Peer-reviewed version available at *Environment International* **2020**, *137*; doi:10.1016/j.envint.2020.105550

In situ **groundwater remediation with bioelectrochemical systems (BES): a 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 may originate from both anthropogenic (e.g., hydrocarbons) and natural compounds (e.g., nitrate and arsenic); to tackle the removal of these contaminants, different technologies have been developed and implemented. Recently, bioelectrochemical systems (BES) have emerged as a potential treatment for groundwater contamination, with reported in situ applications 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, in addition to physical migration due to the electric field generated in a BES. The selection of proper BESs relies on several factors and problems, such as the complexity of groundwater and subsoil environment, scale-up issues, and energy requirements that need to be accounted for. Modeling efforts could help predict case scenarios and select a proper design and approach, while BES-based biosensing could help monitoring remediation processes. In this review, we critically analyze in situ BES applications for groundwater remediation, focusing in particular on different proposed setups, and we identify and discuss the existing research gaps in the field.*

Keywords: bioelectrochemical systems, *in situ* treatment, groundwater remediation, bioelectroremediation, denitrification, microbial electrochemical technologies

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1. Introduction

Groundwater (GW) is highly susceptible to many pollutants, and contamination may render it unsafe or unfit for human or other uses. Contamination might be linked to natural causes, for example, arsenic (As) or nitrate (NO_3^-)-containing rocks (Menció et al., 2016; Tabelin et al., 2018) or, more frequently, to direct or indirect anthropic influence (Burri et al., 2019).

Different treatment technologies have been applied to GW remediation: physical, chemical, and biological, with a 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 are among the most diffused strategies. In this treatment, GW is extracted and subsequently treated outside of the aquifer; this type of solution allows for better process control (i.e., directly observable by the operator); however, it may be highly energy-intensive when the treated, extracted GW does not require immediate use (Favara and Gamlin, 2017). Therefore, much research is focusing on the development of *in situ* treatments, which are generally considered to be more sustainable for the protection of this resource. Compared to P&T, *in situ* treatment requires a more detailed study of the characteristics of the aquifer and its surroundings, since no one-fits-all or standardized solution can be applied with the same success and effectiveness in sites with different characteristics. Therefore, the application of *in situ* GW treatment should be implemented with customized and knowledge-intensive approaches, with a focus on the underlying processes, involving detailed field trials to ensure appropriateness and robustness of the design (Kuppusamy et al., 2016; Majone et al., 2015). Despite the intensive investigation effort required, the application of *in situ* treatments as an alternative to P&T is constantly growing. The latest U.S. EPA Superfund Report showed in fact that *in situ* treatment was chosen as a treatment strategy for GW remediation in 51% of cases, compared to 23% where P&T was selected. A complete reversal of the situation was observed in the year 2000 (EPA, 2017).

A large variety of contaminants and their combinations have been found in GW. As shown in Table 1, these compounds include metals, organic, and inorganic compounds. Pharmaceutically active

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compounds (PhACs) and contaminants of emerging concern (CECs) have also been identified in GW recently (Bexfield et al., 2019).

Table 1. Common contaminants detected in groundwater.

Contaminants		References
Metals	*Metals*	Mahato et al. (2016); Trezzi et al. (2016)
	Metalloids	Kozyatnyk et al. (2016); Luu et al. (2009)
	Explosive metals	Chatterjee et al. (2017); Fuller et al., (2019)
	Radioactive metals	Caridi et al. (2017); Waseem et al. (2015)
	Organometallic pesticides and herbicides	Hakoun et al. (2017); Munira et al. (2018)
VOCs	*Halogenated VOCs*	Plummer et al. (2008); Squillace et al. (2004)
	BTEX	Powers et al. (2001); Rama et al. (2019)
	other non-halogenated VOCs	Plummer et al. (2008); Squillace et al. (2004)
SVOCs	*PCBs*	Coxon et al. (2019); Samia et al. (2018)
	PHAs	Coxon et al. (2019); Samia et al. (2018)
	Organic pesticides and herbicides	Hakoun et al. (2017); Munira et al. (2018)
	Phenols	Han et al. (2016); Rudel et al. (1998)
	Most fuels and distillates	McMahon et al. (2019); Rama et al. (2019)
	Most explosives	Best et al. (1999); Degnan et al. (2016)
	Dioxins and furans	Hofmann and Wendelborn (2007); Thuan et al. (2011)
	Other halogenated and non-halogenated SVOCs	Plummer et al. (2008); Squillace et al. (2004)
Other	Non-metallic inorganics	Cecconet et al. (2018c); Knoll et al. (2019)
	PhACs	Bexfield et al. (2019); Lopez et al. (2015)
	Asbestos	Apollaro et al. (2018); Oskierski et al. (2016)

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), synthesizing 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

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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).

Among different applications of BESs, *in situ* GW bioelectroremediation, i.e., remediation using bioelectrochemical systems, showed to be a promising niche, due to its peculiar characteristics. These include: the option to exploit different redox environments both at anode and cathode, the possibilities to work at different set potentials and to operate as a flexible technology (Modin and Aulenta, 2017). In addition, the combination of anodic and cathodic redox environments with microbial metabolism paves the way for the development of a variety of intriguing and beneficial removal pathways.

