In situ Groundwater Treatment with Bioelectrochemical Systems (BES): Critical Review and Future Perspectives

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Abstract

Groundwater contamination is an ever-growing environmental issue, that has attracted much and undiminished attention for the past half century. Groundwater contamination originates from anthropogenic (e.g. hydrocarbons), natural compounds (e.g. nitrate and arsenic), or both; to tackle these contaminants different technologies have been tested during the years. Recently, bioelectrochemical systems (BESs) have emerged as a potential treatment for groundwater contamination, with in situ applications reported, that showed promising results. Nitrate and hydrocarbons (toluene, phenanthrene, benzene, BTEX and light PAHs) have been successfully removed, due to the interaction of microbial metabolism with poised electrodes, other than physical migration due to the electric field generated in BES. The selection of proper BESs relies on several factors and problems such as complexity of the groundwater, scale-up and energy requirements that need to be taken into account. Modelling efforts could help predict case scenarios and choose an ideal design and approach to solve these issues. In this review, we critically analyze in situ BES applications for groundwater remediation, focusing in particular on the different setups proposed, and we identify and discuss the existing research gaps in the field.

Keywords: bioelectrochemical systems; groundwater remediation; bioelectroremediation; denitrification; *in situ* treatment

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1. Introduction

Groundwater is susceptible to pollutants and its contamination can cause it to become unsafe and unfit for human use. Contamination might be due to natural causes, for example arsenic (As) or nitrate (NO_3^-)-containing rocks (Menció et al., 2016; Tabelin et al., 2018) or more frequently by anthropic activities. Hence, a large variety of contaminants can be found in groundwater: aromatic compounds and chlorinated hydrocarbons (Logeshwaran et al., 2018), inorganic metallic compounds (Galitskaya et al., 2017; Luu et al., 2009), and nutrients (Chen et al., 2016). Recently, pharmaceutically active compounds (PhACs) and contaminants of emerging concern (CECs) have also been identified in groundwater as solutes (Lopez et al., 2015).

Different treatment technologies have been applied to groundwater remediation: physical, chemical and biological, with variable rate of success (Callegari et al., 2018; Dong et al., 2019; O'Connor et al., 2018; Sarkar and Paul, 2016). Application of Pump & Treat (P&T) schemes is among the most diffused strategies, whereby groundwater is extracted and subsequently treated outside of the aquifer; this type of solution allows for a better control of the process (i.e. directly observable by the operator), however this approach may be waste- and energy-intensive when the extracted groundwater is not in need of immediate use (Majone et al., 2015). Therefore, much research is focusing on the development of *in situ* treatments, which are considered to be more sustainable for the general protection of this resource.

Bioelectrochemical systems (BESs) have steadily emerged in the last 15 years as a versatile and promising technology. BESs have been employed in different ways for a variety of tasks: (1) microbial fuel cells (MFC), degrading organic matter and producing electrical energy (Capodaglio et al., 2013), (2) microbial electrolysis cells (MEC), producing valuable hydrogen gas at the cathode (Miller et al., 2019), (3) microbial desalination cells (MDC), providing desalinated water from seawater or brackish water (Brastad and He, 2013), and (4) microbial electrosynthesis systems (MES), synthetizing value-added chemicals and commodities using a poised biocathode (Wang and Ren, 2013). Additionally, BESs have been integrated with other technologies such as membrane

bioreactors, algal photobioreactors and capacitive deionization, in hybrid system configurations to increase overall performance, both in terms of energy consumption/production and contaminant removal (Xiao et al., 2012; Yuan et al., 2012).

Amongst the different applications of BESs, *in situ* groundwater bioelectroremediation, remediation using bioelectrochemical systems, showed to be a promising niche for these systems, due to their peculiar characteristics. These include the possibility to use different redox environments both at the anode and cathode, to work at different set potentials, and the flexibility of the technology (Modin and Aulenta, 2017). In addition, the combination of anodic and cathodic redox environment together with the microbial metabolism paves the way to a variety of intriguing and beneficial removal pathways.

Modin and Aulenta (2017) earlier reviewed the challenges and opportunities of *in situ* bioelectroremediation, mainly focusing on the general process and the biological mechanisms of electron-electrode transfer; however, in this review we shift the focus on different aspects of *in situ* bioelectroremediation. We first focus in depth on different *in situ* applications of bioelectrochemical systems for groundwater remediation, then we discuss the challenges for bioelectroremediation and finally also identify current research gaps and potential future research directions.

2. Practical hurdles in groundwater remediation suggesting BESs as possible solutions

An aquifer is undisputedly a challenging environment, therefore, due to the intrinsic nature of the surrounding environment, groundwater remediation will face several hindrances. Biological water/ wastewater treatment may require electron donors (in case reduction is required) and acceptors (in case oxidation is required). In a scenario of hydrocarbon contaminated groundwater, for instance, limited presence of electron acceptors (NO_3^-, oxygen, and sulfate) may limit contaminant oxidation. In addition, limited mixing within an aquifer allows replenishment of electron acceptors only at the physical boundary of a contaminated plume, where diffusion and dispersion are the predominant mixing factors (Li and Yu, 2015). Due to normally low concentration of organic matter in

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groundwater, a similar behavior can be observed for reduction reactions, such as denitrification, where the limiting electron donor may reduce the possible reaction rates (Shen et al., 2015). In addition, metabolism and growth of microorganisms may be slowed down in these circumstances since the majority of them is attached to soil particles or located in the sediments, where diffusion of electron acceptors and donors might be particularly difficult (Li and Yu, 2015).

Based on these premises, *in situ* bioremediation may become particularly challenging; the application of BESs may become a solution to the problem or at least to a large part of it. The lack of natural onsite electron acceptors and donors can be substituted by insertion of electrodes, acting as virtually inexhaustible electron acceptors (anode) or donors (cathode), thus supporting microbial metabolism (Aulenta et al., 2011). In some cases, addition of chemicals as electron donors/acceptors is chosen, requiring periodical replacement of the spent agents, which is not needed in the case of electrodes. In addition, when reduction reactions are involved, it is possible to set the desired cathodic electrode potential at a reductive level that simply cannot be reached by the sole addition of chemical reagents (Li and Yu, 2015; Williams et al., 2010).

Furthermore, water electrolysis could generate oxygen and hydrogen, which may serve respectively as additional electron acceptor and donor. Electrokinetic enhancement was reported to enhance mixing and mass transport, due to the electric field generated in proximity of the electrodes (Gill et al., 2014). Also, electro-osmosis can induce water displacement with subsequent resuspension of immobilized bacteria and contaminants. This leads to an increase of contact between substrate and bacteria, independently from the hydraulic conductivity of the porous medium (Gill et al., 2014; Jones et al., 2011; Li and Yu, 2015; Lohner et al., 2008; Xu et al., 2010).

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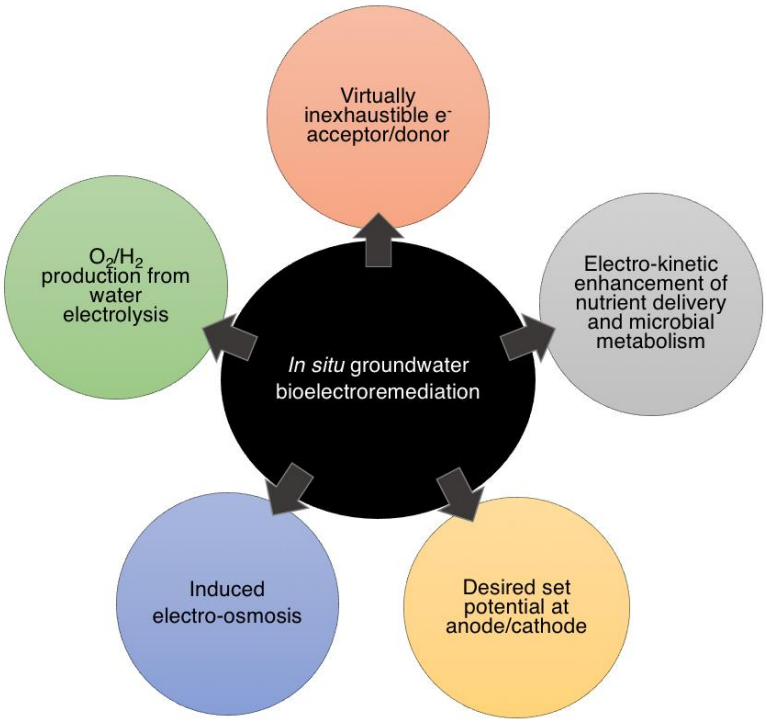

Figure 1: Main advantages of *in situ* bioelectroremediation.

Li and Yu (2015) reported other advantages of BESs application for groundwater *in situ* remediation, namely: electrokinetic enhancement of nutrient delivery and microbial metabolism connected to higher bioavailability, higher bacterial enrichment and adsorption due to large electrodes' surface.

3. *In situ* bioelectroremediation: the quest for the ideal setup

In the last decade, due to the multidisciplinary and faceted nature of BESs, different setups based on BES technology have been developed. The majority of applications have focused on groundwater denitrification and removal of petroleum hydrocarbons (Table 1). Petroleum hydrocarbons are usually removed in BES by oxidation in an anodic compartment; NO_3^- can be reduced in BESs to nitrogen gas via autotrophic denitrification or autohydrogenotrophic denitrification (at the cathode) or via heterotrophic denitrification (at the anode); the presence of organic matter is necessary in the latter case.

