



Electrochemical water softening as pretreatment for nitrate electro bioremediation

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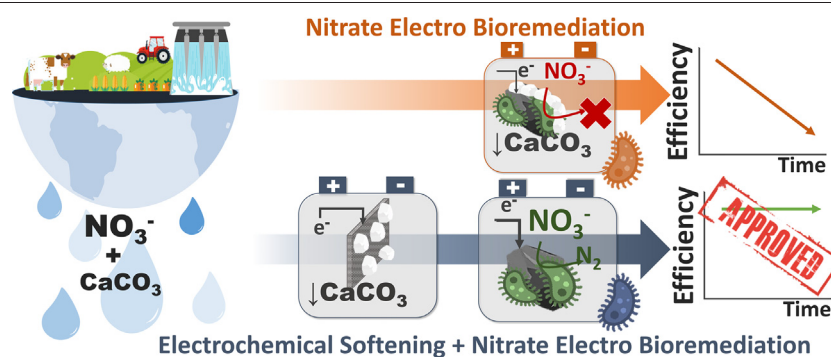
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HIGHLIGHTS

- Electrochemical softening reduced 90% the saturation index of groundwater.
- Softened groundwater reached suitable properties for nitrate electro bioremediation
- Reversal polarity periods increased the electrochemical softening lifetime up to 48%.
- Electrochemical softening with a competitive operational cost

GRAPHICAL ABSTRACT



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ABSTRACT

Electro bioremediation is gaining interest as a sustainable treatment for contaminated groundwater. Nevertheless, the investigation is still at the laboratory level, and before their implementation is necessary to overcome important drawbacks. A prevalent issue is the high groundwater hardness that generates scale deposition on electrodes that irreversibly affects the treatment effectiveness and their lifetime. For this reason, the present study evaluated a novel and sustainable approach combining electrochemical water softening as a preliminary step for electro bioremediation of nitrate-contaminated groundwater. Batch mode tests were performed at mL-scale to determine the optimum reactor configuration (single- or two-chambers) and the suitable applied cathode potential for electrochemical softening. A single-chamber reactor working at a cathode potential of -1.2 V vs. Ag/AgCl was chosen. Continuous groundwater softening under this configuration achieved a hardness removal efficiency of $64 \pm 4\%$ at a rate of 305 ± 17 mg CaCO_3 $\text{m}^{-2}_{\text{cathode}} \text{h}^{-1}$. The saturation index at the effluent of the main minerals susceptible to precipitate (aragonite, calcite, and brucite) was reduced up to 90%. Softening activity plummeted after 13 days of operation due to precipitate deposition (mostly calcite) on the cathode surface. Polarity reversal periods were considered to detach the precipitated throughout the continuous operation. Their implementation every 3–4 days increased the softening lifetime by 48%, keeping a stable hardness removal efficiency. The nitrate content of softened groundwater was removed in an electro bioremediation system at a rate of 1269 ± 30 g NO_3^- $\text{m}^{-2}_{\text{NCC}} \text{d}^{-1}$ (97% nitrate removal efficiency). The energy consumption of the integrated system (1.4 kWh $\text{m}^{-3}_{\text{treated}}$) confirmed the competitiveness of the combined treatment and paves the ground for scaling up the process.

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1. Introduction

Electro bioremediation emerges as a sustainable treatment for contaminated groundwater to treat several pollutants, including organic and inorganic contaminants such as aromatic compounds, chlorinated hydrocarbons, and nutrients (Pous et al., 2018). This treatment is based on microbial electrochemical technologies (METs) and promotes the capacity of electroactive microorganisms to perform oxidation and reduction reactions with solid electron conductors (e.g., electrodes) (Rabaey et al., 2009). Hence, electro bioremediation overcomes the decontamination limitation due to the lack of suitable electron donors or acceptors in the environment, minimizing chemical addition and avoiding brines generation (Sevda et al., 2018; Wang et al., 2020). The electro bioremediation technology readiness level (TRL) is still at proof-of-concept level (TRL 3) since lab scale performances have not been successfully translated to pilot scale level so far. Nevertheless, the technology validation in the relevant environment (TRL 4) is now in progress (Barba et al., 2018; Ceconet et al., 2020; Palma et al., 2018; Tucci et al., 2021; Wang et al., 2020).

The matrix of groundwater is a crucial parameter for a successful implementation in a real environment. A prevalent issue is the high groundwater hardness that generates scale deposition. High local cathode pH enhances the precipitation of hardness ions (carbonate, calcium, and magnesium) usually present in groundwater, coating the electroactive biofilm and the electrode surface (Santini et al., 2017). This issue significantly reduces the effectiveness and lifetime of the treatment. In this context, scale prevention methods (water softening) are required rather than cleaning methods (e.g., acid washing), which would damage microorganisms. Water softening methods are usually based on chemical precipitation and ion exchange resins (Entezari and Tahmasbi, 2009; Oren et al., 2001). Although these technologies are widely used with high efficiencies, they are characterized by the constant addition of chemicals and/or the formation of large volumes of brines (Ariono et al., 2016).

Over the past few years, more sustainable technologies are proposed to reduce hardness ion concentration. Electrochemical water softening has been growing in interest due to its simple operation, low treatment cost (i.e., no chemical dosage), and minimization of brines generation (Clauwaert et al., 2020). The electrochemical water softening principle is based on electrochemical hydroxide generation, which increases the pH near the cathode surface. It promotes calcium and magnesium precipitation by direct reaction with hydroxide (e.g., $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$). The bicarbonate (HCO_3^-) usually present in groundwater also becomes carbonate (CO_3^{2-}), promoting the hardness removal by the formation of insoluble carbonates (e.g., calcium carbonate, CaCO_3). Up to now, research has moved from the understanding of the electrochemical precipitation mechanism (Gabrielli et al., 1996, 1997) to technology application (Clauwaert et al., 2020; Zhang et al., 2020). In recent years, different parameters have been studied to optimize the process such as reactor designs, materials, water composition and operational conditions (Lin et al., 2021; Sanjuán et al., 2019; Wang et al., 2021; Zhang et al., 2020). While these studies were mostly focused on cooling water applications, it has not been proved the applicability of electrochemical water softening as a pretreatment for a biologic groundwater treatment. The pretreated water must achieve specific characteristics for the optimum bioreactor operation such as neutral pH, absence of toxic compounds (i.e., hypochlorite), and nutrients for microorganism growth (i.e., nitrogen, carbon, calcium, magnesium, among others). Moreover, further characteristics are required in electro bioremediation, such as a suitable electrical conductivity to minimize overpotentials that may affect the bioelectrochemical performance (Puig et al., 2012).

In an electrochemical water softener, most of the precipitate gets attached to the cathode surface. This fact avoids further steps to remove suspended precipitate particles. However, the electrode coating by the precipitate leads to higher ohmic resistances and promotes cathode

deactivation that is a key issue for their implementation (Deslouis et al., 1997). Thus, periodical scale detachment is imperative during the continuous operation in the long term. Acid washing (i.e., HCl) is an effective and conventional method to remove the precipitate. However, the stream used during the process must be neutralized for their final disposal. For this reason, complementary techniques to increase the activity time are decisive to reduce the acid wash periodicity and, consequently, improve the sustainability of the treatment. Jin et al. (2019) proposed and tested the polarity reversal method as a detachment approach in mL-scale and short time experiments. In this period, the cathode turns into an anode, generating an oxidative environment that promotes precipitate detachment.

