The anode surface was 0.2 m^2 with a net anode volume (NAC) of 0.43 L. A potentiostat (VSP, BioLogic, France) was used to control the reactor electrically in a potentiostatic mode, with the cathode (working electrode, WE) potential fixed at −0.32 V *vs.* Ag/AgCl to facilitate complete nitrate reduction to nitrogen gas (Pous et al., 2015). Under potentiostatic conditions the working electrode (WE, the cathode in this work) is controlled at a specific value, while the counter electrode (CE, the anode in this work) varies in order to meet the cathode current requirements. Along the operational study, the potentiostat recorded the voltage difference between the anode and the cathode (i.e., cell voltage), which was used to calculate the power requirements of the system.

2.2. Synthetic groundwater

Synthetic nitrate-contaminated groundwater was used in this study. It mimicked the groundwater of the village of Navata (Spain). The synthetic groundwater was prepared with distillate water and contained 203.9 mg L^{-1} NaNO$_3$, 420.0 mg L^{-1} NaHCO$_3$ as inorganic carbon source, 7.5 mg L^{-1} KH$_2$PO$_4$, 1.9 mg L^{-1} Na$_2$HPO$_4$, 100.0 mg L^{-1} NaCl, 75.2 mg L^{-1} MgSO$_4$ × 7H$_2$O, 10.0 mg L^{-1} NH$_4$Cl and 0.1 mL L^{-1} of a trace minerals solution (Balch et al., 1979). In addition, the influent contained 10 % of effluent from a parent denitrifying bioelectrochemical reactor to simulate the presence of microorganisms in the groundwater (Ceballos-Escalera et al., 2021). The inorganic medium only incorporated nitrate as a contaminant (169 ± 5 mg NO$_3^-$ L^{-1}) and bicarbonate as a carbon source. The resulting influent had an electric conductivity of 1.3 ± 0.1 mS cm^{-1} and a pH of 8.0 ± 0.3. The analysis of pathogens revealed that *Enterococcus* was present in the effluent of the parent denitrifying bioelectrochemical reactor. The concentration was 1.3 ± 0.9 ufc per 100 mL^{-1} (Table S1, Supplementary data).

2.3. Reactor continuous operation

The reactor was operated in continuous flow mode. Synthetic groundwater was fed at various hydraulic retention times (HRT) ranging from 7.0 h to 2.1 h. The HRT was reduced by approximately 25 % within one week or until a steady state was achieved. To focus specifically on the cathodic process of nitrate reduction, and make the results comparable to literature, the HRT was also expressed in terms of cathodic hydraulic retention times (HRT$_{cat}$) ranging from 2.4 h to 0.7 h.

Synthetic groundwater was pumped directly through the bottom of the cathode compartment and spilt over the top into the anode compartment towards the bottom where the outlet was located (Fig. 1). The outlet of the cathode compartment was recirculated to the influent at a flow rate of 85 L d^{-1} to improve fluid distribution and enhance mass transfer (Vilà-Rovira et al., 2015). Specifically, recirculation is highly recommended when the electrical conductivity of the water is low, such as in groundwater (Ceballos-Escalera et al., 2021). A pH probe was installed in the cathodic recirculation to control the cathodic pH at 6.8 ± 0.2. Hydrochloric acid (0.2 M HCl) was used for this control as the supplied chloride ions could subsequently be oxidised to chlorine.

2.4. Analyses methods and calculations

Liquid samples were collected and analysed following the standard water measurement methods specified by the American Public Health Association (APHA, 2005). The ion concentration was determined using an ionic chromatography system (ICS 5000, Dionex, USA) with a detection limit of 0.01 mg L^{-1}. Nitrous oxide (N$_2$O) was monitored by a liquid-phase microsensor (Unisense, Denmark) located at the cathodic recirculation. Free chlorine was measured immediately after sampling with a specific kit (Free Chlorine DPD Reagent Powder Pillows, HACH Company, Loveland, CO, USA). Total coliforms, *E. Coli* and *Enterococcus* concentrations were analysed externally (Cat-Gairín Laboratory, Girona). The pH and electrical conductivity of the samples were measured with a pH meter (pH meter basic 20+, Crison, Spain) and a conductivity meter (EC-meter basic 30+, Crison, Spain), respectively.