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Target	Name	Removal pathway (s)	Applied potential/voltage/driving force	Initial conc.	Rem. rate	η	Inoculum	Prevalent microbial species	Ref.
Nitrate	BES	Anodic heterotrophic denitrification	0.8 V (between electrodes)	25 mg NO_3^--N L^{-1}	208.2 ± 13.3 gNO_3^--N m^{-3} d^{-1}	90.50%	Digested sludge	-	Tong and He (2013)
Nitrate	SMDDC	Cathodic autotrophic denitrification	Voltage generated by OM oxidation at the anode	20 mg NO_3^--N L^{-1}	0.483 kgNO_3^--N m^{-3}_{TCV} d^{-1}	90.5% in 12 hrs	Electrodes precolonized in a MFC performing denitrification at the cathode	*Gammaproteobacteria* (*Shewanella*) (anode); *Alphaproteobacteria* and *Sphingobacteria* (cathode)	Zhang and Angelidaki (2013)
Nitrate	BES	Physical migration in a concentrating chamber & successive anodic heterotrophic denitrification	0.8 V (between electrodes)	21.4 mgNO_3^--N L^{-1}	N/A	55% in 17 hrs	Anaerobic sludge	-	Tong and He (2014)
Nitrate	Biocathode buried in simulated aquifer	Cathodic autotrophic denitrification	-0.7 V vs SHE	50 mg NO_3^--N L^{-1}	322.6 mg m^{-2} d^{-1}	-	Anaerobic sludge	*Thiobacillus*, *Paracoccus*	Nguyen et al. (2016a)
Nitrate	Biocathode buried in sand or gravel	Cathodic autotrophic denitrification	-0.303 V vs SHE	30 mg NO_3^--N L^{-1}	35.35 mgNO_3^--N m^{-2} d^{-1}	97%	Parent biocathode	-	Ceccone et al. (2019a)
			1.0 V (between anode and cathode)	30 mg NO_3^--N L^{-1}	36.23 mgNO_3^--N m^{-2} d^{-1}	100%	Parent biocathode	-	

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Nitrate	SMFC-BER	Cathodic autotrophic denitrification	0.27 mA, powered by a SMFC	30 mg NO_3^--N L^{-1}	3.87 mgN L^{-1} h^{-1}	-	Ground water	*Hyphomicrobium*, *Terrimicrobium*, *Teridiphaera*, *Prosthecobacter*	Liu et al. (2019)
Phenantrene and benzene	MFC	Anodic oxidation	MFC setup	100 ppm (phenantrene), 2000 ppm (benzene)	-	>80% (phenantrene, >90% (benzene)	Parent MFC	-	Adelaja et al. (2017)
Phenol	Bioelectric well	Anodic phenol oxidation	+0.2 V vs SHE (anode potential)	25 mg L^{-1}	59 ± 3 mg L^{-1} d^{-1}	99.5 ± 0.4%	Refinery wastewater	*Geobacter*	Palma et al. (2018a)
Toluene	Bioelectric well	Anodic toluene oxidation	+0.2 V vs SHE (anode potential)	25 mg L^{-1}	67.2 ± 5.7 mg L^{-1} d^{-1}	100%	Refinery wastewater	*Geobacter*	Palma et al. (2018b)
Benzene, toluene, ethyl-benzene, xylene	Bioelectric well	Anodic oxidation	+0.2 V vs SHE (anode potential)	5 mg L^{-1} (benzene), 14 mg L^{-1} (toluene), 2 mg L^{-1} (ethyl-benzene), 4 mg L^{-1} (xylene)	31.3± 1.5 mg L^{-1} d^{-1} (toluene), 6.1±0.3 mg L^{-1} d^{-1} (benzene), 3.3±0.1 mg L^{-1} d^{-1} (ethyl-benzene), 4.5±0.2 mg L^{-1} d^{-1} (xylene)	-	Refinery wastewater	*Geobacter*	Palma et al. (2019)
Light PAHs	GAC-BES	Anodic oxidation and adsorption on GAC	MFC setup	1546 mg L^{-1}	N/A	99%	Contaminated groundwater	*Beta-proteobacteria* (in particular *Pseudomanadaceae*)	Kirmizakis et al. (2019)

Table 1: Specifications of BES performing in situ groundwater treatment

Tong and He (2013) developed a BES, placed within the aquifer medium, able to attract NO_3^- in the anode chamber, and remove it by heterotrophic denitrification (Figure 2A); tests were carried

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out with both synthetic and real groundwater. Anode and cathode chambers consisted of separated porous tubes wrapped by anionic (AEM) and cationic (CEM) exchange membranes respectively. The anode chamber was fed with synthetic/real groundwater while the cathodic one with buffer solution. The system was operated in both MFC and MEC modes; application of 0.8 V potential between anode and cathode led to the best results, obtaining NO_3^- removal rates up to 208.2 ± 13.3 gNO_3^--N m^{-3} d^{-1}. Competition between ion exchange and electricity-driven migration was observed, leading to NO_3^- removal rate of 158.2± 4.2 gNO_3^--N m^{-3} d^{-1} in open circuit condition. In this case, electricity generation prevented the migration of undesired ions into groundwater by ion exchange inhibition. Higher current densities were recorded when the system was operated with real groundwater, due to the natural presence of other ions that enhanced ion movement and assisted electricity generation (Tong and He, 2013). In a follow-up study by Tong and He (2014), the current flow generated by a tubular BES induced NO_3^- migration out of groundwater, accumulating it in a concentration chamber, defined by the presence of CEM and AEM. The BES setup was similar to that of a tubular MDC (Figure 2C). Electrons generated by organic matter oxidation at the anode flowed to the cathode, while cations migrated to the concentration chamber from the anode. Simultaneously, anions, including the target pollutant NO_3^-, reached the concentration chamber through the AEM, where they were retained due to the presence of the CEM preventing their intrusion into the anode chamber. In this case, rather than biological denitrification, NO_3^- removal from groundwater was due mainly to the physical migration induced by the generated electric current, with a subsequent treatment needed to denitrify the concentrated feed afterwards (Tong and He, 2014). Zhang and Angelidaki (2013) proposed a modification of the MDC setup: bioelectricity was used to attract NO_3^- into the anodic chamber through an AEM, then NO_3^- was transferred to the cathode chamber, where it was reduced *via* autotrophic denitrification (Figure 2B). NO_3^- removal rate of 90.5% was obtained with HRT of 12 hours; in this case the ionic strength of groundwater was a limiting factor for NO_3^- removal. The addition of a nitrification step in the loop transferring NO_3^- from anode to cathode was beneficial to both bioelectricity production and NO_3^- attraction, removing ammonia (NH_3/NH_4^+) that appeared in

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the anode chamber due to the lack of aeration. The setup proved to be versatile, and capable, with minor modifications, to remove NH_3 from anaerobic reactors, at the same time balancing NH_3 inhibition (Zhang and Angelidaki, 2015a, 2015b)

Denitrification processes using biocathodes buried in a simulated aquifer have been investigated by Nguyen et al. (2016a), showing that NO_3^- removal rates depend on the burial percentage of the electrode; the electrodes were immersed in sand at a variable submersion percentage (10, 50 and 100%, plus a control without sand). 30% decrease in NO_3^- removal rates was observed and reported when recirculation was impeded by the addition of sand at the bottom of the cathode chamber (Nguyen et al., 2016a) (Figure 2D).

The need for local recirculation was discussed by Jain and He (2018), where, in order to achieve good BES performances, recirculation was indicated as an essential step to promote contact between substrate and biomass, while decreasing overpotentials. The required energy contribution of stirring in small reactors, or pumping in bigger reactors, cannot be however neglected, and may massively affect the overall energy balance of the application (Jacobson et al., 2015; Zou and He, 2018). Recently, Cecconet et al. (2019a) confirmed the decrease in NO_3^- removal rates reported by Nguyen et al. (2016a) by operating buried biocathodes completely immersed in sand and gravel, assisted by a potentiostat or power supply. The biocathodes operated in gravel achieved better results due to greater possibility of water movement compared to the one with sand. In addition, higher accumulation of intermediate nitrogen species was found in biocathodes operated by potentiostat, compared with those operated by power supply. Increased accumulation of intermediate nitrogen species, e.g. nitrous oxide (N_2O), has been shown in other studies to be a potential route of nitrogen loss in bioelectroremediation systems (Srinivasan et al., 2016; Van Doan et al., 2013; Vilar-Sanz et al., 2013). This is likely due to the intrinsic behavior of biofilms and their microbial stratification, interactions, substrate gradients and interaction allowing for biotic and abiotic formation of N_2O (Sabba et al., 2018). The results of Cecconet et al. (2019a) and Nguyen et al. (2016a) suggest that the

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177 insertion of electrodes in a porous medium, even though feasible and simple, presents some
178 limitations that could be corrected and eliminated with a more dedicated design (Figure 2D).

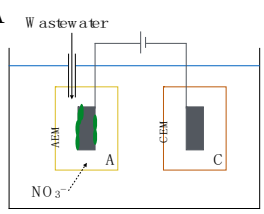
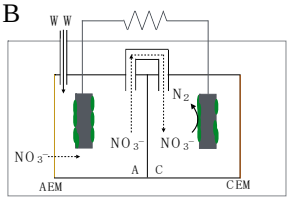
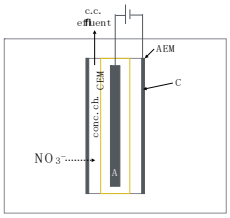
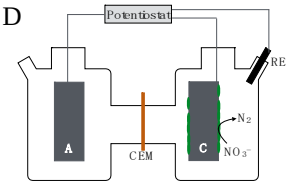
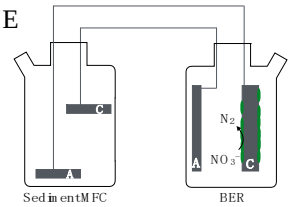
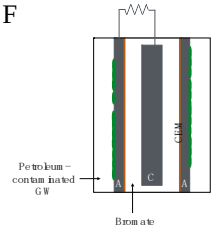
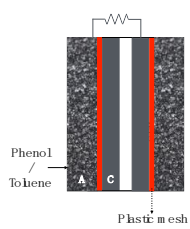
Target	Setup	Pros	Cons	Ref.
NO_3^-	A 	Heterotrophic denitrification (higher kinetics compared to autotrophic)	Necessity of power supply despite OM oxidation; wastewater as anolyte may contaminate the aquifer	Tong and He (2013)
NO_3^-	B 	Versatile	Use of wastewater as anolyte may contaminate the aquifer	Zhang and Angelidaki (2013)
NO_3^-	C 	Tubular, adapt to be used in wells	N physically concentrated, and not biologically removed	Tong and He (2014)
NO_3^-	D 	Simulation of an aquifer remediation	Membrane use not feasible, low performances	Nguyen et al. (2016a); Cecconet et al. (2019a)
NO_3^-	E 	Synergic remediation of sediment and groundwater	No need of wastewater or power supply to fuel the system	Liu et al. (2019)
Phenanthrene and benzene	F 	High performances in PAH removal	Use of bromate as catholyte is not sustainable	Adelaja et al. (2017)
Phenol, toluene, BTEX	G 	High performances, internal recirculation, absence of expensive membrane	Granular graphite may possess non-scalable properties	Palma et al . (2018a, 2018b, 2019)

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Figure 2: Advantages and disadvantages of different BES setups for *in situ* groundwater denitrification

A BES setup, known as "bioelectric well", was proposed for *in situ* remediation of hydrocarbon contaminated groundwater (Palma et al., 2018b) (Figure 2G). This setup consisted of a granular graphite anode and a stainless steel mesh cathode; physically separated by a polyethylene mesh, while hydraulic connection was maintained. The system, operated at the set anode potential of +0.2 V vs Standard Hydrogen Electrode (SHE), obtained nearly complete (99.5%) phenol removal. This BES showed an average degradation rate of 59 ± 3 mg L^{-1} d^{-1} when inoculated with refinery wastewater; lower performances, i.e. 23±1 mg L^{-1} d^{-1}, were recorded when municipal activated sludge was used as inoculum. In both cases, *Geobacter* species were predominant in the mature biofilm on the surface of the graphite granules at the anode.