The present study raised the treatment for nitrate-contaminated groundwater with a high degree of hardness ($325 \pm 10 \text{ mg CaCO}_3 \text{ L}^{-1}$), combining electrochemical water softening as pretreatment to prevent scale deposition in the following nitrate electro bioremediation. Groundwater contamination by nitrate is widely extended due to intensive agriculture and livestock (Fewtrell, 2004). World Health Organization is defined nitrate as a dangerous inorganic pollutant (WHO, 2017) and the Nitrates Directive (91/676/EU) sets a nitrate concentration limit of $50 \text{ mg NO}_3^- \text{ L}^{-1}$ in drinking water for human health and safety. Against this backdrop, nitrate electro bioremediation is being investigated for moving to a real environment. The treatment is based on autotrophic denitrification to dinitrogen gas as an end-product using only the cathode as the electron donor and inorganic carbon as the carbon source (Ceballos-Escalera et al., 2021; Majone et al., 2015; Pous et al., 2015).

This research evaluated an electrochemical water softening reactor to achieve optimal characteristics for nitrate electro bioremediation. The experimental procedure for electrochemical softening was divided into the batch and continuous mode tests. Batch mode tests were performed at mL-scale to determine the optimum reactor configuration (single- and two-chambers) and the applied cathode potential to obtain suitable water characteristics for the following bioelectrochemical treatment. The energy consumption, the calcium precipitation rate, and the final water characteristics such as pH and hardness were monitored to choose the best reactor settings. Subsequently, a L-scale electrochemical water softening reactor was operated in continuous flow mode treating real nitrate-contaminated groundwater. Furthermore, the implementation of polarity reversal periods in the continuous softening as a cleaning method was tested to increase the cathode activity lifetime and, consequently, the softening time. Finally, the softened groundwater was treated in the nitrate electro bioremediation to assess the feasibility of the overall process.

2. Materials and methods

2.1. Electrochemical water softening setups

2.1.1. Batch setup

Two different electrochemical water softening configurations were assembled: single- and two-chambers (Fig. 1A). The single-chamber setup used a three-neck bottle with a total volume of 250 mL. The two-chamber setup had an H-type configuration of 250 mL total volume, where the anode and the cathode were separated by a cation exchange membrane ($2 \times 10^{-4} \text{ m}^2$, CEM, CMI-7000, Membranes Int., USA). Recirculation flow of 15 L d^{-1} was applied on the whole setup (single-chamber setup) or in the cathodic chamber (two-chamber setup) to improve the hydrodynamics and promote mass transfer. In both configurations, stainless steel mesh with a surface of $1.5 \times 10^{-2} \text{ m}^2$ (1.0 mm of light path and 0.4 mm of wire diameter, CISA, Spain) was used as the cathode, and the anode was a Ti-MMO electrode rod ($225 \times 6 \text{ mm}$, NMT electrodes, South Africa). The inter-electrode gap was 35 mm and 70 mm in the single- and two-chamber setup, respectively. The setups were equipped with an Ag/AgCl sat. KCl reference electrode (+0.197 V vs. standard hydrogen electrode,

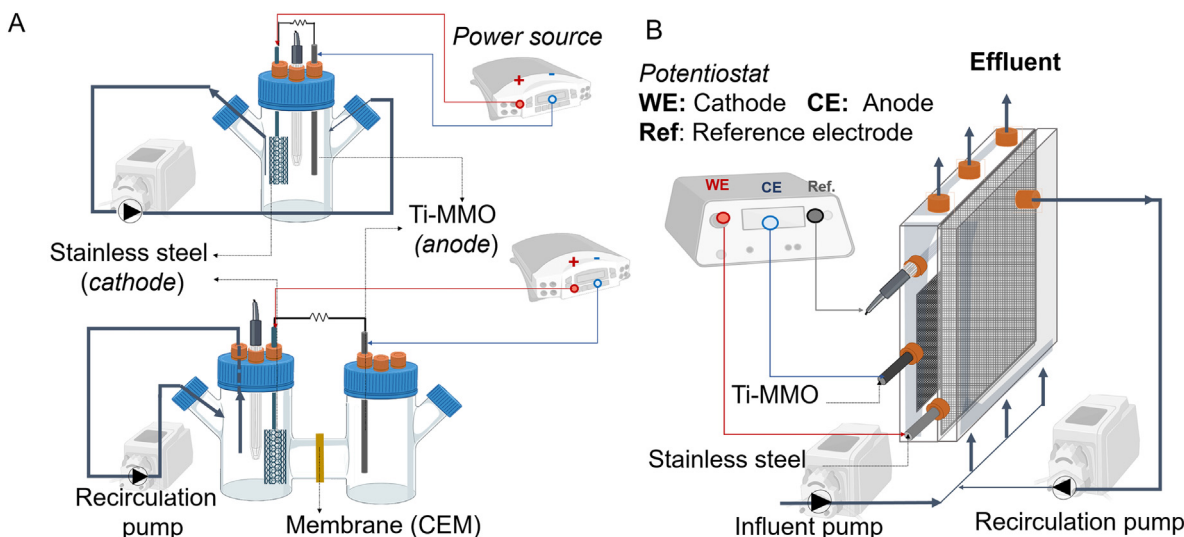


Fig. 1. Electrochemical water softening setups. (A) Scheme of batch tests setup, single-chamber on the top and two-chamber configuration on the bottom; (B) scheme of continuous electrochemical setup.

SHE, SE 11, Xylem Analytics Germany Sales GmbH & Co. KG Sensortechnik Meinsberg, Germany). A power source (TENMA 72–2715, Farnell, Spain) was used to control the cathode potential. Both setups were working under chronoamperometry mode. Two different cathode potentials were tested (-0.6 and -1.2 V vs. Ag/AgCl) following the results observed in other studies (Gabrielli et al., 2006). If not stated otherwise, all redox potentials were provided in respect of Ag/AgCl.

2.1.2. Continuous setup

A single-chamber reactor ($20 \times 20 \times 3$ cm³ internal dimension methacrylate frame, 1.2 L working volume) was used for continuous electrochemical water softening. Fig. 1B presents a scheme of the reactor setup. The cathode and the anode had an interelectrode gap of 15 mm. Two stainless steel mesh layers (20×20 cm² each layer, 1 mm mesh sizes, and 0.4 mm wire diameter, CISA, Spain) were assembled as the cathode with a total surface of 2.0×10^{-1} m². Ti-MMO mesh anode (10×10 cm², 2 mm light path and 1 mm wire diameter, NMT electrodes, South Africa) with a total surface of $6.3 \cdot 10^{-2}$ m² was used. Both electrode surfaces were calculated assuming each mesh wire. The reactor was equipped with an Ag/AgCl sat. KCl reference electrode ($+0.197$ V vs. SHE, SE 11, Xylem Analytics Germany Sales GmbH & Co. KG Sensortechnik Meinsberg, Germany) resulting in a three-electrode setup. The working electrode (cathode) was poised at -1.2 V vs. Ag/AgCl through a potentiostatic control using a potentiostat (VSP, Bio-Logic, France). The influent was directly pumped upwards through three different points to ensure accurate flux distribution. A recirculation flow of 50 L d⁻¹ was applied to promote the mass transfer and improve the hydrodynamics.

2.2. Groundwater characteristics

Two kinds of feed solutions were employed: (i) synthetic groundwater mimicking groundwater from Navata (Girona, Spain) and (ii) the real Navata groundwater.

Synthetic groundwater was used for electrochemical softening batch tests. The solution was prepared using distillate water with 360 mg L⁻¹ CaCl₂ (130 mg Ca²⁺ L⁻¹), 203 mg L⁻¹ MgSO₄ × 7H₂O (20 mg Mg²⁺ L⁻¹), 420 mg L⁻¹ NaHCO₃, 7 mg L⁻¹ KH₂PO₄, 2 mg L⁻¹ Na₂HPO₄ and 100 mg L⁻¹ NaCl. The average hardness was 400 ± 20 mg CaCO₃ L⁻¹. The electric conductivity and the pH values were 1.5 ± 0.1 mS cm⁻¹ and 7.5 ± 0.4 , respectively.