The performance of electro-bioremediation was assessed based on various factors, including nitrate removal efficiency, energy consumption, free chloride concentration, and operational costs. The nitrate reduction rate was determined (Eq. S1, Supplementary data) and normalised by the net cathode volume (kg NO$_3^-$ m^{-3} d^{-1}). Energy consumption was calculated (Eq. S5, Supplementary data) and expressed relative to the amount of nitrate removed (kWh kg NO$_3^-$) or the volume of water treated (kWh m^{-3}). The calculation of the cathodic coulombic efficiency considered the presence of potential intermediates such as nitrite and nitrous oxide (Eq. S6, Supplementary data) (Pous et al., 2017).

Two main costs were considered in the estimation of the operational cost for the treatment: (i) the cost of hydrochloric acid and (ii) the energy consumption from the power supply to sustain the electrochemical reactions. The price of hydrochloric acid was determined by its commercial concentrate cost (1.40 € L^{-1}, 35 % HCl, Ref. 13235T-00/B02, Vadequimica, Spain). The energy cost in this study was estimated using the electricity price for industrial consumers from the second period of 2022 in Europe (Eurostat statistics, 0.20 € kWh^{-1}).

3. Results and discussion

3.1. Quality of treated groundwater: compliance with drinking water standards

For the first time, the overall characteristics of the treated water in the electro-bioremediation process were evaluated in accordance with the European Directive 2020/2184 (Table 1). This directive establishes both chemical and microbiological standards to ensure drinking water quality.

The nitrate concentration in the treated water remained below the safe limit of 50 mg NO$_3^-$ L^{-1}, with a concentration range of 4.5 ± 0.6 to 15.1 ± 7.7 mg NO$_3^-$ L^{-1} between the HRT$_{cat}$ from 2.4 to 0.7 h. Besides, the treatment exhibited high selectivity to nitrogen gas (<99 %). Harmful denitrifying by-products, neither nitrate nor ammonium, were detected in the effluent, and the concentrations remained below the prescribed limits of 0.5 mg NO$_2^-$ L^{-1} and 0.5 mg NH$_4^+$ L^{-1}. Furthermore, the absence of nitrous oxide in the liquid phases, a greenhouse gas, reinforces the environmental sustainability of the treatment. Hence, the treatment effectively eliminated nitrate without producing any harmful by-products in the treated groundwater.

In parallel, the free chlorine concentration in the effluent increased from 0.3 ± 0.1 to 4.4 ± 1.4 mg Cl$_2$ L^{-1} as the HRT$_{cat}$ decreased from 2.4 h to 0.7 h. In this scenario, chlorine was considered suitable as a disinfectant due to the absence of organic matter in the groundwater, preventing the formation of toxic by-products (Mazhar et al., 2020). The typical residual chlorine concentration in conventional potable water plants ranges from 0.2 to 2.0 mg L^{-1}, with a possible increase in dosage during extreme contamination scenarios (Brandt et al., 2017). Thus, it was assumed that the chlorine production attained in this study was satisfactory for the *in-situ* disinfection, ensuring the microbiological

Table 1

Treatment performances and water characteristics according to the different HRT_{cat} tested (n ≥ 2). The water characteristics are represented with a colour-coded according to the fulfilment of drinking water standards (Directive EU, 2020/ 2184). Neither nitrite, ammonium, nor nitrous oxide were accumulated. NaN: Not a Number.

Operation performance			Treatment performance				
HRT_{cat}	Current	Cell voltage	Nitrate reduction rate	Nitrate reduction efficiency	Energy consumption	HCl consumption [a]	
[h]	[mA]	[V]	[kg NO_3^- m^{-3}_{NCC} d^{-1}]	[%]	[KWh m^{-3}_{water}]	[L m^{-3}_{water}]	
2.4	35 ± 1	1.81 ± 0.02	1.7 ± 0.0	97 ± 1	0.69 ± 0.03	0.76 ± 0.17	
1.6	49 ± 1	2.10 ± 0.12	2.6 ± 0.1	98 ± 0	0.73 ± 0.03	0.66 ± 0.07	
1.3	53 ± 5	2.08 ± 0.12	2.9 ± 0.1	95 ± 2	0.63 ± 0.07	0.66 ± 0.10	
0.9	92 ± 5	2.43 ± 0.08	4.3 ± 0.0	98 ± 1	0.95 ± 0.02	0.89 ± 0.10	
0.7	104 ± 5	2.37 ± 0.12	5.0 ± 0.3	90 ± 4	0.83 ± 0.06	0.99 ± 0.12	

(right margin: PARAMETRIC VALUE — Drinking water — < / >)