In a follow-up study, Palma et al. (2018a) using the same, previously applied anode potential for phenol removal, tested the bioelectric well during long term operation to remove toluene, achieving the highest toluene removal rate reported so far for anaerobic toluene oxidation (67.2 ± 5.7 mg L^{-1} d^{-1}) (Figure 2G). *Geobacter* species acted as catalyzer for the oxidation, initiated by fumarate addition, a common removal pathway for hydrocarbon-degrading anaerobic microorganisms (Palma et al., 2018a). Recently, a bioelectric well showed to successfully remove mixtures of benzene, toluene, ethyl-benzene and xylenes (BTEX) from groundwater (Palma et al., 2019). Compared to other applications previously described, the bioelectric well has, due to its vertical design, the advantage of being easily adaptable for placement in existing groundwater wells. In addition, the setup could be easily scalable, and built to include internal recirculation. However, the use of granular graphite as electrode material might require some attention due to the material's non-scalable properties, as reported by other researchers (Rozendal et al., 2008; Zhou et al., 2011), and the tendency to form dead volumes in the bed with subsequent loss in performance (Cecconet et al.,

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2018b); therefore, the application of other 3-D, scalable electrode materials (e.g., carbon or graphite foam) should be further investigated.

Recently, Kirmizakis et al. (2019) proposed a BES for gasworks groundwater *in situ* remediation, designed with a graphite electrode chamber (in place of the conventional non-conductive material) coupled with granular activated carbon (GAC) to increase available anode surface area. A latex membrane was used to divide the anode from the cathode chamber. This GAC-BES showed 99% removal of aliphatic and aromatic compounds with rapid bacterial colonization. The main class of bacteria found in the system was betaproteobacteria with specific PAH-degrading *Pseudomonadaceaea*, commonly detected in gasworks-contaminated groundwater (Kirmizakis et al., 2019).

In situ treatment of phenantrene and benzene contaminated groundwater with a MFC was reported by Adelaja et al. (2017), where a tubular MFC was designed with carbon felt anode exposed to the contaminated groundwater and used for long term operation (about 155 days) (Figure 2F). The system was able to remove up to 90% petroleum hydrocarbons at the anode and up to 79% bromate (BrO_3^-) at the cathode (added as catholyte). The MFC was tested under copiotrophic (high concentration of organic C $\simeq$ 1500 ppm for benzene and 100 ppm for phenanthrene) and oligotrophic (low concentration of organic carbon $\simeq$ 50 ppb for both the considered contaminants) conditions. The highest (0.76 mW m^{-2}) and lowest (0.01 mW m^{-2}) power densities were achieved in copiotrophic and oligotrophic conditions respectively, while contaminants removal remained constantly high (higher than 80% for benzene and phenantrene in copiotrophic conditions).

Despite these interesting results, due to the toxicity of BrO_3^- (a known carcinogen, Hutchinson et al., 1997) and the possibility of leaks, the use of BrO_3^- as catholyte in *in situ* applications should be avoided, and should be strictly restricted to *ex situ* treatment. The presence of BrO_3^- in groundwater has been reported (Butler et al., 2005), originating mainly as byproduct of potabilization processes (Butler et al., 2006). *Ex situ* treatments would allow a combined treatment of both contaminants, maintaining separate streams.

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Recently, a 3-chamber BES was proposed by Liu et al. (2019), where a sediment MFC was used to drive NO_3^- reduction in a bioelectrochemical reactor, whose electrodes were connected to the sediment MFC's electrodes (Figure 2E). The connection of the two systems enhanced both performances, allowing a 66% decrease of organic matter content in the sediment and an observed denitrification rate of 3.7 mgN L^{-1} h^{-1}. These results were achieved in both simulated groundwater and at even higher levels with real groundwater. The presence of the microcurrent positively influenced establishment of naturally occurring groundwater denitrifying microorganisms (Liu et al., 2019).

Based on existing literature analysis, the main characteristics of an optimal BES for *in situ* groundwater treatment can be identified as shown in Figure 3. These include the possibility to be placed in existing wells or trenches, avoiding expensive excavations; the ability to intercept groundwater flow; the lack of membranes to reduce maintenance and costs; internal recirculation to allow proper contact between biomass and substrate; large surface electrodes to allow biofilm growth; use of a power supply or potentiostat to set a desired potential and avoid limitations linked to anodic organic matter oxidation rate; easily scalable and/or modular setup.

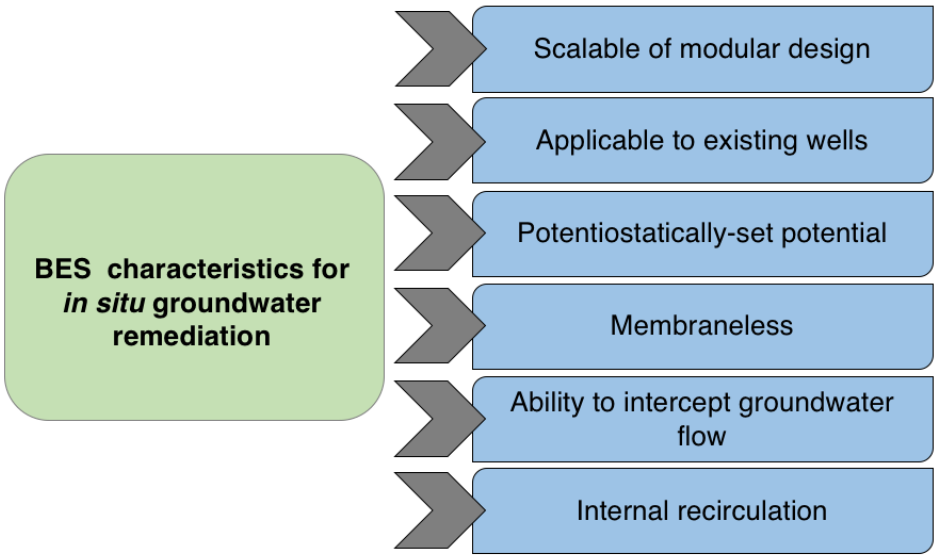

Figure 3: BES characteristics for *in situ* bioelectroremediation

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4. Discussion and future perspectives

4.1. Evolution of permeable reactive barriers: a future for BES development?

Among the options for remediation of contaminated groundwater plumes, the use of permeable reactive barriers (PRB), and in particular because of their biological declination, biobarriers have been promoted and applied in the past. A PRB is built by introducing reactive media orthogonally to the established trajectory of the contaminated groundwater plume; driven by the natural hydraulic gradient, the plume passively migrates through the PBR, allowing contact of the transported contaminants with the reactive material within the PBR, and thus leading to their fixation, transformation or precipitation to a neutral or less environmentally harmful form (Obiri-Nyarko et al., 2014).

Integration of PRBs with microbial metabolism allows the creation of "biobarriers", or bio-PRBs. These consist of materials that enhance, support and stimulate microbial metabolism, allowing *in situ* bioremediation of contaminated groundwater (Obiri-Nyarko et al., 2014). Usually, microbial populations, necessary for degradation of target compound, are already present in the contaminated area (Careghini et al., 2013), while in their absence, properly enriched, preadapted bacteria can be introduced (Sarkar et al., 2017).

Several contaminants could be removed by biobarriers: reduced compounds, such as petroleum hydrocarbons, whereby oxygen (serving as terminal electron acceptor) is added via air sparging, or by addition of oxygen-releasing compounds such as CaO_2, MgO_2, H_2O_2 (Careghini et al., 2013); oxidized compounds, whereby low-cost organic matter (woodchips, alfalfa, leaves, sawdust, composted municipal sewage sludge, mulch) is added into the biobarrier (Liu et al., 2013), acting as electron donor.

Advantages of using PRBs and biobarriers are numerous and include the passivity of the technology, the possible combinations of multiple barriers to remove different specific contaminants, the avoidance of groundwater extraction (and related energy consumption), the possibility of using on site above ground areas for other purposes (Obiri-Nyarco et al., 2014; Careghini et al., 2013). One

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of the disadvantages conversely, is that reactive materials ought to be periodically removed/ replaced for perduring operation, and the need for long-term monitoring.

The integration of BES with reactive permeable barriers have been proposed by Palma et al. (2018b), as a possible application of their bioelectric well (Figure 4A). Such setup could provide an efficient treatment for groundwater, while saving energy by using natural groundwater flow to achieve contact between substrate and bioelectrodes, without the need for a dedicated pumping systems to attract groundwater. The aquifer flow may also (completely or partially) substitute the need for recirculation, with an additional decrease in the overall system energy consumption.

3-D electrodes built with new materials such as carbon foam or granular graphite could be a good option for these applications, as they offer a porous medium that allows water to flow, while still offering ample surface for biofilm growth, combined with an excellent electrical conductivity. Microbial populations able to perform direct or indirect electron-electrode transfer, necessary for the establishment of a BES, have been already reported to naturally occur in groundwater and used as inoculum, meaning that the addition of exogenous bacteria may not be necessary (Kirmizakis et al., 2019; Liu et al., 2019; Yang et al., 2015).

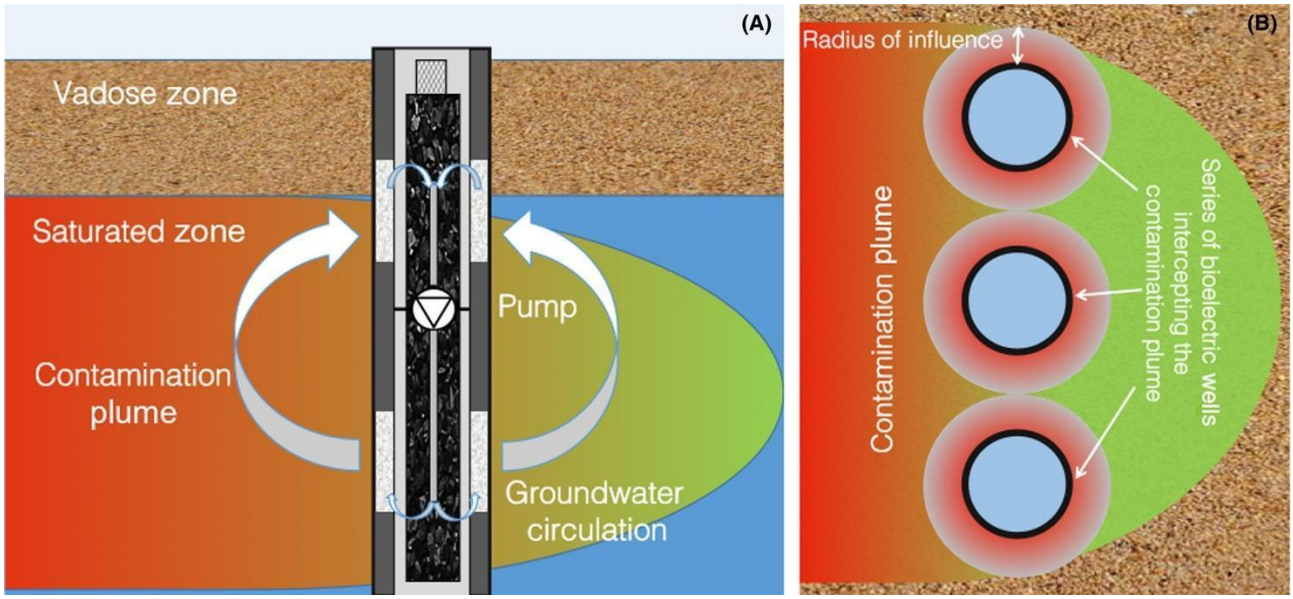

Figure 4: Scheme of the bioelectrochemical barriers proposed by Palma et al. (2018b).