Real nitrate-contaminated groundwater extracted from Navata (Spain) was treated in the continuous electrochemical softening setup for the next nitrate electro bioremediation. The average hardness was 325 ± 10 mg CaCO₃ L⁻¹, the hardness ion concentration was 127 ± 21 mg Ca²⁺ L⁻¹ and 11 ± 4 mg Mg²⁺ L⁻¹, and nitrate concentration was 110 ± 6 mg NO₃⁻ L⁻¹ (composition showed in Supplementary data, Table S1). The pH was 7.5 ± 0.2 , and the electric conductivity was 0.7 ± 0.1 mS cm⁻¹.

2.3. Electrochemical water softening procedure

2.3.1. Batch mode test

Four different batch tests in duplicate were performed to evaluate the combination of two setup configurations (single- and two-chambers) and two cathode potentials (-0.6 and -1.2 V vs. Ag/AgCl). All experiments used 150 mL of synthetic groundwater per chamber and lasted 24 h at room temperature (25 ± 1 °C).

2.3.2. Continuous electrochemical water softening operation

The single-chamber reactor was operated under continuous flow mode at an hydraulic retention time (HRT) of 4.1 h (flow-rate of 7.1 L d⁻¹), based on the hardness removal rate obtained under batch conditions (325 ± 10 mg CaCO₃ L⁻¹) and aiming to achieve a hardness reduction of around 60% (target removal to reduce the saturation index by >90% of some problematic minerals such as calcite and aragonite). The operation was divided into two periods: (i) precipitation and (ii) detachment periods. Through the precipitation period, the system was operated under chronoamperometry mode at a cathode potential of -1.2 V vs. Ag/AgCl to promote the hydroxyl formation and hardness ions precipitation. The detachment period employed polarity reversal cycles, where the cathode (working electrode) was turned into an anode to remove the precipitate formed on the working electrode and increase its activity time. During polarity reversal, the influent was stopped, and the working electrode was poised at $+1.2$ V vs. Ag/AgCl for 10 min. After the detachment step, the medium was replaced with effluent to restart the operation condition before the precipitation period.

The reactor was operated under three different approaches (Fig. 2). The first strategy (A) was performed without any detachment period. The following B1 and B2 strategies were operated with periodical detachment periods (reverse polarity cycles). Strategy B1 tested polarity reversal cycles every 3–4 days, and it was tested every day in Strategy B2. Each strategy was carried out until the calcium precipitation efficiency dropped below 50%. Before each new strategy, the reactor was

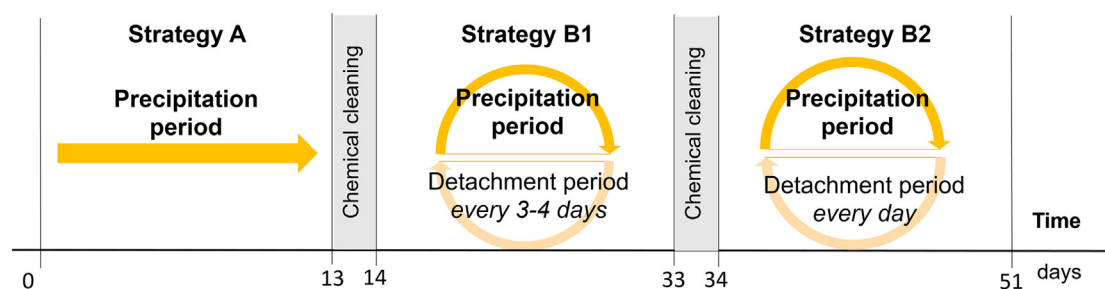


Fig. 2. Timeline of continuous electrochemical water softening operation.

chemically cleaned by recirculating hydrochloric acid solution (1.5 L of 0.1 M HCl, per cleaning) for a minimum of 3 h to remove the scale layer.

2.4. Coupling electrochemical water softening with nitrate electro bioremediation

The softened groundwater resulting from the continuous softening operation was used to feed the nitrate electro bioremediation reactor. The bioelectrochemical reactor was a fixed-bed tubular reactor previously started-up (Ceballos-Escalera et al., 2021). The cathode (inner part) and anode (outer part) compartments were filled with granular graphite. Electrodes surface of 0.51 m² (cathode) and 0.29 m² (anode) were estimated assuming granular graphite as spherical particles (average diameter of 3.25 mm) with a fixed-bed porosity of 50%. The net cathode (NCC) and anode (NAC) liquid volumes were 0.3 L and 0.15 L, respectively. The setup was equipped with an Ag/AgCl sat. KCl reference electrode (+0.197 V vs. standard hydrogen electrode, SHE, SE 11, Xylem Analytics Germany Sales GmbH & Co. KG Sensortechnik Meinsberg, Germany). The system was electrically operated under chronoamperometry mode, poisoning the cathode potential at -0.320 V vs. Ag/AgCl using a potentiostat (VSP, BioLogic, France). The cathode and the anode were hydraulically connected. The softened groundwater was pumped upwards through the cathode compartment at a flow-rate of 3.4 ± 0.1 L d⁻¹ (HRT_{cat} 2.1 ± 0.1 h) aiming to achieve nitrate conversions >90% based on previous experience (Ceballos-Escalera et al., 2021). It spilled over at the cathode top to the anode, and the treated effluent left through the bottom of the anode compartment. A fraction of the effluent was recirculated at 85 L d⁻¹ to the influent to increase the fluid distribution. This study presents the results of 15 days operating with electrochemical softened groundwater.

2.5. Analyses methods and calculations

Liquid-phase samples of effluent and influent during the continuous operations were taken periodically three times per week. As well, a minimum of three samples were taken throughout the 24-h batch tests. 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. Water hardness, calcium, and magnesium concentration were analyzed by a DR2800 spectrophotometer using a specific water hardness kit (LCK327, HACH Company, Loveland, CO, USA). In addition, some samples were analyzed according to APHA standard water measurements (APHA, 2005) to determine the anions (NO₃⁻, NO₂⁻, Cl⁻, PO₄³⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, and K⁺) composition by ionic chromatography (ICS 5000, Dionex, USA). Nitrous oxide (N₂O) was measured once a week in the bioelectrochemical setup using an N₂O liquid-phase microsensor (Unisense, Denmark) located in the effluent of the reactor.

The electrochemical water softening was evaluated in terms of total water hardness and hardness ions (calcium and magnesium) removal rate from the liquid phase. All softening rates were normalized by the cathode surface (mg h⁻¹ m⁻²). The energy consumption for the external power supply was normalized by the total hardness removed (kWh

kg⁻¹ CaCO₃). The nitrate electro bioremediation performance was evaluated in terms of nitrate removal rate normalized by the net cathode compartment volume (g NO₃⁻ m_{NCC}⁻³ d⁻¹), where the denitrification occurred. The cathodic coulombic efficiency and specific energy consumption for the external energy supply (kWh kg⁻¹ NO₃⁻) were calculated as proposed by (Pous et al., 2017). The total energy consumption for the combined treatment was normalized by the treated groundwater volume (kWh m⁻³). The main energy consumers considered were: (i) pumping system for feeding and recirculation in both reactors and (ii) external power supply. The energy consumption of pumps for each subunit was calculated as proposed by (Zou and He, 2018) (Supplementary data, Energy calculation). Finally, the construction cost (CAPEX) was estimated, assuming the electrodes and the membranes as the main cost. The reactor structure and other equipment such as pumps and sensors were not considered due to the design variability relying on the materials and the operational requirements. Besides, operation cost (OPEX) was also calculated considering: power supply for bio- and electrochemical reactions, power for other equipment (pumping system), and reagents. European electricity price in the second period of 2020 was assumed for the energy cost (0.21 € kWh⁻¹, Eurostat, 2020). The reagent was attributed to hydrochloric acid needed during the chemical cleaning in the electrochemical water softening, which was considered in the utilization of concentrated acid (HCl 20%) with a market price of 1.16 € L⁻¹. All calculations are shown in Supplementary data, Economic calculation.