Water characteristics								
HRT_{cat}	pH	Electrical conductivity	Nitrate	Chloride	Free chlorine	T. coliforms	*E. coli*	*Enterococcus*
[h]		[mS cm^{-1}]	[mg NO_3^- L^{-1}]	[mg Cl^- L^{-1}]	[mg Cl_2 L^{-1}]	[ufc 100 mL^{-1}]	[ufc 100 mL^1]	[ufc 100 mL^{-1}]
Untreated groundwater								
-	8.0 ± 0.3	1.3 ± 0.1	169.9± 5.3	93 ± 1	0.0 ± 0.0	0 ± 0	0 ± 0	1.3 ± 0.9
Treated groundwater								
2.4	6.5 ± 0.1[b]	1.4 ± 0.1	4.5 ± 0.6	385 ± 1	0.3 ± 0.1	*NaN*	*NaN*	*NaN*
1.6	6.8 ± 0.2[b]	1.5 ± 0.2	3.8 ± 0.6	380 ± 7	0.8 ± 0.1	*NaN*	*NaN*	*NaN*
1.3	6.6 ± 0.2[b]	1.7 ± 0.1	8.2 ± 3.5	395 ± 6	1.7 ± 0.8	0 ± 0	0 ± 0	0 ± 0
0.9	4.0 ± 0.2[b]	1.9 ± 0.3	2.7 ± 1.8	361 ± 33	4.1 ± 1.2	*NaN*	*NaN*	*NaN*
0.7	3.0 ± 0.1[b]	2.0 ± 0.1	15.1 ± 7.7	399 ± 29	4.4 ± 1.4	*NaN*	*NaN*	*NaN*

quality of the treated water up to the point of use. The disinfection capacity was also evaluated during the HRT_{cat} test of 1.3 h, with a free chlorine concentration of 1.7 ± 0.8 mg Cl_2 L^{-1}. This analysis revealed the absence of Total coliforms, *E. coli,* and *Enterococcus*, as the European Directive 2020/2184 required.

The European Directive 2020/2184 indicates other less stringent parameters for monitoring and ensuring human health protection. Some of these quantitative and qualitative parameters are pH, electrical conductivity, other ion content, colour, taste and odour. The pH was maintained at neutral levels, as recommended by the same guideline (6.5 < pH < 9.5), for HRT_{cat} higher than 1.3 h (Table 1 and Fig. 2). Only when the $HRTs_{cat}$ were lower than 1.3 h the pH was dropped below 6.5. At these conditions, the higher current densities exacerbated the pH difference between the anode-cathode, implying: (i) higher anode potential from 1.49 ± 0.02 (HRTcat of 2.4 h) to 2.05 ± 0.12 V *vs.* Ag/AgCl (HRTcat of 0.7 h) and (ii) higher requirement for acid dosage (Table 1).
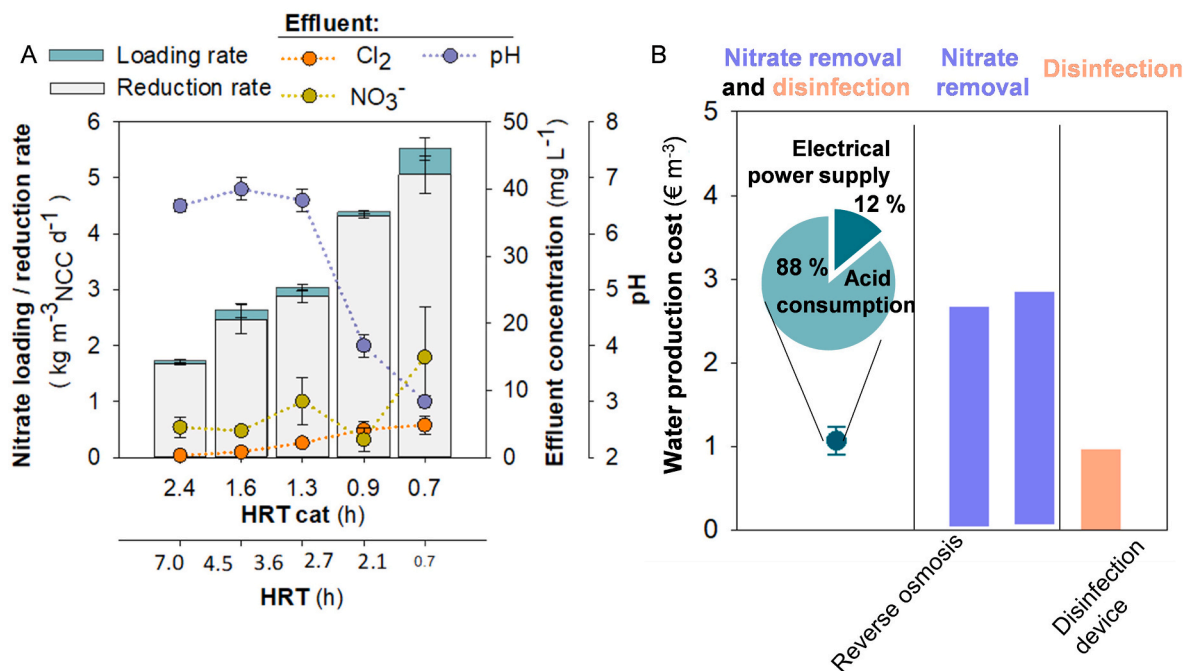