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One advantage of the integration of BES with PRBs rely on both anode and cathode acting as virtually inexhaustible electron sink and donor, respectively. Therefore, no replacement of the reactive materials/chemicals is needed. However, a thick biofilm could change the conductivity of such electrodes which may create the necessity of washing or replacing them after some time. On the other hand, Czurda and Haus (2002) reported that the integration of electrochemical processes in biobarriers may reduce the fouling induced by excessive microbial growth, and remove undesired biomolecules and precipitates. Based on this idea, the existing permeable barriers may be retrofitted and offer the possibility of oxidation and reduction of a variety of contaminants.

Palma et al. (2018a, 2018b) proposed the combined use of several units of their tubular-designed bioelectric well. An upgrade of this system could be the use of possible setups able to intercept the groundwater flow, similarly to the diffused funnel and gate or open channel design of PRBs (Fig. 4B).

4.2. Energy consumption: an often-neglected parameter

Zou and He (2018) recently analyzed the energy sustainability of bioelectrochemical systems for multiple purposes (desalination, wastewater treatment, hydrogen production) considering the additional energy costs due to the recirculation and feeding/extraction of influents/effluents. A similar analysis of *in* and *ex situ* treatment with MFC and power supply-assisted biocathodes was conducted by Cecconet et al. (2018c), showing that *in situ* denitrification using MFC can be energy-positive. The performances of the poised biocathodes were far higher than the MFC's in terms of nitrogen removal rates (around 30% higher). Based on that calculation, it is possible to consider the use of MFC for long-term groundwater denitrification (or biocathodic reduction of other chemicals). Electrons produced by anodic organic matter oxidation could be used for cathodic reduction, and the limitation of removal rates would be acceptable for an *in situ* treatment, where the spatial dimension of the contamination is high. One issue to be tackled is the use of organic matter as anolyte, and the need to avoid further contamination. On the other hand, in an *ex situ* configuration the use of a poised

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biocathode would benefit from higher removal rates, being able to ensure higher flow rates for different purposes. More attention should be given to the actual energy consumption of BESs, by means of a life cycle assessment (LCA) of the technology, where all the different aspects such as recirculation, pumping, etc. are considered.

Recently, the microbial electrochemical snorkel emerged as a novel BES type (Figure 5). A snorkel is a short-circuited MFC, where a microbial anode is directly coupled with a biotic or abiotic cathode. The snorkel does not produce (or require) power, but it works at the maximum current sustainable by the system, and at the same time, hence, at the maximum electrochemical reaction rate (Hoareau et al., 2019). This systems is characterized by its extreme simplicity, as it may be constituted by a single rod (graphite, steel or carbon), exposed to two different redox environments (Viggi et al., 2017, 2015). Snorkels have been used to degrade organic matter from wastewater (Aguirre-Sierra et al., 2016) and NO_3^- from low-organic wastewater, in addition to remediating hydrocarbon-contaminated sediments (Yang et al., 2015).

The application of a snorkel for groundwater remediation would allow treatment where no external energy is provided, and where simplicity would suggest its use for *in situ* applications. However, the snorkel is a relatively new type of BESs, and some challenges might be unsolved, such as the inability of fully controlling the electrode potential, the lack of accurate delimitation of anodic and cathodic zones, and the possible presence of oxygen in the anodic zone. Some solutions, including numerical and mathematical modelling and use of anocathodophilic biofilms have been proposed (Hoareau et al., 2019).

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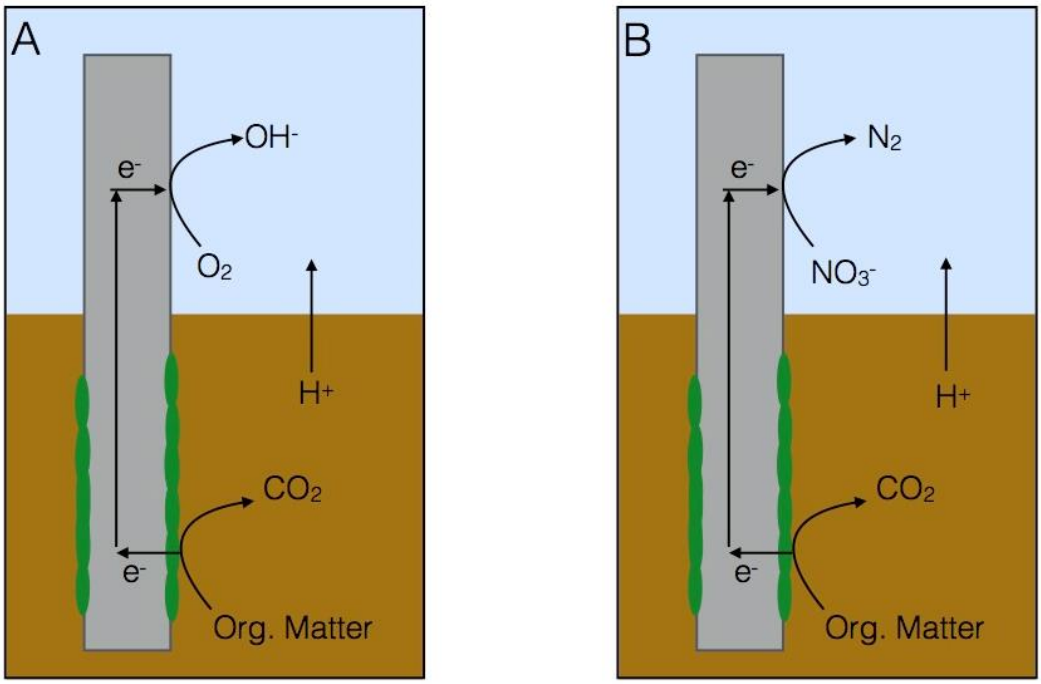

338

339 **Figure 5**: Microbial electrochemical snorkel. (A) Oxygen and (B) nitrate as electron acceptor.

340

341 **4.3. Complex groundwater with multiple contaminants**

342 Different and/or concomitant anthropic activities (i.e. agriculture, industry) may contaminate
343 groundwater with different pollutants (Bartzas et al., 2015; Han et al., 2016; Venkatramanan et al.,
344 2016). Therefore, working on single contaminants can be interesting and useful to understand the
345 single component removal pathway and its related kinetics but it might not be useful for real
346 applications.

347 Earlier attempts of using BESs for the removal of multiple contaminants from groundwater
348 have been reported: Butler et al. (2010) first studied the interaction and competition of NO_3^- and
349 perchlorate as terminal electron acceptors (these compounds are often associated in groundwater) in
350 a BES biocathode; Xie et al. (2014) showed the inhibition of perchlorate reduction in presence of 2.1
351 mM of NO_3^-, and a slowed reduction at lower NO_3^- concentrations. Nguyen et al. (2016b) carried out
352 research on the As oxidation at the anode and denitrification at the cathode of BES, maintaining a
353 strict separation of the streams (i.e. the anodic and cathodic influents). The competition between

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vanadium and chromium in BES cathodes has also been investigated (Zhang et al., 2012) while Lai et al. (2015) performed reductive BES-based dechlorination of cis-dichloroethylene (cis-DCE) in NO_3^- and sulfate contaminated real groundwater with a simultaneous reduction of all three compounds.

In order to enhance sustainability of treatment, the multi-contaminant approach should be implemented, considering industry-originated organic carbon sources or organic contaminants commonly detected in groundwater (e.g., petroleum hydrocarbons). Potential inhibition effects due to the combination of different contaminants should also be assessed. The use of BESs with separated chambers should be carefully evaluated, as the separation of reduced and oxidized contaminants in groundwater is not as feasible as in lab setups. A flow-through setup, similar to the one descripted by Pous et al. (2017), may represent an option: in this case the contaminated stream would first be exposed to the anode, allowing oxidation processes, and then to the cathode where reduction would occur. Another option is the use of anocathodophilic bacteria that employ electrodes as both electron acceptors and donors based on redox conditions; some examples have been reported for biofilms capable of catalyzing organic matter oxidation and NO_3^- or chromium reduction (Beretta et al., 2018; Molognoni et al., 2017; Pous et al., 2016).

4.4. Need for additional modeling efforts

Modeling MFC operation has advanced extensively with the possibility to predict both organic matter removal and energy production (Capodaglio et al., 2017; Gadkari et al., 2018; Pinto et al., 2010). In addition, MEC and MDC processes have been successfully modeled (Ping et al., 2014; Pinto et al., 2011) and latter models evaluated integration of BESs with membrane bioreactors and algal photobioreactors (Li and He, 2016; Luo et al., 2017). Statistical methods have also been applied to BES technology to improve knowledge on the operation (Cecconet et al., 2018a; Luo et al., 2016).

Up to date, only a single modeling effort has been reported for groundwater treatment using BES. Srinivasan et al. (2016) developed a model for groundwater denitrification based on the model

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proposed by Pan et al. (2013), showing a competition between NO_3^- and nitrite for electrons in the biocathode of an MFC. Based on existing models, the removal of the considered contaminants in groundwater could be simulated, taking into account competition between different electron acceptors.

4.5. Scaling-up

BES applications at full scale for wastewater treatment have been reported (Table 2), but no data are yet available for full scale applications for groundwater treatment. Most of the data for such BES applications are still at laboratory scale. Recently, Wang and He (2019) discussed the dimension that a BES should reach in order to be referred to as "pilot scale", concluding that a large part of the examples of pilot scale BES reactors available in literature should not be considered as such, based on their practical flow or hydraulic capacity: a pilot reactor should have between 0.1 and 5% of the full scale application flow rate. This concept is difficult to be applied in the case of *in situ* groundwater bioelectroremediation due to the impossibility to identify a flow-rate for the reactors. In contrast, a range of flow rate values can be calculated for *ex situ* on site applications. In the case of drinking water treatment plants built to serve small or medium communities (with a flow rate in the 500-5000 $m^3\ d^{-1}$ range), no reported BES was able to meet the 0.5-250 $m^3\ d^{-1}$ required flow-rate. A different scenario should be considered for decentralized applications: if we consider an isolated household housing four people, a daily water consumption of 400 L d^{-1} can be calculated based on the World Health Organization (WHO) requirement of 100 L d^{-1} per capita as the minimum daily water intake necessary to avoid any level of health concern connected to the available water quantity (Howard and Bartram, 2003). Therefore, a pilot scale BES reactor for such a decentralized household should guarantee a flow rate higher than 0.4-20 L d^{-1}. This condition has been met by BES performing groundwater treatment, with flow rate values exceeding 12 L d^{-1} in the denitrifying BES operated by Pous and co-workers (2017). Based on that, it is possible to state that BES for groundwater treatment have reached the pilot scale level (even though limited to decentralized applications) and are no longer confined to laboratory settings.