The main minerals that can precipitate in the present study were predicted from the saturation index at pH 8. The data was calculated from the ionic groundwater composition using the freeware chemical equilibrium model Visual MINTEQ ver. 3.1 (KTH Royal Institute of Technology, Sweden). After testing strategies A and B2, the precipitate formed on the cathode surface was collected and analyzed. The phase composition of precipitates was analyzed by powder X-ray diffraction (XRD) (mod. D8 Quest Eco, Bruker); the analysis was carried out by Research Technical Services (STR) at of the University of Girona.

3. Results and discussion

3.1. Single- versus two-chamber systems for electrochemical water softening

Two configurations (single- and two-chamber) at different cathode potentials (-0.6 and -1.2 V) were assessed for electrochemical water softening as a pretreatment step for the nitrate electro bioremediation treatment. Table 1 summarizes the results obtained in batch mode experiments.

The cathode potential is a critical parameter for electrochemical reactions and energy consumption. Hydroxyl groups may be formed through two different reactions in large potentials range: (i) oxygen reduction ($E^{\circ} = +0.6$ V vs. Ag/AgCl, pH 7); and (ii) water reduction ($E^{\circ} = -0.6$ V vs. Ag/AgCl, pH 7). At practical level, oxygen reduction requires a cathode potential higher than water reduction, but dissolved oxygen diffusion from the liquid to the cathode surface is a constraining

Table 1

Batch tests to determine the suitable reactor configuration and applied cathode potential for electrochemical softening. Experimental time: 24 h.

	Cell configuration				Units
	Two-chamber		Single-chamber		
Cathode potential	−0.60	−1.20	−0.60	−1.20	V vs. Ag/AgCl
Final hardness	382 ± 19	102 ± 8	358 ± 18	108 ± 9	mg CaCO ₃ L ^{−1}
Calcium removal efficiency	12 ± 5	85 ± 6	3 ± 2	76 ± 2	%
Magnesium removal efficiency	30 ± 10	44 ± 6	19 ± 9	55 ± 6	%
Hardness removal efficiency	10 ± 4	74 ± 2	4 ± 6	73 ± 2	%
Maximum hardness removal rate	77 ± 66	371 ± 60	33 ± 32	252 ± 51	mg CaCO ₃ m ^{−2} h ^{−1}
Final electric conductivity	1.3 ± 0.0	0.4 ± 0.1	1.4 ± 0.0	0.4 ± 0.1	mS cm ^{−1}
Final pH	8.7 ± 0.0	10.1 ± 0.4	8.6 ± 0.0	6.8 ± 0.7	–
Cell voltage	1.7 ± 0.3	5.8 ± 0.7	0.5 ± 0.3	2.6 ± 0.2	V
Energy consumption	925 ± 529	2061 ± 469	155 ± 56	306 ± 177	kWh kg ^{−1} CaCO ₃

step. While at a more negative cathode potential (< 1.1 V vs. Ag/AgCl), water reduction takes more relevance, a process hindered by a lower mass transfer than oxygen reduction (Gabrielli et al., 2006). Consequently, the present study assessed two different cathode potentials (-0.6 and -1.2 V). The results are presented in Table 1. The maximum hardness removal rate increased around 5-fold in the two-chamber setup and 8-fold in the single-chamber setup operating at -1.2 V versus -0.6 V. Consequently, the hardness removal efficiency was below 10% in the test under -0.6 V and it was enhanced to 70% by decreasing the potential until -1.2 V. This is in agreement with other authors that identified this potential as the optimal for CaCO₃ with stainless steel as a cathode (Dirany et al., 2016). Therefore, the cathode potential of -1.2 V was chosen for softening, assuming water reduction as the main cathode reaction.

The reactor configuration is another important operational parameter. There are several approaches for electrochemical water softening reactors. Concerning the separation of the electrodes, it can be classified as a single- (Jin et al., 2019; Yu et al., 2019) or two-chamber system (Clauwaert et al., 2020; Hasson et al., 2010). Both configurations were tested in this study, reaching the same hardness removal efficiency of around 70% after each batch test under a cathode potential of -1.2 V. Nevertheless, the two-chamber configuration showed a hardness removal rate (371 ± 60 mg CaCO₃ h^{−1} m^{−2}) higher than the single-chamber system (252 ± 51 mg CaCO₃ m^{−2} h^{−1}), while the energy consumption was 85% lower when operating with a single-chamber reactor (Table 1). In addition, the two-chamber reactor presented a significant pH difference between both compartments (pH of 5.4 ± 1.5 and 10.1 ± 0.4 in the anodic and cathodic chambers, respectively). This pH gradient and further ohmic resistances (e.g., large interelectrode gap distance) were derived on a cell voltage (5.8 ± 0.7 V) higher than in the single-chamber reactor (2.6 ± 0.2 V).

Altogether, the potential of the cathode was considered the most decisive variable. The higher softening performances were observed in the tests at -1.2 V (Table 1). However, when considering electrochemical softening as a pretreatment for nitrate electro bioremediation, other parameters must be taken into account. Neutral pH is a strict characteristic for biological treatments, and it was only reached in the single-chamber setup (6.8 ± 0.7). Nevertheless, the two-chamber configuration presented a higher pH difference between the anode (5.4 ± 1.5) and the cathode (10.1 ± 0.4) because of the low proton diffusion through the cation exchange membrane. Hence, the single-chamber configuration was considered more suitable for the combined treatment proposed here. In addition, the simplification of the reactor configuration also reduces the setup costs (Kokabian and Gude, 2015).

3.2. Continuous groundwater softening

A 1.2 L single-chamber reactor was operated in continuous flow mode at a cathode potential of -1.2 V, treating real groundwater under different operational strategies (Fig. 2). The results obtained are shown in Fig. 3 and Table 2.

The application of strategy A allowed to reach a stable hardness removal rate of 305 ± 17 mg CaCO₃ m^{−2} h^{−1} (hardness removal of $66 \pm 4\%$), which corresponded to a calcium and magnesium precipitation efficiencies of 72 ± 5 and $40 \pm 6\%$, respectively. The average energy consumption was 3.6 ± 0.9 kWh Kg^{−1} CaCO₃ and the trend was progressively decreased throughout each operation due to cathode scaling. At the same time, the hardness reduction performance was kept until 12 days (Fig. 3) since crystals could still grow, although hydroxyl formation was reduced. Finally, the hardness reduction efficiency was drastically reduced to 30% after 13 days of operation. It is worth noting that the present study evaluates the hardness removal performance during a time frame of days instead of hours. The resulting cathodic precipitate was composed of calcium (65% calcite and 28% aragonite) and magnesium minerals (7% brucite) (Table 3). The prevalence of calcite was probably due to the low water conductivity (e.g., groundwater) and high Ca²⁺/Mg²⁺ ratio (Sanjuán et al., 2019).

The inactivation of the cathode is the main drawback in electrochemical water softening systems. In the present study, the softening activity was recovered between the different strategies using chemical cleaning. A chemical cleaning was carried out after Strategy A, and the hardness removal efficiency was recovered ($62 \pm 7\%$, strategy B1, days 15–18, Fig. 3). Although the chemical cleaning method was effective, it required the consumption of chemicals and generated an acid stream that needed to be neutralized for the final deposition. Hence, methods for extending the duration of softening before a chemical cleaning were required.