Fig. 2. Main results at the different HRT_{cat} tested (A) and economic assessment of the presented treatment (electro-bioremediation) compared with the range of the operational cost of other conventional treatments for nitrate removal at very small scale (10–190 m^3 d^{-1}) (Jensen et al., 2012) and chlorination-based disinfection devices (1–3 m^3 d^{-1}) (Dossegger et al., 2021) (B). Cost values were converted from dollars to euros using the exchange rate of the year of publication. 2-column fitting image.

The electrical conductivity gradually increased due to the addition of acid, reaching 2.0 ± 0.1 mS cm^{-1} at the lower HRT$_{cat}$ of 0.7 h. However, it never surpassed the recommended value of 2.5 mS cm^{-1}. Meanwhile, chloride concentration overcame the suggested value of 250 mg Cl^{-} L^{-1}, increasing from 92 ± 1 mg Cl^{-} L^{-1} in the influent to 387 ± 24 mg Cl^{-} L^{-1} in the effluent. Finally, this chloride concentration should not have any health risks. Finally, the colour appears unchanged, while chlorine accumulation would only slightly influence the taste and odour.

In conclusion, electro-bioremediation is a powerful treatment to meet the mandatory drinking water requirements. Specifically, the more sustainable HRT$_{cat}$ to meet the neutral pH was 1.3 h (Table 1). Nevertheless, to sustain operation at lower HRTs$_{cat}$ and achieve a higher treatment rate, a viable approach is to blend the treated groundwater with a fraction of untreated groundwater. This method, commonly used in drinking water services, would balance the pH in lower HRTs$_{cat}$ and decrease chloride levels while maintaining safe nitrate levels.

3.2. Techno-economical implications for decentralised water treatment

Electro-bioremediation is a promising option for sustainable decentralised water treatment, even though its real applicability is currently being evaluated. The success of this transition relies on the treatment's effectiveness, competitiveness, and feasibility. Therefore, after verifying the satisfactory quality of the treated water, the present study carefully evaluated key factors such as reaction rates, efficiency and costs to assess the competitiveness of the treatment (Fig. 2).

3.2.1. Improving nitrate reduction performance

Nitrate removal in the presented treatment was achieved through the denitrifying biocathode, utilising the cathode as the sole electron donor. Previously, a cathode potential of -0.32 V *vs.* Ag/AgCl was identified as the optimal potential for achieving the highest nitrate reduction rate in similar bioelectrochemical reactors (Pous et al., 2015). Specifically, the biocathode used to inoculate the reactor in this study exhibited a robust electroactive response at a cathode potential of -0.32 V *vs.* Ag/AgCl in the presence of nitrate in the media. Further electrochemical characterisation by cyclic voltammetry revealed a formal potential of approximately -0.20 V *vs.* Ag/AgCl associated with nitrate reduction (Fig. S1, Supplementary Data) (Ceballos-Escalera et al., 2021). Meanwhile, testing similar denitrifying biocathodes with cyclic voltammetry indicated a clear electrochemical response in the presence of nitrate, with a wide range of formal redox potentials between -0.200 V and -0.70 V *vs.* Ag/AgCl (pH 7.0–8.0) (Ceballos-Escalera et al., 2024; Korth et al., 2022; Pous et al., 2014, 2016). Moreover, the electric current of the reactor was enhanced by reducing the HRT$_{cat}$, which resulted in higher nitrate reduction rates (Table 1). At the same time, the reactor demonstrated a remarkable coulombic efficiency in nitrate reduction, assuming the cathode as the sole electron donor, with an average of 101 ± 6 % observed in all tests (data not shown). This highlights the strong selectivity of nitrate removal using the electrode as the electron source.