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406 Recently, application of small scale BESs in series has been proposed as an alternative to the
407 increase in size for technology upscaling (Greenman and Ieropoulos, 2017). Series application of
408 several small-scale BESs may be a feasible option to both remove different contaminants (e.g.,
409 biocathodes poised at different potential focused each on a different contaminant, similar to the setup
410 reported by Huang et al. (2015) and increase energy production. This sequential approach was tested
411 by Cecconet et al. (2019b) for groundwater denitrification. The sequential coupling of two
412 denitrifying biocathodes showed to be particularly promising in terms of energy sustainability: the
413 specific energy consumption (SEC) of the system decreased at the increase of the NO_3^- load, showing
414 that such a system was more energy-efficient when operated at low HRTs (advantageous aspect for
415 a full-scale treatment technology).
416 The possibility of connecting two or more BES units represent another aspect of the flexibility
417 of the technology; applications of stacked MFCs have been reported (Kim et al., 2017; Vilajeliu-Pons
418 et al., 2017; Wu et al., 2016), as also the applications of MFC to supply enough voltage to allow MEC
419 processes (Choi et al., 2014; Liu et al., 2016).
420

BES type	Dimension (L)	Influent	Modularized?	N° of modules	Reference
MFC	1000	Brewery WW	Yes	12	Logan (2010)
MFC	90	Brewery WW	Yes	5	Dong et al. (2015)
MFC	200	Municipal WW	Yes	96	Ge and He (2016)
MFC	250	Municipal WW	No	-	Feng et al. (2014)
MEC	130	Urban WW	Yes	10	Baeza et al. (2017)
MFC	300	Urine	Yes	432	Ieropoulos et al. (2016)

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MFC	1000	Artificial and real WW	Yes	50	Liang et al. (2018)
MFC	700	Domestic WW	Yes	18	Valladares Linares et al., (2019)
MES[1]	1500	Municipal WW	Yes	336	He et al., (2019)

Table 2: notable examples of full and pilot scale BES. [1]: The reactor was denominated Microbial Electrochemical System (MES), and showed a setup similar to an MFC.

Few examples of commercial application of the BES technology have been reported so far (e.g. Plant-e, spinoff of Wageningen University, Netherlands; Cambrian water), mainly related to the production of bioenergy using MFCs, or hydrogen production using MECs. The cost of the materials (membrane and electrode mainly) is still a hard-to-overcome issue (Foley et al., 2010; Pant et al., 2011), and only large-scale commercialization of BESs could lower those costs. An alternative is represented by the application of natural materials in place of membranes and electrodes (Goglio et al., 2019), but these still offer far lower performance than engineered or conventional materials. Based on the above, major cuts on the materials' costs (i.e. membranes) are needed in order to allow BES to become an established technology for groundwater denitrification.

4.6. Contaminants of emerging concern

CECs are a class of substances used for a variety of purposes: personal care, food production, human and animal health (pharmaceuticals), industrial manufacturing and fire suppression (Richardson and Kimura, 2017). CECs have been detected worldwide in groundwater: their presence has been reported in Europe (Jurado et al., 2012; Stuart et al., 2012), Americas (Montes-Grajales et al., 2017), Asia (Lapworth et al., 2018), Africa (Arukwe et al., 2012) and Oceania (Sui et al., 2015), in developed and developing countries alike. Their occurrence in groundwater is to be ascribed to anthropic activities (Lapworth et al., 2012); therefore, CECs can be used as tracers to identify groundwater contamination

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due to wastewater infiltration (McCance et al., 2018). As most of the world relies on the use of groundwater for drinking water production, and CECs' regulations have not been issued yet (at least in the European Union), much debate on the matter is going on (Lapworth et al., 2019).

BESs proved to be able to remove CECs with high performance, in some cases higher than conventional water and wastewater treatments (e.g., biological process), scoring interesting results in particular in the removal of recalcitrant contaminants due to the combination of microbial metabolisms with different redox conditions offered by anode and cathode, respectively (Cecconet et al., 2017). Therefore, the investigation on the removal of CECs from groundwater should be intensified, taking into consideration the particularities of groundwater (general low conductivity, and low concentration of nutrients and organic matter); in addition, the removal of those contaminants should be considered in combination with the presence of other contaminants that may occur in the aquifer, especially if there are orders of magnitude of difference between their concentrations.

4.7. Biosensing

Recently, much attention has been attracted by the development of BES-based biosensors for environmental monitoring (Ivars-Barceló et al., 2018). Therefore, some researchers have shifted their focus on applications for contaminants detection and monitoring in groundwater. Velasquez-Orta and co-workers (2017) designed an MFC-based biosensor for the online monitoring of fecal and organic pollution in shallow groundwater wells, obtaining responsive increases in the current produced; the system was sensitive to temperature fluctuations but not to changes in salinity or modifications of the external resistance (and thus to longer wiring for the connections of the electrodes). Field tests highlighted the influence of water level oscillations in the wells causing air exposition at the cathode (Velasquez-Orta et al., 2017). Organic matter presence in an aquifer undergoing bioremediation was ascertained by the increase in current density in a BES-based biosensor; current quickly dropped when organic matter presence was discontinued, suggesting that the system was able to monitor subsurface microbial activity during in situ bioremediation (Williams et al., 2010). The electrodes

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were able to produce detectable current despite the long separation of anode and cathode (6 m), and electron transfer was attributed to *Geobacter* species (Williams et al., 2010).

Bio-current generated by a bioanode poised at +0.2 V vs SHE was reported being linearly correlated with the increase in concentration of biogenic Fe(II), serving thus as indicator; Fe(II) is widely used chemical in groundwater remediation, and the system could monitor the concentration of the compound in an effective way (Feng et al., 2013). A BES-based biosensor for As was developed by Webster et al. (2014) using an engineered *Shewanella oneidensis* strain, allowing an arsenite detection limit of 40 µM and a linear range up to 100 µM. A BES-based biosensor able to monitor NO_3^- concentrations in real-time was proposed by Su et al. (2019), but designed for monitoring secondary effluents of wastewater treatment plants, and thus requiring organic matter to properly work; such design could not be adapted to groundwater monitoring. Biosensors developed to monitor microbial activity in anoxic sediments (Wardman et al., 2014) could, with some modifications in the setup, be applied to groundwater monitoring.

The development of BES-based biosensors is of extreme interest to the research community, due to the possibility of operating in off-grid and decentralized applications, and the suitability for *in situ* and on site testing, other than requiring less time and advanced technological skills compared to conventional analytical techniques (Grattieri et al., 2017).

5. Conclusions

Amongst the different technologies applicable for *in situ* treatment of contaminated groundwater, BESs showed to be a suitable and feasible option. The analysis of the different setups reported so far in literature highlighted that it is crucial to properly design a BES to be operated in a harsh and challenging environment such as the aquifer, and that the simple adaptation of *ex situ* BES setups may not be sufficient to achieve the desired results.

Research in the field mainly focused on denitrification and hydrocarbons removal, showing excellent results due to the interaction of microbial metabolism and poised electrodes. In the near

494 future research should focus on emerging topics such as the interaction between multiple
495 contaminants (both reduced and oxidized), accurate estimation of the energy consumption for *in situ*
496 treatment with BES, development of reliable models to simulate and predict the processes and
497 possible integration of BES with PRBs for the interception and treatment of contaminated plumes.
498 The integration of these research gaps with the existing BES technology could lead to the
499 development of reliable and resilient BES for *in situ* bioelectroremediation.
500

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504

505 **Declaration of competing interest**

506 The authors declare that they have no known competing financial interests or personal relationships
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508

509 **References**

510 Adelaja, O., Keshavarz, T., Kyazze, G., 2017. Treatment of phenanthrene and benzene using
511 microbial fuel cells operated continuously for possible in situ and ex situ applications. Int.
512 Biodeterior. Biodegrad. 116, 91–103. doi:10.1016/j.ibiod.2016.10.021
513 Aguirre-Sierra, A., Bacchetti-De Gregoris, T., Berná, A., Salas, J.J., Aragón, C., Esteve-Núñez, A.,
514 2016. Microbial electrochemical systems outperform fixed-bed biofilters in cleaning up urban
515 wastewater. Environ. Sci. Water Res. Technol. 2, 984–993. doi:10.1039/C6EW00172F
516 Arukwe, A., Eggen, T., Möder, M., 2012. Solid waste deposits as a significant source of contaminants
517 of emerging concern to the aquatic and terrestrial environments — A developing country case
518 study from Owerri, Nigeria. Sci. Total Environ. 438, 94–102.
519 doi:10.1016/j.scitotenv.2012.08.039

520 Aulenta, F., Tocca, L., Verdini, R., Reale, P., Majone, M., 2011. Dechlorination of trichloroethene in
521 a continuous-flow bioelectrochemical reactor: Effect of cathode potential on rate, selectivity,
522 and electron transfer mechanisms. Environ. Sci. Technol. 45, 8444–8451.
523 doi:10.1021/es202262y
524 Baeza, J.A., Martínez-Miró, À., Guerrero, J., Ruiz, Y., Guisasola, A., 2017. Bioelectrochemical
525 hydrogen production from urban wastewater on a pilot scale. J. Power Sources 356, 500–509.
526 doi:10.1016/j.jpowsour.2017.02.087
527 Bartzas, G., Tinivella, F., Medini, L., Zaharaki, D., Komnitsas, K., 2015. Assessment of groundwater
528 contamination risk in an agricultural area in north Italy. Inf. Process. Agric. 2, 109–129.
529 doi:10.1016/j.inpa.2015.06.004
530 Beretta, G., Mastorgio, A., Espinoza, A., Pedrali, L., Daghio, M., Sezenna, E., Franzetti, A., Saponaro,
531 S., Ferrari, G., 2018. Microbial assisted hexavalent chromium removal in the cathodic chamber
532 of a Microbial Electrolysis Cell, in: Proceedings of the 4th European Meeting of the International
533 Society for Microbial Electrochemistry and Technology (4th EU-ISMET), 12th-14th September.
534 Newcastle upon Tyne (UK), p. 152.
535 Brastad, K.S., He, Z., 2013. Water softening using microbial desalination cell technology.
536 Desalination 309, 32–37. doi:10.1016/j.desal.2012.09.015
537 Butler, C.S., Clauwaert, P., Green, S.J., Verstraete, W., Nerenberg, R., 2010. Bioelectrochemical
538 Perchlorate Reduction in a Microbial Fuel Cell. Environ. Sci. Technol. 44, 4685–4691.
539 doi:10.1021/es901758z
540 Butler, R., Ehrenberg, S., Godley, A.R., Lake, R., Lytton, L., Cartmell, E., 2006. Remediation of
541 bromate-contaminated groundwater in an ex situ fixed-film bioreactor. Sci. Total Environ. 366,
542 12–20. doi:10.1016/j.scitotenv.2005.12.013
543 Butler, R., Godley, A., Lytton, L., Cartmell, E., 2005. Bromate environmental contamination: Review
544 of impact and possible treatment. Crit. Rev. Environ. Sci. Technol. 35, 193–217.
545 doi:10.1080/10643380590917888