The present study implemented reverse polarity periods as a detachment strategy to increase the cathode activity lifetime and, consequently, the softening time. It was considered two different detachment periodicity strategies during the continuous softening operation: (i) every 3–4 days, B1; and (ii) every day, B2 (Fig. 3, Table 2). On the one hand, the hardness removal performance (291 ± 24 mg CaCO₃ m^{−2} h^{−1}, $61 \pm 2\%$) and the energy consumption (3.2 ± 0.2 kWh kg CaCO₃) were kept up during the precipitation period of strategies B1 and B2. On the other hand, the current density during the detachment period reached values ca. 700 mA m^{−2} with an energy consumption of $8 \pm 3 \times 10^{-5}$ kWh cycle^{−1}. The primary reaction under this condition was water oxidation, generating oxygen in the working electrode. This oxygen may form bubbles that create pressure on the scale deposition, leading to scale breaking and detachment (Yu et al., 2018). As pursued, the softening lifetime increased by 48% and 33% for strategy B1 and B2 compared to strategy A, respectively. The purge of the cathode surface by polarity reversal was effective, but the periodicity of this shock needs to be further optimized by taking into account that prolonged exposure to an oxidative environment may damage the stainless steel electrode (Jin et al., 2019). In fact, the application of polarity reversal with a periodicity of 3–4 days (strategy B1) was more beneficial than daily polarity reversal (strategy B2), but there is still room for improvement by exploring different alternative periodicities. A balance between cathode cleaning and

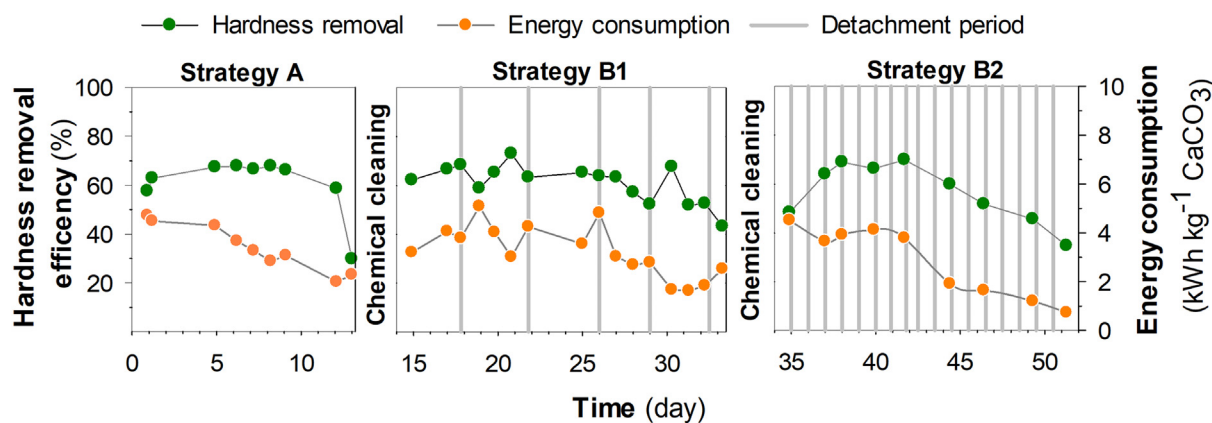


Fig. 3. Hardness removal efficiency and energy consumption evolution during the continuous water softening through the precipitation period. The system was operated under different strategies: Strategy A without detachment period; B1 with detachment period by applying polarity reversal every 3–4 days; and B2 with detachment period by applying polarity reversal every day. The grey line represents the detachment step (data not shown).

cathode protection, as well as the seek for the more appropriate electrode materials, will be key factors for the maximum exploitation of polarity reversal cleaning strategy.

The analysis of the precipitate extracted after the polarity reversal tests showed a slight change in the composition compared to strategy A (Table 3). The brucite fraction increased from 6.8 to 29.0%. This change could be due to higher magnesium precipitation (Table 2) and/or a more significant detachment of calcium minerals during polarity reversal periods. In addition, brucite precipitates present a porosity higher than calcite, which could have contributed to the increment of cathode activity lifetime (Sanjuán et al., 2019).

The electrochemical water softening is presented in the literature as a treatment environmental-friendlier than conventional treatments (i.e. ion exchange) due to the lower chemical requirements but with a high range of energy consumption according to the characteristics of the reactor ($1.5\text{--}27.1 \text{ kWh kg}^{-1} \text{ CaCO}_3$, Clauwaert et al., 2020; Luan et al., 2019; Zhang et al., 2020). The treatment presented in the current study showed a competitive energy consumption ($3.3 \pm 1.1 \text{ kWh kg}^{-1} \text{ CaCO}_3$, strategy B1), even though groundwater was treated instead of recirculating cooling water. The electrochemical water softening effectiveness on groundwater was also confirmed by the drastic reduction of the saturated index by 90% (Table 3). Softened water presented further characteristics suitable for nitrate electro bioremediation (Supplementary data, Table S1). For instance, nitrate content was not modified during the electrochemical water softening, and macronutrients for bacteria growth (e.g., phosphorous and potassium) remained present in the treated groundwater. A neutral pH, optimal for denitrification (Clauwaert et al., 2009) was maintained (6.5 ± 0.5). The low electrical conductivity ($0.4 \pm 0.0 \text{ mS cm}^{-1}$) was the

most limiting factor and it could reduce the effectiveness of the electro bioremediation treatment due to a limited ion diffusion capacity (Puig et al., 2012). Taking all results together, electrochemical softening presented the appropriate characteristics as a pretreatment for nitrate electro bioremediation.

3.3. Coupling electrochemical water softening to nitrate electro bioremediation

A bioelectrochemical reactor for nitrate electro bioremediation, which had successfully treated synthetic groundwater in previous work (Ceballos-Escalera et al., 2021), was switched to treat the softened groundwater. Table 4 compares the main characteristics and results of the electro bioremediation for nitrate removal operating with synthetic and softened groundwater at HRT_{cat} of 2.1 h. Treatment effectiveness had similar values treating softened groundwater or synthetic medium. Nitrate removal efficiency remained at $97 \pm 1\%$ with a nitrate removal rate of $1269 \pm 30 \text{ g NO}_3^- \text{ m}_{\text{NCC}}^{-3} \text{ d}^{-1}$ and a cathodic coulombic efficiency of $89 \pm 5\%$. The effluent nitrate concentration remained at values below $15 \pm 7 \text{ mg NO}_3^- \text{ L}^{-1}$, and neither nitrite nor nitrous oxide were detected. Hence, the effluent achieved the drinking water standards in terms of nitrates and nitrites (Nitrates Directive, 91/ 767 /EU). The low conductivity of softened groundwater (0.4 mS cm^{-1}) did not affect significantly the nitrate removal performance, but it generated overpotentials that increased the cell voltage of the system (Table 4). Consequently, the specific energy consumption increased by 23% from 5.1 ± 0.4 to $6.3 \pm 0.3 \text{ kWh kg}^{-1} \text{ NO}_3^-$ compared with the operation treating synthetic groundwater ($1.3 \pm 0.2 \text{ mS cm}^{-1}$). Nevertheless, the low conductivity did not become a

Table 2

Summary of the results corresponding to detachment and precipitation periods in the continuous flow mode. Strategy A without any detachment period, strategy B1 with detachment period by applying polarity reversal every 3–4 days, and strategy B2 with detachment period by applying polarity reversal every day.