The nitrate removal efficiency remained consistently above 90 % in all tests. Complete reduction to nitrogen gas was achieved without accumulating intermediates such as nitrite or nitrous oxide. As a result, by decreasing the HRT$_{cat}$ from 2.4 h to 0.7 h, the nitrate removal rate increased from 1.7 ± 0.0 to 5.0 ± 0.3 kg NO$_3^-$ m$_{NCC}^{-3}$ d^{-1} (Table 1, Fig. 2). Although the highest nitrate reduction rate, while maintaining the recommended neutral pH according to the European Directive 2020/2184, was achieved at an HRT$_{cat}$ of 1.3 h with a rate of $2.9 \pm 0.$ kg NO$_3^-$ m$_{NCC}^{-3}$ d^{-1}. As far as the author knows, this study has achieved the highest reported nitrate reduction rate in a bioelectrochemical system, reaching a maximum rate of 5.0 ± 0.3 kg NO$_3^-$ m$_{NCC}^{-3}$ d^{-1}. Previous studies have reported a maximum nitrate reduction of up to 3.7 kg NO$_3^-$ m$_{NCC}^{-3}$ d^{-1} at HRT$_{cat}$ of 0.5 h (Pous et al., 2017).

The intensification of the process in the cathode compartment can be mainly attributed to two key operating procedures: (i) applying pH control at the cathode and (ii) implementing internal recirculation. pH

plays a critical role in the denitrifying bioelectrochemical reactor, with neutrality being identified as the optimal pH (Rogińska et al., 2023). In particular, a more fundamental study of denitrifying biocathodes has shown a suitable pH in the range of 6–8 (Korth et al., 2022). Furthermore, nitrate reduction is a pH-dependent process that consumes protons. This consumption leads to an increase in pH within the cathodic compartment. This is particularly challenging when dealing with groundwater due to the low electrical conductivity, which also limits proton transport from the anode to the cathode. Additionally, internal recirculation enhances reactor hydrodynamics, overcoming mass transfer limitations inherent in systems with low electrical conductivity (Ceballos-Escalera et al., 2021). This improvement enhances reactor homogeneity, reducing pH and substrate (i.e., nitrate) gradients along the biocathode.

3.2.2. In-situ chloride recovery for disinfection

After the reduction of nitrate in the cathode compartment, the treated groundwater flowed into the anode compartment, where two potential abiotic reactions could occur due to the presence of the anode material (Ti-MMO) and the operational anode potential ($> +1.49 \pm 0.02$ V *vs.* Ag/AgCl): (i) water oxidation to oxygen (E$^o_{H2O/O2}$ = $+1.03$ V *vs.* Ag/AgCl) and (ii) chloride oxidation to chlorine (E$^o_{Cl-/Cl2}$ = $+1.16$ V *vs.* Ag/AgCl). While oxygen has a low economic interest, chlorine is widely used as a disinfectant in drinking water systems (Bereiter et al., 2021). Specifically, in the context of groundwater with low organic matter content, chlorination is a sustainable disinfection method due to its minimal risk of toxic by-product formation (Mazhar et al., 2020). Additionally, the present system took advantage of the addition of hydrochloric acid in the cathodic compartment, which increased the chloride concentration (385 ± 25 mg Cl^{-} L^{-1}, Table 1). The rise in chloride concentration promoted the *in-situ* electrochemical production of chlorine.

In all HRTs$_{cat}$ tested, the effluent consistently kept an adequate free chlorine concentration to ensure effective *in-situ* disinfection. This concentration progressively increased from 0.3 ± 0.1 to 4.4 ± 1.4 mg Cl$_2$ L^{-1} by decreasing the HRT$_{cat}$ (Fig. 2). Lower HRTs$_{cat}$ induced higher nitrate reduction rates associated with higher current densities. Under such conditions, the anode potential increased from 1.49 ± 0.02 (HRT$_{cat}$ of 2.4 h) to 2.05 ± 0.12 V *vs.* Ag/AgCl (HRT$_{cat}$ of 0.7 h) to sustain this current, promoting chlorine accumulation on the effluent. Besides, the low pH under lower HRTs$_{cat}$ (pH of 3.0 ± 0.1 at 0.7 h) forces a displacement of the chemical equilibrium (hypochlorite) to chlorine.