546 Callegari, A., Ferronato, N., Rada, E.C., Capodaglio, A.G., Torretta, V., 2018. Assessment of arsenic
547 removal efficiency by an iron oxide-coated sand filter process. Environ. Sci. Pollut. Res. 1–9.
548 doi:10.1007/s11356-018-2674-y
549 Capodaglio, A.G., Cecconet, D., Molognoni, D., 2017. An Integrated Mathematical Model of
550 Microbial Fuel Cell Processes: Bioelectrochemical and Microbiologic Aspects. Processes 5, 73.
551 doi:10.3390/pr5040073
552 Capodaglio, A.G., Molognoni, D., Dallago, E., Liberale, A., Cella, R., Longoni, P., Pantaleoni, L.,
553 2013. Microbial fuel cells for direct electrical energy recovery from urban wastewaters. Sci.
554 World J. 2013. doi:10.1155/2013/634738
555 Careghini, A., Saponaro, S., Sezenna, E., 2013. Biobarriers for groundwater treatment: A review.
556 Water Sci. Technol. 67, 453–468. doi:10.2166/wst.2012.599
557 Cecconet, D., Bolognesi, S., Callegari, A., Capodaglio, A.G., 2019a. Simulation tests of in situ
558 groundwater denitrification with aquifer-buried biocathodes. Heliyon 5, e02117.
559 doi:10.1016/j.heliyon.2019.e02117
560 Cecconet, D., Bolognesi, S., Callegari, A., Capodaglio, A.G., 2019b. Controlled sequential
561 biocathodic denitrification for contaminated groundwater bioremediation. Sci. Total Environ.
562 651, 3107–3116. doi:10.1016/j.scitotenv.2018.10.196
563 Cecconet, D., Bolognesi, S., Daneshgar, S., Callegari, A., Capodaglio, A.G., 2018a. Improved
564 process understanding and optimization by multivariate statistical analysis of Microbial Fuel
565 Cells operation. Int. J. Hydrogen Energy 43, 16719–16727. doi:10.1016/j.ijhydene.2018.07.056
566 Cecconet, D., Bolognesi, S., Molognoni, D., Callegari, A., Capodaglio, A.G., 2018b. Influence of
567 reactor's hydrodynamics on the performance of microbial fuel cells. J. Water Process Eng. 26,
568 281–288. doi:10.1016/j.jwpe.2018.10.019
569 Cecconet, D., Molognoni, D., Callegari, A., Capodaglio, A.G., 2017. Biological combination
570 processes for efficient removal of pharmaceutically active compounds from wastewater: A
571 review and future perspectives. J. Environ. Chem. Eng. 5, 3590–3603.

572 doi:10.1016/j.jece.2017.07.020
573 Cecconet, D., Zou, S., Capodaglio, A.G., He, Z., 2018c. Evaluation of energy consumption of treating
574 nitrate-contaminated groundwater by bioelectrochemical systems. Sci. Total Environ. 636, 881–
575 890. doi:10.1016/j.scitotenv.2018.04.336
576 Chen, J., Wu, H., Qian, H., 2016. Groundwater Nitrate Contamination and Associated Health Risk
577 for the Rural Communities in an Agricultural Area of Ningxia, Northwest China. Expo. Heal. 8,
578 349–359. doi:10.1007/s12403-016-0208-8
579 Choi, C., Hu, N., Lim, B., 2014. Cadmium recovery by coupling double microbial fuel cells.
580 Bioresour. Technol. 170, 361–369. doi:10.1016/j.biortech.2014.07.087
581 Czurda, K.A., Haus, R., 2002. Reactive barriers with fly ash zeolites for in situ groundwater
582 remediation. Appl. Clay Sci. 21, 13–20. doi:10.1016/S0169-1317(01)00088-6
583 Dong, H., Li, L., Lu, Y., Cheng, Y., Wang, Y., Ning, Q., Wang, B., Zhang, L., Zeng, G., 2019.
584 Integration of nanoscale zero-valent iron and functional anaerobic bacteria for groundwater
585 remediation: A review. Environ. Int. 124, 265–277. doi:10.1016/j.envint.2019.01.030
586 Dong, Y., Qu, Y., He, W., Du, Y., Liu, J., Han, X., Feng, Y., 2015. A 90-liter stackable baffled
587 microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode.
588 Bioresour. Technol. 195, 66–72. doi:10.1016/j.biortech.2015.06.026
589 Feng, C., Yue, X., Li, F., Wei, C., 2013. Bio-current as an indicator for biogenic Fe(II) generation
590 driven by dissimilatory iron reducing bacteria. Biosens. Bioelectron. 39, 51–56.
591 doi:10.1016/j.bios.2012.06.037
592 Feng, Y., He, W., Liu, J., Wang, X., Qu, Y., Ren, N., 2014. A horizontal plug flow and stackable
593 pilot microbial fuel cell for municipal wastewater treatment. Bioresour. Technol. 156, 132–138.
594 doi:10.1016/j.biortech.2013.12.104
595 Foley, J.M., Rozendal, R.A., Hertle, C.K., Lant, P.A., Rabaey, K., 2010. Life cycle assessment of
596 high-rate anaerobic treatment, microbial fuel cells, and microbial electrolysis cells. Environ. Sci.
597 Technol. 44, 3629–3637. doi:10.1021/es100125h

598 Gadkari, S., Gu, S., Sadhukhan, J., 2018. Towards automated design of bioelectrochemical systems:
599 A comprehensive review of mathematical models. Chem. Eng. J. 343, 303–316.
600 doi:10.1016/j.cej.2018.03.005
601 Galitskaya, I.V., Mohan, K.R., Krishna, A.K., Batrak, G.I., Eremina, O.N., Putilina, V.S., Yuganova,
602 T.I., 2017. Assessment of soil and Groundwater Contamination by Heavy Metals and Metalloids
603 in Russian and Indian Megacities. Procedia Earth Planet. Sci. 17, 674–677.
604 doi:10.1016/j.proeps.2016.12.180
605 Ge, Z., He, Z., 2016. Long-term performance of a 200 liter modularized microbial fuel cell system
606 treating municipal wastewater: treatment, energy, and cost. Environ. Sci. Water Res. Technol.
607 2, 274–281. doi:10.1039/C6EW00020G
608 Gill, R.T., Harbottle, M.J., Smith, J.W.N., Thornton, S.F., 2014. Electrokinetic-enhanced
609 bioremediation of organic contaminants: A review of processes and environmental applications.
610 Chemosphere 107, 31–42. doi:10.1016/j.chemosphere.2014.03.019
611 Goglio, A., Tucci, M., Rizzi, B., Colombo, A., Cristiani, P., Schievano, A., 2019. Microbial recycling
612 cells (MRCs): A new platform of microbial electrochemical technologies based on
613 biocompatible materials, aimed at cycling carbon and nutrients in agro-food systems. Sci. Total
614 Environ. 649, 1349–1361. doi:10.1016/j.scitotenv.2018.08.324
615 Grattieri, M., Hasan, K., Minteer, S.D., 2017. Bioelectrochemical Systems as a Multipurpose
616 Biosensing Tool: Present Perspective and Future Outlook. ChemElectroChem 4, 834–842.
617 doi:10.1002/celc.201600507
618 Greenman, J., Ieropoulos, I.A., 2017. Allometric scaling of microbial fuel cells and stacks: The
619 lifeform case for scale-up. J. Power Sources 356, 365–370. doi:10.1016/j.jpowsour.2017.04.033
620 Han, Z., Ma, H., Shi, G., He, L., Wei, L., Shi, Q., 2016. A review of groundwater contamination near
621 municipal solid waste landfill sites in China. Sci. Total Environ. 569–570, 1255–1264.
622 doi:10.1016/j.scitotenv.2016.06.201
623 Hoareau, M., Erable, B., Bergel, A., 2019. Microbial electrochemical snorkels (MESs): A budding

technology for multiple applications. A mini review. Electrochem. commun. doi:10.1016/j.elecom.2019.05.022

Huang, L., Wang, Q., Jiang, L., Zhou, P., Quan, X., Logan, B.E., 2015. Adaptively Evolving Bacterial Communities for Complete and Selective Reduction of Cr(VI), Cu(II), and Cd(II) in Biocathode Bioelectrochemical Systems. Environ. Sci. Technol. 49, 9914–9924. doi:10.1021/acs.est.5b00191

Hutchinson, T.H., Hutchings, M.J., Moore, K.W., 1997. A review of the effects of bromate on aquatic organisms and toxicity of bromate to oyster (Crassostrea gigas) embryos. Ecotoxicol. Environ. Saf. 38, 238–243. doi:10.1006/eesa.1997.1584

Ieropoulos, I.A., Stinchcombe, A., Gajda, I., Forbes, S., Merino-Jimenez, I., Pasternak, G., Sanchez-Herranz, D., Greenman, J., 2016. Pee power urinal-microbial fuel cell technology field trials in the context of sanitation. Environ. Sci. Water Res. Technol. 2, 336–343. doi:10.1039/c5ew00270b

Ivars-Barceló, F., Zuliani, A., Fallah, M., Mashkour, M., Rahimnejad, M., Luque, R., 2018. Novel Applications of Microbial Fuel Cells in Sensors and Biosensors. Appl. Sci. 8, 1184. doi:10.3390/app8071184

Jacobson, K.S., Kelly, P.T., He, Z., 2015. Energy balance affected by electrolyte recirculation and operating modes in microbial fuel cells. Water Environ. Res. 87, 252–7. doi:10.2175/106143015X14212658613235

Jain, A., He, Z., 2018. "NEW" resource recovery from wastewater using bioelectrochemical systems: Moving forward with functions. Front. Environ. Sci. Eng. 12, 1. doi:10.1007/s11783-018-1052-9

Jones, E.H., Reynolds, D.A., Wood, A.L., Thomas, D.G., 2011. Use of Electrophoresis for Transporting Nano-Iron in Porous Media. Ground Water 49, 172–183. doi:10.1111/j.1745-6584.2010.00718.x

Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012.