Operational strategy	A	B1	B2	Units
Detachment period of 10 min: Polarity reversal setting				
Periodicity	Never	Every 3–4 days	Every day	–
Energy consumption	–	$8 \pm 2 \times 10^{-5}$	$7 \pm 3 \times 10^{-5}$	kWh cycle^{-1}
Precipitation period				
Softening time	13	19	17	days
Effluent hardness	115 ± 15	127 ± 22	126 ± 30	$\text{mg CaCO}_3 \text{ L}^{-1}$
Hardness removal efficiency	64 ± 4	62 ± 7	60 ± 10	%
Calcium removal efficiency	71 ± 5	64 ± 7	67 ± 7	%
Magnesium removal efficiency	29 ± 5	47 ± 13	50 ± 8	%
Hardness removal rate	305 ± 17	308 ± 33	274 ± 44	$\text{mg CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$
Effluent electric conductivity	0.4 ± 0.0	0.4 ± 0.0	0.4 ± 0.0	mS cm^{-1}
Effluent pH	6.0 ± 0.1	6.4 ± 0.4	7.1 ± 0.6	–
Energy consumption	3.6 ± 0.9	3.3 ± 1.1	3.1 ± 1.3	$\text{kWh kg}^{-1} \text{ CaCO}_3$

Table 3

Saturation index (pH = 8) of the main minerals that can precipitate in the untreated groundwater and after the electrochemical treatment. Data obtained from the freeware chemical equilibrium model Visual MINTEQ ver. 3.1 (KTH Royal Institute of Technology, Sweden). The phase composition of precipitate formed on the cathode surface after strategies A and B2. Solid analyzed by powder X-ray diffraction (XRD) (mod. D8 Quest Eco, Bruker).

Mineral	Saturation index (=log IAP – log Ks)		Precipitate composition (%)	
	Untreated groundwater	Treated groundwater	Strategy A	Strategy B2
Aragonite (CaCO ₃)	1.18	−0.07	27.8	14.3
Calcite (CaCO ₃)	1.32	0.07	65.4	56.7
Dolomite, disordered (CaMg(CO ₃) ₂)	1.75	−0.54	n.d.	n.d.
Dolomite, ordered (CaMg(CO ₃) ₂)	2.30	0.01	n.d.	n.d.
Vaterite (CaCO ₃)	0.75	−0.50	n.d.	n.d.
Brucite (Mg(OH) ₂)	−4.24	−4.61	6.8	29.0

critical factor for the overall nitrate removal performance. The hardness accumulation rate in the bioelectrochemical reactor with the softened groundwater was minimal (24 ± 7 g CaCO₃ m_{NCC}^{−3} d^{−1}, $1.4 \pm 0.4\%$), avoiding the massive scale formation in the bioreactor. These results prove the applicability of the electrochemical water softener as a pretreatment of nitrate electro bioremediation.

3.4. Cost-benefit analysis of the combined treatment

Cost analysis is a decisive parameter to assess a new technology. Thus, this study performed a preliminary construction (CAPEX) and operational (OPEX) cost evaluation to show the combined treatment feasibility (Fig. 4). The electrodes and the ion exchange membrane were considered the main cost in the electrochemical reactor construction. While, the operational cost of the electrochemical-based treatments was calculated assuming three main costs: power supply for bio- and electrochemical reactions, power for other equipment (pumping system), and reagents.

Electrochemical water softening was demonstrated to be an adaptable method as a pretreatment for electro bioremediation. On the one hand, the investment cost around 60 € considering only the electrodes and the estimated operational cost of 0.37 € m^{−3} emphasized the potentiality of the proposed treatment. The main reactor cost was the anode electrode (Ti-MMO, 700 € m^{−2}), but it is expected to have a long lifetime. Whereas the cathode electrode can be faster damaged. On the other hand, the operational cost balance showed the critical point on the reagents (HCl) for the periodical chemical cleaning (60% of the total cost). Hence, cleaning optimization or increasing softening lifetime promises to reduce the operating cost significantly. In this sense, the present study increased the softening time around 48% before the chemical cleaning by applying reversal polarity periods with a cost lower than 0.01 € m^{−3}. The second important parameter on OPEX was the power supply for the electrochemical reactions, consuming 0.69 kWh m^{−3} of treated groundwater (0.14 € m^{−3}). The cost is competitive compared to other conventional treatments such as chemical precipitation or ion exchange softening, the cost is competitive. For instance, Van der Bruggen et al. (2009) approximated the reagents cost for CaCO₃

precipitation using NaOH addition in a pellet reactor at 3.18 € m^{−3}. Ion exchange softening presented a lower cost (0.15 € m^{−3}, calculation in Supplementary data), although the resin regeneration had an intrinsic environmental desalination cost that was not considered in that balance.

For nitrate electro bioremediation, the estimated CAPEX for the electrodes materials and the membrane was reduced to 12 €, being the membrane the main cost. In the same way, the operational cost was estimated to be 0.14 € m^{−3} considering the principal cost in the power supply for the bioelectrochemical reactions (0.69 kWh m^{−3}). In contrast, the energy consumption for the pumping was calculated to be <0.01 € m^{−3} (Supplementary data). Thus, the combined treatment presented a low-cost construction and operation with an estimated total CAPEX of <70 € and OPEX of 0.51 € m^{−3}. The energy consumption is also an important parameter to evaluate. The calculated energy consumption of 1.4 kWh m^{−3} demonstrated the competitiveness of the combined treatment compared with other conventional treatments that also separate nitrate and other ions, such as reverse osmosis (0.9 – 2.2 kWh m^{−3}, Twomey et al., 2010). Nevertheless, nitrate treatments are currently moving from the non-specific separation to the complete reduction for their transformation or recovery (Vilardi, 2019; Vilardi et al., 2020). In this sense, electro bioremediation increases the value of the treatment in terms of complete nitrate reduction to dinitrogen gas (inert gas) in front of concentrated brines generated in reverse osmosis.

4. Conclusions

A novel treatment for nitrate in hard groundwater was developed by coupling an electrochemical softener and nitrate electro bioremediation. Electrochemical water softening was demonstrated to be suitable as a preliminary step for nitrate electro bioremediation. Batch mode tests determined that a single-chamber reactor with a cathode potential of -1.2 V vs. Ag/AgCl was the best configuration to obtain an effluent with suitable characteristics for the following electro bioremediation treatment. Continuous flow-mode studies achieved a hardness removal efficiency of around 60% resulting in a reduction of the saturation index

Table 4

Average of the results obtained nitrate electro bioremediation using synthetic groundwater and electrochemical water softening.

	Synthetic groundwater (Ceballos-Escalera et al., 2021)	Softened groundwater	Units
Cathodic hydraulic retention time	2.0 ± 0.1	2.1 ± 0.1	h
Influent electric conductivity	1.3 ± 0.0	0.4 ± 0.0	mS cm ^{−1}
Influent pH	8.2 ± 0.1	7.0 ± 0.2	
Influent nitrate concentration	156 ± 4	114 ± 3	mg NO ₃ [−] L ^{−1}
Nitrate loading rate	1909 ± 95	1291 ± 30	g NO ₃ [−] m _{NCC} ^{−3} d ^{−1}
Nitrate reduction rate	1906 ± 97	1269 ± 30	g NO ₃ [−] m _{NCC} ^{−3} d ^{−1}
Nitrate reduction efficiency	99 ± 0	97 ± 1	%
Coulombic efficiency	106 ± 10	89 ± 5	%
Cell voltage	-2.21 ± 0.01	-3.20 ± 0.05	V
Energy consumption	5.3 ± 0.5	6.3 ± 0.3	kWh kg ^{−1} NO ₃ [−]
Hardness accumulation rate	–	24 ± 7	g CaCO ₃ m _{NCC} ^{−3} d ^{−1}