3.2.3. Operational costs

The sustainability of electro-bioremediation relies on minimising reagent usage and substituting them with electrochemical reactions to reduce treatment costs. This reduction in reagent dependency also enables the implementation of the treatment in remote areas. The operational costs of the presented treatment were attributed to the hydrochloric acid for pH control and the electrical power required to maintain the bio- and electrochemical reactions. It is important to note that previous studies have identified the power supply as the primary energy consumer in bioelectrochemical reactors (Cecconet et al., 2018b; Zou and He, 2018). The operational cost estimation does not include additional costs associated with external pumping systems or personnel costs. Additionally, expenses can vary based on the specific settings used in each scenario, as well as variations in reagent and electricity costs in different regions. However, the price structure is expected to remain the same.

The estimated operational cost was 1.05 ± 0.16 € m^{-3} based on the outcome achieved at an HRT$_{cat}$ of 1.3 h, which kept a neutral effluent pH while achieving the highest nitrate reduction rate. The breakdown of costs reveals that power supply accounted for about 12 % of the total cost, equivalent to 0.13 ± 0.01 € m^{-3}. Additionally, the low energy demand (0.63 ± 0.07 KWh m^{-3}) and the resilience of the bioelectrochemical systems to power fluctuation support the feasibility of

using renewable energy sources (Rovira-Alsina et al., 2021). This opens up the possibility of utilising solar panels to achieve self-sufficiency and reduce the operational costs associated with energy consumption. On the other hand, the cost of hydrochloric acid accounted for 88 % of the operating costs. Considering the hydrochloric acid market price, the estimated cost was approximately $0.92 \pm 0.15 \, \text{€} \, \text{m}^{-3}$.

It is worth noting that electro-bioremediation presents a competitive cost compared to other commonly used nitrate removal treatments such as reverse osmosis (0.04–2.67 € m^{-3}) and ion-exchange resin (0.07–2.85 € m^{-3}) (Jensen et al., 2012). Moreover, electro-bioremediation offers a lower environmental impact by removing nitrate instead of concentrating it in brines (Fig. 2). Furthermore, this process combines the reduction of nitrates with disinfection, removing the requirement for further treatment to achieve potable water. Decentralised water treatment systems often require separate chlorination-based disinfection devices, resulting in a cost between 0.01 and 0.93 € m^{-3} (Dossegger et al., 2021). The main operating cost associated with acid consumption (88 %) was recovered by utilising in-situ chlorine production. Besides, the need for transporting and handling hazardous disinfectant chemicals was eliminated. Thus, this approach may reduce costs and enhance the overall sustainability and safety of the treatment.

4. Conclusions

This study optimised the cost-effectiveness of treating nitrate-contaminated groundwater through electro-bioremediation, effectively merging nitrate reduction and chlorine production in a single unit. The nitrate reduction rate was enhanced by implementing cathodic pH control at 6.8 ± 0.2, reaching the maximum reported rate in the literature so far ($5.0 \pm 0.3 \, \text{kg} \, \text{NO}_3^- \, \text{m}_{\text{NCC}}^{-3} \, \text{d}^{-1}$ at an HRT$_{\text{cat}}$ of 0.7 h). Subsequently, the hydrochloric acid utilised to control the cathodic pH was recovered to produce chlorine *in-situ* with a final concentration ranging from 0.3 ± 0.1 to $4.4 \pm 1.4 \, \text{mg} \, \text{Cl}_2 \, \text{L}^{-1}$. Chlorine evolution allowed a correct disinfection of effluent water. For the first time in electro-bioremediation, the overall quality of treated water has been assessed taking into account both the chemical and biological requirements for drinking water. The results demonstrated nitrate and nitrite concentrations below the specified limits and the absence of pathogens such as T. coliforms, *E. coli,* and *Enterococcus*. Finally, the competitiveness of electro-bioremediation compared with conventional treatments was demonstrated by the estimated operating cost of $1.07 \pm 0.17 \, \text{€} \, \text{m}^{-3}$ and the lower environmental impact. In addition, the technology is attractive for meeting drinking water standards in rural areas due to its minimal chemical dependency and complete absence of residue formation. In conclusion, these results strongly encourage further research into electro-bioremediation of nitrate-contaminated groundwater and open the door to real implementation of this technology in the rural areas.

CRediT authorship contribution statement

Alba Ceballos-Escalera: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Narcís Pous:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – review & editing. **M. Dolors Balaguer:** Conceptualization, Funding acquisition, Supervision, Validation, Writing – review & editing. **Sebastià Puig:** Conceptualization, Funding acquisition, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.141370.

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