650 Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence
651 and fate in a European context. Sci. Total Environ. 440, 82–94.
652 doi:10.1016/j.scitotenv.2012.08.029
653 Kim, B., Choi, S., Jang, J.K., Chang, I.S., 2017. Self-recoverable voltage reversal in stacked microbial
654 fuel cells due to biofilm capacitance. Bioresour. Technol. 245, 1286–1289.
655 doi:10.1016/j.biortech.2017.08.163
656 Kirmizakis, P., Doherty, R., Mendonça, C.A., Costeira, R., Allen, C.C.R., Ofterdinger, U.S., Kulakov,
657 L., 2019. Enhancement of gasworks groundwater remediation by coupling a bio-electrochemical
658 and activated carbon system. Environ. Sci. Pollut. Res. 1–11. doi:10.1007/s11356-019-04297-
659 w
660 Lai, A., Verdini, R., Aulenta, F., Majone, M., 2015. Influence of nitrate and sulfate reduction in the
661 bioelectrochemically assisted dechlorination of cis-DCE. Chemosphere 125.
662 doi:10.1016/j.chemosphere.2014.12.023
663 Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in
664 groundwater: A review of sources, fate and occurrence. Environ. Pollut. 163, 287–303.
665 doi:10.1016/j.envpol.2011.12.034
666 Lapworth, D.J., Das, P., Shaw, A., Mukherjee, A., Civil, W., Petersen, J.O., Gooddy, D.C., Wakefield,
667 O., Finlayson, A., Krishan, G., Sengupta, P., MacDonald, A.M., 2018. Deep urban groundwater
668 vulnerability in India revealed through the use of emerging organic contaminants and residence
669 time tracers. Environ. Pollut. 240, 938–949. doi:10.1016/j.envpol.2018.04.053
670 Lapworth, D.J., Lopez, B., Laabs, V., Kozel, R., Wolter, R., Ward, R., Vargas Amelin, E., Besien,
671 T., Claessens, J., Delloye, F., Ferretti, E., Grath, J., 2019. Developing a groundwater watch list
672 for substances of emerging concern: a European perspective. Environ. Res. Lett. 14, 035004.
673 doi:10.1088/1748-9326/aaf4d7
674 Li, J., He, Z., 2016. Development of a dynamic mathematical model for membrane
675 bioelectrochemical reactors with different configurations. Environ. Sci. Pollut. Res. 23, 3897–

3906. doi:10.1007/s11356-015-5611-3

Li, W.W., Yu, H.Q., 2015. Electro-assisted groundwater bioremediation: Fundamentals, challenges and future perspectives. Bioresour. Technol. doi:10.1016/j.biortech.2015.07.074

Liang, P., Duan, R., Jiang, Y., Zhang, X., Qiu, Y., Huang, X., 2018. One-year operation of 1000-L modularized microbial fuel cell for municipal wastewater treatment. Water Res. 141, 1–8. doi:10.1016/J.WATRES.2018.04.066

Liu, R., Zheng, X., Li, M., Han, L., Liu, X., Zhang, F., Hou, X., 2019. A three chamber bioelectrochemical system appropriate for in-situ remediation of nitrate-contaminated groundwater and its reaction mechanisms. Water Res. 158, 401–410. doi:10.1016/j.watres.2019.04.047

Liu, S.J., Zhao, Z.Y., Li, J., Wang, J., Qi, Y., 2013. An anaerobic two-layer permeable reactive biobarrier for the remediation of nitrate-contaminated groundwater. Water Res. 47, 5977–5985. doi:10.1016/j.watres.2013.06.028

Liu, Y., Zhang, B., Tian, C., Feng, C., Wang, Z., Cheng, M., Hu, W., 2016. Optimization of enhanced bioelectrical reactor with electricity from microbial fuel cells for groundwater nitrate removal. Environ. Technol. 37, 1008–1017. doi:10.1080/09593330.2015.1096962

Logan, B.E., 2010. Scaling up microbial fuel cells and other bioelectrochemical systems. Appl. Microbiol. Biotechnol. 85, 1665–1671. doi:10.1007/s00253-009-2378-9

Logeshwaran, P., Megharaj, M., Chadalavada, S., Bowman, M., Naidu, R., 2018. Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches. Environ. Technol. Innov. 10, 175–193. doi:10.1016/j.eti.2018.02.001

Lohner, S.T., Katzoreck, D., Tiehm, A., 2008. Electromigration of microbial electron acceptors and nutrients: (II) Transport in groundwater. J. Environ. Sci. Heal. Part A 43, 922–925. doi:10.1080/10934520801974442

Lopez, B., Ollivier, P., Togola, A., Baran, N., Ghestem, J.P., 2015. Screening of French groundwater

for regulated and emerging contaminants. Sci. Total Environ. 518–519, 562–573. doi:10.1016/j.scitotenv.2015.01.110

Luo, S., Sun, H., Ping, Q., Jin, R., He, Z., 2016. A Review of Modeling Bioelectrochemical Systems: Engineering and Statistical Aspects. Energies 9, 111. doi:10.3390/en9020111

Luo, S., Wang, Z.W., He, Z., 2017. Mathematical modeling of the dynamic behavior of an integrated photo-bioelectrochemical system for simultaneous wastewater treatment and bioenergy recovery. Energy 124, 227–237. doi:10.1016/j.energy.2017.02.039

Luu, T.T.G., Sthiannopkao, S., Kim, K.W., 2009. Arsenic and other trace elements contamination in groundwater and a risk assessment study for the residents in the Kandal Province of Cambodia. Environ. Int. 35, 455–460. doi:10.1016/j.envint.2008.07.013

Majone, M., Verdini, R., Aulenta, F., Rossetti, S., Tandoi, V., Kalogerakis, N., Agathos, S., Puig, S., Zanaroli, G., Fava, F., 2015. In situ groundwater and sediment bioremediation: barriers and perspectives at European contaminated sites. N. Biotechnol. 32, 133–146. doi:10.1016/j.nbt.2014.02.011

McCance, W., Jones, O.A.H., Edwards, M., Surapaneni, A., Chadalavada, S., Currell, M., 2018. Contaminants of Emerging Concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. Water Res. 146, 118–133. doi:10.1016/j.watres.2018.09.013

Menció, A., Mas-Pla, J., Otero, N., Regàs, O., Boy-Roura, M., Puig, R., Bach, J., Domènech, C., Zamorano, M., Brusi, D., Folch, A., 2016. Nitrate pollution of groundwater; all right…, but nothing else? Sci. Total Environ. 539, 241–251. doi:10.1016/j.scitotenv.2015.08.151

Miller, A., Singh, L., Wang, L., Liu, H., 2019. Linking internal resistance with design and operation decisions in microbial electrolysis cells. Environ. Int. 126, 611–618. doi:10.1016/j.envint.2019.02.056

Modin, O., Aulenta, F., 2017. Three promising applications of microbial electrochemistry for the water sector. Environ. Sci. Water Res. Technol. 3, 391–402. doi:10.1039/C6EW00325G

728 Molognoni, D., Devecseri, M., Cecconet, D., Capodaglio, A.G., 2017. Cathodic groundwater
729 denitrification with a bioelectrochemical system. J. Water Process Eng. 19, 67–73.
730 doi:10.1016/j.jwpe.2017.07.013
731 Montes-Grajales, D., Fennix-Agudelo, M., Miranda-Castro, W., 2017. Occurrence of personal care
732 products as emerging chemicals of concern in water resources: A review. Sci. Total Environ.
733 595, 601–614. doi:10.1016/j.scitotenv.2017.03.286
734 Nguyen, V.K., Park, Y., Yu, J., Lee, T., 2016a. Bioelectrochemical denitrification on biocathode
735 buried in simulated aquifer saturated with nitrate-contaminated groundwater. Environ. Sci.
736 Pollut. Res. 23, 15443–15451. doi:10.1007/s11356-016-6709-y
737 Nguyen, V.K., Park, Y., Yu, J., Lee, T., 2016b. Simultaneous arsenite oxidation and nitrate reduction
738 at the electrodes of bioelectrochemical systems. Environ. Sci. Pollut. Res. 23, 19978–19988.
739 doi:10.1007/s11356-016-7225-9
740 O'Connor, D., Hou, D., Ok, Y.S., Song, Y., Sarmah, A.K., Li, X., Tack, F.M.G., 2018. Sustainable
741 in situ remediation of recalcitrant organic pollutants in groundwater with controlled release
742 materials: A review. J. Control. Release 283, 200–213. doi:10.1016/j.jconrel.2018.06.007
743 Obiri-Nyarko, F., Grajales-Mesa, S.J., Malina, G., 2014. An overview of permeable reactive barriers
744 for in situ sustainable groundwater remediation. Chemosphere 111, 243–259.
745 doi:10.1016/j.chemosphere.2014.03.112
746 Palma, E., Daghio, M., Espinoza Tofalos, A., Franzetti, A., Cruz Viggi, C., Fazi, S., Petrangeli Papini,
747 M., Aulenta, F., 2018a. Anaerobic electrogenic oxidation of toluene in a continuous-flow
748 bioelectrochemical reactor: process performance, microbial community analysis, and
749 biodegradation pathways. Environ. Sci. Water Res. Technol. 4, 2136–2145.
750 doi:10.1039/C8EW00666K
751 Palma, E., Daghio, M., Franzetti, A., Petrangeli Papini, M., Aulenta, F., 2018b. The bioelectric well:
752 a novel approach for in situ treatment of hydrocarbon-contaminated groundwater. Microb.
753 Biotechnol. 11, 112–118. doi:10.1111/1751-7915.12760

754 Palma, E., Tofalos, A.E., Daghio, M., Franzetti, A., Tsiota, P., Cruz Viggi, C., Papini, M.P., Aulenta,
755 F., 2019. Bioelectrochemical treatment of groundwater containing BTEX in a continuous-flow
756 system: substrate interactions, microbial community analysis, and impact of sulfate as a co-
757 contaminant. N. Biotechnol. 53, 41–48. doi:10.1016/j.nbt.2019.06.004
758 Pan, Y., Ni, B.-J., Yuan, Z., 2013. Modeling Electron Competition among Nitrogen Oxides Reduction
759 and N 2 O Accumulation in Denitrification. Environ. Sci. Technol. 47, 11083–11091.
760 doi:10.1021/es402348n
761 Pant, D., Singh, A., Van Bogaert, G., Gallego, Y.A., Diels, L., Vanbroekhoven, K., 2011. An
762 introduction to the life cycle assessment (LCA) of bioelectrochemical systems (BES) for
763 sustainable energy and product generation: Relevance and key aspects. Renew. Sustain. Energy
764 Rev. 15, 1305–1313. doi:10.1016/j.rser.2010.10.005
765 Ping, Q., Zhang, C., Chen, X., Zhang, B., Huang, Z., He, Z., 2014. Mathematical Model of Dynamic
766 Behavior of Microbial Desalination Cells for Simultaneous Wastewater Treatment and Water
767 Desalination. Environ. Sci. Technol. 48, 13010–13019. doi:10.1021/es504089x
768 Pinto, R.P., Srinivasan, B., Escapa, A., Tartakovsky, B., 2011. Multi-Population Model of a Microbial
769 Electrolysis Cell. Environ. Sci. Technol. 45, 5039–5046. doi:10.1021/es104268g
770 Pinto, R.P., Srinivasan, B., Manuel, M.-F., Tartakovsky, B., 2010. A two-population bio-
771 electrochemical model of a microbial fuel cell. Bioresour. Technol. 101, 5256–5265.
772 doi:10.1016/j.biortech.2010.01.122
773 Pous, N., Carmona-Martínez, A.A., Vilajeliu-Pons, A., Fiset, E., Bañeras, L., Trably, E., Balaguer,
774 M.D., Colprim, J., Bernet, N., Puig, S., 2016. Bidirectional microbial electron transfer:
775 Switching an acetate oxidizing biofilm to nitrate reducing conditions. Biosens. Bioelectron. 75,
776 352–358. doi:10.1016/j.bios.2015.08.035
777 Pous, N., Puig, S., Balaguer, M.D., Colprim, J., 2017. Effect of hydraulic retention time and substrate
778 availability in denitrifying bioelectrochemical systems. Environ. Sci. Water Res. Technol.
779 doi:10.1039/C7EW00145B