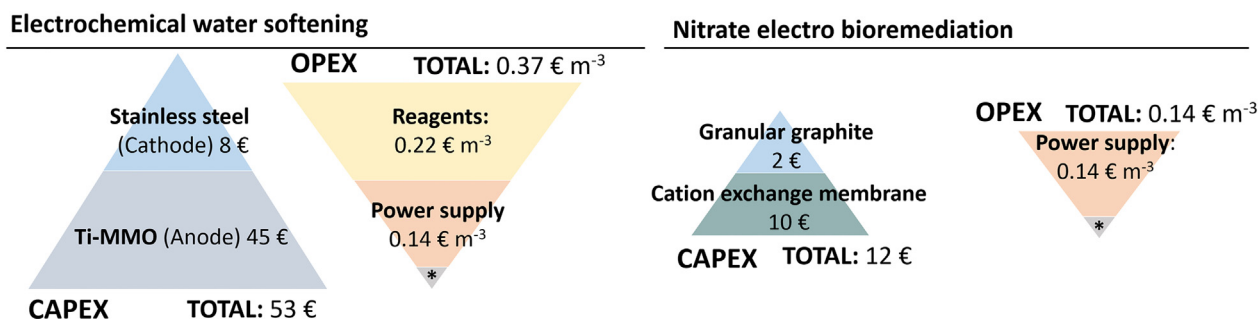


Fig. 4. Preliminary analysis of construction (CAPEX) and operational cost of the combined treatment based on electrochemical water softening and nitrate electro bioremediation.

of calcium and magnesium minerals up to 90%. Periods of reverse polarity were implemented to increase the softening active time, overcoming the main drawback of the electrochemical water softening. The application of reverse polarity periods every 3–4 days increased the softening time by 48% at low cost ($< 0.01 \text{ € m}^{-3}$), and reduced the need of chemical cleanings (main operation cost, 60%). Finally, the softened groundwater was treated by electro bioremediation, with a high conversion of nitrate into dinitrogen gas (97 ± 1 ; $1269 \pm 30 \text{ g NO}_3^- \text{ m}^{-3} \text{ d}^{-1}$). Consequently, the combined treatment produced an effluent that achieved the standards for drinking water in terms of both nitrates and nitrite at a competitive cost.

CRediT authorship contribution statement

The manuscript was written through the contributions of all authors. A. Ceballos-Escalera: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft; N. Pous: Conceptualization, Investigation, Methodology, Supervision, Writing – Review & Editing; M. D. Balaguer: Conceptualization, Methodology, Supervision, Funding acquisition, Writing – Review & Editing; S. Puig: Conceptualization, Methodology, Supervision, Funding acquisition, Writing – Review & Editing. All authors have given approval to the final version of the manuscript.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.150433>.

References

- APHA, 2005. *Standard Methods for the Examination of Water and Wastewater*. 19th ed. Am. Public Heal. Assoc, Washingt. DC, USA.
- Ariono, D., Purwasmita, M., Wenten, I.G., 2016. Brine effluents: characteristics, environmental impacts, and their handling. *J. Eng. Technol. Sci.* 48 (9), 367–387. <https://doi.org/10.5614/j.eng.technol.sci.2016.48.4.1>.
- Barba, S., López-Vizcaíno, R., Saez, C., Villaseñor, J., Cañizares, P., Navarro, V., Rodrigo, M.A., 2018. Electro-bioremediation at the prototype scale: what it should be learned for the scale-up. *Chem. Eng. J.* 334, 2030–2038. <https://doi.org/10.1016/j.cej.2017.11.172>.

- Ceballos-Escalera, A., Pous, N., Chiluita-Ramos, P., Korth, B., Harnisch, F., Bañeras, L., Balaguer, M.D., Puig, S., 2021. Electro-bioremediation of nitrate and arsenite polluted groundwater. *Water Res.* 190, 116748. <https://doi.org/10.1016/j.watres.2020.116748>.
- Ceconet, D., Sabba, F., Devecseri, M., Callegari, A., Capodaglio, A.G., 2020. In situ groundwater remediation with bioelectrochemical systems: a critical review and future perspectives. *Environ. Int.* 137, 105550. <https://doi.org/10.1016/j.envint.2020.105550>.
- Clauwaert, P., Desloover, J., Shea, C., Nerenberg, R., Boon, N., Verstraete, W., 2009. Enhanced nitrogen removal in bio-electrochemical systems by pH control. *Biotechnol. Lett.* 31, 1537–1543. <https://doi.org/10.1007/s10529-009-0048-8>.
- Clauwaert, P., De Paepe, J., Jiang, F., Alonso-Fariñas, B., Vaiopoulou, E., Verliefd, A., Rabaey, K., 2020. Electrochemical tap water softening: a zero chemical input approach. *Water Res.* 169, 115263. <https://doi.org/10.1016/j.watres.2019.115263>.
- Deslouis, C., Gabrielli, C., Keddad, M., Khalil, A., Rosset, R., Tribollet, B., Zidoune, M., 1997. Impedance techniques at partially blocked electrodes by scale deposition. *Electrochim. Acta* 42 (8), 1219–1233. [https://doi.org/10.1016/S0013-4686\(96\)00290-3](https://doi.org/10.1016/S0013-4686(96)00290-3).
- Dirany, A., Drogui, P., El Khakani, M.A., 2016. Clean electrochemical deposition of calcium carbonate to prevent scale formation in cooling water systems. *Environ. Chem. Lett.* 14, 507–514. <https://doi.org/10.1007/s10311-016-0579-x>.
- Entezari, M.H., Tahmasbi, M., 2009. Water softening by combination of ultrasound and ion exchange. *Ultrason. Sonochem.* 16 (3), 356–360. <https://doi.org/10.1016/j.ultsonch.2008.09.008>.
- Eurostat, 2020. Statistics explained: electricity price statistics second period. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_price_statistics.
- Fewtrell, L., 2004. Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ. Health Perspect.* 112 (14). <https://doi.org/10.1289/ehp.7216>.
- Gabrielli, C., Keddad, M., Perrot, H., Khalil, A., Rosset, R., Zidoune, M., 1996. Characterization of the efficiency of antiscaling treatments of water. part I: chemical processes. *J. Appl. Electrochem.* 26, 1125–1132. <https://doi.org/10.1007/BF00243737>.
- Gabrielli, C., Keddad, M., Khalil, A., Rosset, R., Zidoune, M., 1997. Study of calcium carbonate scales by electrochemical impedance spectroscopy. *Electrochim. Acta* 42 (8), 1207–1218. [https://doi.org/10.1016/S0013-4686\(96\)00289-7](https://doi.org/10.1016/S0013-4686(96)00289-7).
- Gabrielli, C., Maurin, G., Francy-Chausson, H., Thery, P., Tran, T.T.M., Tlili, M., 2006. Electrochemical water softening: principle and application. *Desalination* 201 (1–3), 150–163. <https://doi.org/10.1016/j.desal.2006.02.012>.
- Hasson, D., Sidorenko, G., Semiat, R., 2010. Calcium carbonate hardness removal by a novel electrochemical seeds system. *Desalination* 263 (1–3), 285–289. <https://doi.org/10.1016/j.desal.2010.06.036>.
- Jin, H., Yu, Y., Zhang, L., Yan, R., Chen, X., 2019. Polarity reversal electrochemical process for water softening. *Sep. Purif. Technol.* 210, 943–949. <https://doi.org/10.1016/j.seppur.2018.09.009>.
- Kokabian, B., Gude, V.G., 2015. Role of membranes in bioelectrochemical systems. *Membr. Water Treat.* 6 (1), 53–75. <https://doi.org/10.12989/mwt.2015.6.1.053>.
- Lin, W., Wang, Z., Wang, W., Chen, Q., Xu, J., Yu, J., 2021. Comparative analysis the performance of electrochemical water softening between high frequency electric fields and direct current electric fields based on orthogonal experimental methods. *Water Sci. Technol.* 83, 1677–1690. <https://doi.org/10.2166/WST.2021.084>.
- Luan, J., Wang, L., Sun, W., Li, X., Zhu, T., Zhou, Y., Deng, H., Chen, S., He, S., Liu, G., 2019. Multi-meshes coupled cathodes enhanced performance of electrochemical water softening system. *Sep. Purif. Technol.* 217 (15), 128–136. <https://doi.org/10.1016/j.seppur.2019.01.054>.
- Majone, M., Verdini, R., Aulenta, F., Rossetti, S., Tandoi, V., Kalogerakis, N., Agathos, S., Puig, S., Zanolari, G., Fava, F., 2015. In situ groundwater and sediment bioremediation: barriers and perspectives at european contaminated sites. *New Biotechnol.* 32 (1), 133–146. <https://doi.org/10.1016/j.nbt.2014.02.011>.
- Oren, Y., Katz, V., Daltrophe, N.C., 2001. Improved compact accelerated precipitation softening (CAPS). *Desalination* 139 (1–3), 155–159. [https://doi.org/10.1016/S0011-9164\(01\)00305-8](https://doi.org/10.1016/S0011-9164(01)00305-8).
- Palma, E., Daghighi, M., Franzetti, A., Petrangeli Papini, M., Aulenta, F., 2018. The bioelectric well: a novel approach for in situ treatment of hydrocarbon-contaminated groundwater. *Microb. Biotechnol.* 11, 112–118. <https://doi.org/10.1111/1751-7915.12760>.
- Pous, N., Puig, S., Dolores Balaguer, M., Colprim, J., 2015. Cathode potential and anode electron donor evaluation for a suitable treatment of nitrate-contaminated groundwater in bioelectrochemical systems. *Chem. Eng. J.* 263, 151–159. <https://doi.org/10.1016/j.cej.2014.11.002>.