780 Richardson, S.D., Kimura, S.Y., 2017. Emerging environmental contaminants: Challenges facing our
781 next generation and potential engineering solutions. Environ. Technol. Innov. 8, 40–56.
782 doi:10.1016/j.eti.2017.04.002
783 Rozendal, R.A., Hamelers, H.V.M., Rabaey, K., Keller, J., Buisman, C.J.N., 2008. Towards practical
784 implementation of bioelectrochemical wastewater treatment. Trends Biotechnol. 26, 450–459.
785 doi:10.1016/j.tibtech.2008.04.008
786 Sabba, F., Terada, A., Wells, G., Smets, B.F., Nerenberg, R., 2018. Nitrous oxide emissions from
787 biofilm processes for wastewater treatment. Appl. Microbiol. Biotechnol. 102, 9815–9829.
788 doi:10.1007/s00253-018-9332-7
789 Sarkar, A., Paul, B., 2016. The global menace of arsenic and its conventional remediation - A critical
790 review. Chemosphere 158, 37–49. doi:10.1016/j.chemosphere.2016.05.043
791 Sarkar, P., Roy, A., Pal, S., Mohapatra, B., Kazy, S.K., Maiti, M.K., Sar, P., 2017. Enrichment and
792 characterization of hydrocarbon-degrading bacteria from petroleum refinery waste as potent
793 bioaugmentation agent for in situ bioremediation. Bioresour. Technol. 242, 15–27.
794 doi:10.1016/j.biortech.2017.05.010
795 Shen, Y., Chapelle, F.H., Strom, E.W., Benner, R., 2015. Origins and bioavailability of dissolved
796 organic matter in groundwater. Biogeochemistry 122, 61–78. doi:10.1007/s10533-014-0029-4
797 Srinivasan, V., Weinrich, J., Butler, C., 2016. Nitrite accumulation in a denitrifying biocathode
798 microbial fuel cell. Environ. Sci. Water Res. Technol. 2, 344–352. doi:10.1039/C5EW00260E
799 Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging
800 contaminants in UK groundwater. Sci. Total Environ. doi:10.1016/j.scitotenv.2011.11.072
801 Su, S., Cheng, H., Zhu, T., Wang, H., Wang, A., 2019. A novel bioelectrochemical method for real-
802 time nitrate monitoring. Bioelectrochemistry 125, 33–37.
803 doi:10.1016/j.bioelechem.2018.09.002
804 Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., Yu, G., 2015. Occurrence, sources and fate of
805 pharmaceuticals and personal care products in the groundwater: A review. Emerg. Contam. 1,

14–24. doi:10.1016/j.emcon.2015.07.001

Tabelin, C.B., Igarashi, T., Villacorte-Tabelin, M., Park, I., Opiso, E.M., Ito, M., Hiroyoshi, N., 2018. Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies. Sci. Total Environ. 645, 1522–1553. doi:10.1016/j.scitotenv.2018.07.103

Tong, Y., He, Z., 2014. Current-driven nitrate migration out of groundwater by using a bioelectrochemical system. RSC Adv. 4, 10290. doi:10.1039/c3ra47851c

Tong, Y., He, Z., 2013. Nitrate removal from groundwater driven by electricity generation and heterotrophic denitrification in a bioelectrochemical system. J. Hazard. Mater. 262, 614–619. doi:10.1016/j.jhazmat.2013.09.008

Van Doan, T., Lee, T.K., Shukla, S.K., Tiedje, J.M., Park, J., 2013. Increased nitrous oxide accumulation by bioelectrochemical denitrification under autotrophic conditions: Kinetics and expression ofdenitrification pathway genes. Water Res. 47, 7087–7097. doi:10.1016/j.watres.2013.08.041

Velasquez-Orta, S.B., Werner, D., Varia, J.C., Mgana, S., 2017. Microbial fuel cells for inexpensive continuous in-situ monitoring of groundwater quality. Water Res. 117, 9–17. doi:10.1016/j.watres.2017.03.040

Venkatramanan, S., Chung, S.Y., Kim, T.H., Kim, B.W., Selvam, S., 2016. Geostatistical techniques to evaluate groundwater contamination and its sources in Miryang City, Korea. Environ. Earth Sci. 75, 1–14. doi:10.1007/s12665-016-5813-0

Viggi, C.C., Matturro, B., Frascadore, E., Insogna, S., Mezzi, A., Kaciulis, S., Sherry, A., Mejeha, O.K., Head, I.M., Vaiopoulou, E., Rabaey, K., Rossetti, S., Aulenta, F., 2017. Bridging spatially segregated redox zones with a microbial electrochemical snorkel triggers biogeochemical cycles in oil-contaminated River Tyne (UK) sediments. Water Res. 127, 11–21. doi:10.1016/j.watres.2017.10.002

Viggi, C.C., Presta, E., Bellagamba, M., Kaciulis, S., Balijepalli, S.K., Zanaroli, G., Papini, M.P.,

832 Rossetti, S., Aulenta, F., 2015. The “Oil-Spill Snorkel”: An innovative bioelectrochemical
833 approach to accelerate hydrocarbons biodegradation in marine sediments. Front. Microbiol. 6,
834 1–11. doi:10.3389/fmicb.2015.00881
835 Vilajeliu-Pons, A., Puig, S., Salcedo-Dávila, I., Balaguer, M.D., Colprim, J., 2017. Long-term
836 assessment of six-stacked scaled-up MFCs treating swine manure with different electrode
837 materials. Environ. Sci. Water Res. Technol. 3, 947–959. doi:10.1039/c7ew00079k
838 Vilar-Sanz, A., Puig, S., García-Lledó, A., Trias, R., Balaguer, M.D., Colprim, J., Bañeras, L., 2013.
839 Denitrifying Bacterial Communities Affect Current Production and Nitrous Oxide
840 Accumulation in a Microbial Fuel Cell. PLoS One 8, e63460. doi:10.1371/journal.pone.0063460
841 Wang, H., Ren, Z.J., 2013. A comprehensive review of microbial electrochemical systems as a
842 platform technology. Biotechnol. Adv. 31, 1796–1807. doi:10.1016/j.biotechadv.2013.10.001
843 Wardman, C., Nevin, K.P., Lovley, D.R., 2014. Real-time monitoring of subsurface microbial
844 metabolism with graphite electrodes. Front. Microbiol. 5, 1–7. doi:10.3389/fmicb.2014.00621
845 Webster, D.P., TerAvest, M.A., Doud, D.F.R., Chakravorty, A., Holmes, E.C., Radens, C.M., Sureka,
846 S., Gralnick, J.A., Angenent, L.T., 2014. An arsenic-specific biosensor with genetically
847 engineered Shewanella oneidensis in a bioelectrochemical system. Biosens. Bioelectron. 62,
848 320–324. doi:10.1016/j.bios.2014.07.003
849 Williams, K.H., Nevin, K.P., Franks, A., Englert, A., Long, P.E., Lovley, D.R., 2010. Electrode-
850 Based Approach for Monitoring In Situ Microbial Activity During Subsurface Bioremediation.
851 Environ. Sci. Technol. 44, 47–54. doi:10.1021/es9017464
852 Wu, S., Li, H., Zhou, X., Liang, P., Zhang, X., Jiang, Y., Huang, X., 2016. A novel pilot-scale stacked
853 microbial fuel cell for efficient electricity generation and wastewater treatment. Water Res. 98,
854 396–403. doi:10.1016/j.watres.2016.04.043
855 Xiao, L., Young, E.B., Berges, J.A., He, Z., 2012. Integrated Photo-Bioelectrochemical System for
856 Contaminants Removal and Bioenergy Production. Environ. Sci. Technol. 46, 11459–11466.
857 doi:10.1021/es303144n

858 Xie, D., Yu, H., Li, C., Ren, Y., Wei, C., Feng, C., 2014. Competitive microbial reduction of
859 perchlorate and nitrate with a cathode directly serving as the electron donor. Electrochim. Acta
860 133, 217–223. doi:10.1016/j.electacta.2014.04.016
861 Xu, W., Wang, C., Liu, H., Zhang, Z., Sun, H., 2010. A laboratory feasibility study on a new
862 electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil. J.
863 Hazard. Mater. 184, 798–804. doi:10.1016/j.jhazmat.2010.08.111
864 Yang, Q., Zhao, H., Liang, H.H., 2015. Denitrification of overlying water by microbial
865 electrochemical snorkel. Bioresour. Technol. 197, 512–514. doi:10.1016/j.biortech.2015.08.127
866 Yuan, L., Yang, X., Liang, P., Wang, L., Huang, Z.-H., Wei, J., Huang, X., 2012. Capacitive
867 deionization coupled with microbial fuel cells to desalinate low-concentration salt water.
868 Bioresour. Technol. 110, 735–738. doi:10.1016/j.biortech.2012.01.137
869 Zhang, B., Feng, C., Ni, J., Zhang, J., Huang, W., 2012. Simultaneous reduction of vanadium (V) and
870 chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J. Power
871 Sources 204, 34–39. doi:10.1016/j.jpowsour.2012.01.013
872 Zhang, Y., Angelidaki, I., 2015a. Counteracting ammonia inhibition during anaerobic digestion by
873 recovery using submersible microbial desalination cell. Biotechnol. Bioeng. 112, 1478–1482.
874 doi:10.1002/bit.25549
875 Zhang, Y., Angelidaki, I., 2015b. Recovery of ammonia and sulfate from waste streams and
876 bioenergy production via bipolar bioelectrodialysis. Water Res. 85, 177–184.
877 doi:10.1016/j.watres.2015.08.032
878 Zhang, Y., Angelidaki, I., 2013. A new method for in situ nitrate removal from groundwater using
879 submerged microbial desalination–denitrification cell (SMDDC). Water Res. 47, 1827–1836.
880 doi:10.1016/j.watres.2013.01.005
881 Zhou, M., Chi, M., Luo, J., He, H., Jin, T., 2011. An overview of electrode materials in microbial
882 fuel cells. J. Power Sources 196, 4427–4435. doi:10.1016/j.jpowsour.2011.01.012
883 Zou, S., He, Z., 2018. Efficiently “pumping out” value-added resources from wastewater by

884 bioelectrochemical systems: A review from energy perspectives. Water Res. 131, 62–73.
885 doi:10.1016/j.watres.2017.12.026
886