- Pous, N., Puig, S., Balaguer, M.D., Colprim, J., 2017. Effect of hydraulic retention time and substrate availability in denitrifying bioelectrochemical systems. *Environ. Sci.: Water Res. Technol.* 3, 922–929. <https://doi.org/10.1039/c7ew00145b>.
- Pous, N., Balaguer, M.D., Colprim, J., Puig, S., 2018. Opportunities for groundwater microbial electro-remediation. *Microb. Biotechnol.* 11, 119–135. <https://doi.org/10.1111/1751-7915.12866>.
- Puig, S., Coma, M., Desloover, J., Boon, N., Colprim, J., Balaguer, M.D., 2012. Autotrophic denitrification in microbial fuel cells treating low ionic strength waters. *Environ. Sci. Technol.* 46 (4), 2309–2315. <https://doi.org/10.1021/es2030609>.
- Rabaey, K., Angenent, L., Schröder, U., Keller, J., 2009. *Bioelectrochemical Systems: From Extracellular Electron Transfer to Biotechnological Application*. Water Intelligence Online. IWA Publishing, London <https://doi.org/10.2166/9781780401621>.
- Sanjuán, I., Benavente, D., Expósito, E., Montiel, V., 2019. Electrochemical water softening: influence of water composition on the precipitation behaviour. *Sep. Purif. Technol.* 211, 857–865. <https://doi.org/10.1016/j.seppur.2018.10.044>.
- Santini, M., Marzorati, S., Fest-Santini, S., Trasatti, S., Cristiani, P., 2017. Carbonate scale deactivating the biocathode in a microbial fuel cell. *J. Power Sources* 356, 400–407. <https://doi.org/10.1016/j.jpowsour.2017.02.088>.
- Sevda, S., Sreekishnan, T.R., Pous, N., Puig, S., Pant, D., 2018. Bioelectroremediation of perchlorate and nitrate contaminated water: a review. *Bioresour. Technol.* 255, 331–339. <https://doi.org/10.1016/j.biortech.2018.02.005>.
- Tucci, M., Carolina, C.V., Resitano, M., Matturro, B., Crognale, S., Pietrini, I., Rossetti, S., Harnisch, F., Aulenta, F., 2021. Simultaneous removal of hydrocarbons and sulfate from groundwater using a “bioelectric well”. *Electrochim. Acta* 388, 138636. <https://doi.org/10.1016/j.ELECTACTA.2021.138636>.
- Twomey, K.M., Stillwell, A.S., Webber, M.E., 2010. The unintended energy impacts of increased nitrate contamination from biofuels production. *J. Environ. Monit.* 12 (218), 224. <https://doi.org/10.1039/b913137j>.
- Van der Bruggen, B., Goossens, H., Everard, P.A., Stembé, K., Rogge, W., 2009. Cost-benefit analysis of central softening for production of drinking water. *J. Environ. Manag.* 91, 541–549. <https://doi.org/10.1016/j.jenvman.2009.09.024>.
- Vilardi, G., 2019. Mathematical modelling of simultaneous nitrate and dissolved oxygen reduction by cu-nZVI using a bi-component shrinking core model. *Powder Technol.* 343, 613–618. <https://doi.org/10.1016/j.POWTEC.2018.11.082>.
- Vilardi, G., De Caprariis, B., Stoller, M., Di Palma, L., Verdone, N., 2020. Intensified water denitrification by means of a spinning disk reactor and stirred tank in series: kinetic modelling and computational fluid dynamics. *J. Water Process Eng.* 34, 101147. <https://doi.org/10.1016/j.JWPE.2020.101147>.
- Wang, X., Aulenta, F., Puig, S., Esteve-Núñez, A., He, Y., Mu, Y., Rabaey, K., 2020. Microbial electrochemistry for bioremediation. *Environ. Sci. Ecotechnol.* 1, 100013. <https://doi.org/10.1016/j.ese.2020.100013>.
- Wang, W., Chen, Q., Lin, W., Zheng, X., Xu, J., Yu, J., 2021. Effect of operational parameters and material properties on hardness removal efficiency by electrochemical technique. *Water Supply* <https://doi.org/10.2166/WS.2021.105>.
- WHO, 2017. *Guidelines for Drinking-water Quality: Fourth Edition Incorporating the First Addendum*. World Health Organization <https://doi.org/10.5942/jawwa.2017.109.0087>.
- Yu, Y., Jin, H., Jin, X., Yan, R., Zhang, L., Chen, X., 2018a. Current pulsed electrochemical precipitation for water softening. *Ind. Eng. Chem. Res.* 57 (18), 6585–6593. <https://doi.org/10.1021/acs.iecr.8b00448>.
- Yu, Y., Jin, H., Quan, X., Hong, B., Chen, X., 2019. Continuous multistage electrochemical precipitation reactor for water softening. *Ind. Eng. Chem. Res.* 58 (1), 461–468. <https://doi.org/10.1021/acs.iecr.8b04200>.
- Zhang, C., Tang, J., Zhao, G., Tang, Y., Li, J., Li, F., Zhuang, H., Chen, J., Lin, H., Zhang, Y., 2020. Investigation on an electrochemical pilot equipment for water softening with an automatic descaling system: parameter optimization and energy consumption analysis. *J. Clean. Prod.* 276, 123178. <https://doi.org/10.1016/j.jclepro.2020.123178>.
- Zou, S., He, Z., 2018. Efficiently “pumping out” value-added resources from wastewater by bioelectrochemical systems: a review from energy perspectives. *Water Res.* 131, 62–73. <https://doi.org/10.1016/j.watres.2017.12.026>.