Modin and Aulenta (2017) reviewed challenges and opportunities of *in situ* bioelectroremediation, mainly focusing on the general process and the biological mechanisms of electron-electrode transfer; however, the focus of this review will concentrate on different aspects of *in situ* bioelectroremediation. The first in-depth assessment is on different *in situ* applications of bioelectrochemical systems for GW remediation, then critical bioelectroremediation challenges and current research gaps and potential future research directions, including energy consumption and scaling-up will be identified and discussed.

2. Practical obstacles in GW remediation suggesting BESs application

An aquifer is undisputedly a challenging environment, and therefore, due to its intrinsic nature, GW remediation will face several practical issues. Biological water/wastewater treatment requires electron donors (in case of reductive processes) and acceptors (in case of oxidation). In a hydrocarbon-contaminated aquifer scenario, for instance, the limited presence of electron acceptors (NO_3^-, oxygen, sulfate) could limit contaminant oxidation. In addition, insufficient intra-aquifer mixing allows replenishment of electron acceptors only at a contaminated plume's physical boundary, where diffusion and dispersion are the predominant mixing factors (Li and Yu, 2015). Due to ordinarily low concentration of organic matter in GW, similar behavior can be observed for reduction reactions, such as denitrification, where the limiting electron donor may limit potential reaction rates (Shen et al., 2015). Besides,

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metabolism and growth rates of microorganisms may be slowed down in such circumstances, since the majority of biota is attached to soil particles in the sediment, where diffusion of electron acceptors/donors might be particularly difficult (Li and Yu, 2015).

According to these premises, *in situ* bioremediation may become particularly challenging. In addition, a few technologies developed so far often contemplate the addition of (expensive) chemicals, nutrients, and oxygen or introduction/augmentation of microbial communities adapted to the selective degradation of target contaminants. Some of these processes require post-treatments or are efficient only on a limited range of contaminants. These drawbacks may render an *in situ* remediation process quite complex. Some of these issues are summarized in Table 2.

Table 2. Advantages and drawbacks of some commonly applied technology for *in situ* GW remediation.

Technology	Advantages	Drawbacks	References
Heating	Increases performance of the technology used in post-treatment	Necessarily followed by another remediation technology	(Baker et al., 2016)
Permeable reactive barriers	Intercepts GW flow, long-lasting, variety of setups and solutions	Strongly dependent on the site characteristics, necessary addition of chemicals/nutrients	(Obiri-Nyarko et al., 2014)
Air Sparging	Simple, rapid and economical	Not applicable to nonvolatile contaminants; not suited for confined aquifers	(Bass et al., 2000)
Natural Attenuation	Uses naturally-occurring processes	Long remediation time, needs appropriate conditions	(Weatherill et al., 2018)
Bioaugmentation	Pre-adapted bacteria are able to remove target contaminants, mimics natural process	Long remediation time, not suitable for large-scale sites, may need addition of nutrients, oxygen	(Lyon et al., 2013)
Biostimulation	use of naturally-present bacteria	Not suited for highly-polluted sites addition of nutrients, oxygen supply may be costly in the long period	(Prasad and Prasad, 2012)
Nanoremediation	Reactive materials catalyze and reduce contaminants, nanoparticles diffuse well in aquifer	May be linked to ecotoxicological effects on flora and fauna	(Ingle et al., 2014)
Chemical oxidation/reduction	Highly effective	High cost	(Borden et al., 2011)
Bioelectroremediation	No chemicals addition, electrodes acting as electron donor/acceptor, use of indigenous microbial consortia, low	Still at lab or pilot scale	(Pous et al., 2018)

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energy demand can be supplied by renewable sources

BES application may become a solution to the challenges mentioned above or at least a large part of them. The lack of natural onsite electron acceptors and donors required by bioremediation can be substituted electrodes inserted in the soil matrix, acting as "virtually" inexhaustible electron acceptors (anode) or donors (cathode) and supporting microbial metabolism (Aulenta et al., 2011). In other solutions, chemicals acting as electron donors/acceptors are added instead (e.g., reactive barriers), requiring periodic replacement of spent agents. In addition, when reduction reactions are involved, BESs allow setting the desired cathodic electrode potential at reductive levels that cannot be reached by the mere addition of chemical reagents (Li and Yu, 2015; Williams et al., 2010).

Concomitant phenomena may amplify the effectiveness of BES applications. Water electrolysis (occurring at the electrodes' surface) may generate oxygen and hydrogen, which could serve as an additional electron acceptor and donor, respectively. Such electrokinetic enhancement was reported to enhance mixing and mass transport due to the electric field generated in electrodes' proximity (Gill et al., 2014). Electro-osmosis effects may induce water displacement with subsequent resuspension of immobilized bacteria and contaminants, leading to enhanced contact between substrate and bacteria, independently of 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). Li and Yu (2015) reported other advantages of BESs application for GW *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.

As shown in Figure 1, an additional advantage of BES application for *in situ* remediation is their higher environmental sustainability; this is mainly due to the general lack of chemicals addition. This aspect becomes especially relevant when BESs are compared to other technologies where a constant/intermittent supply of electron donors/acceptors and chemicals is an operational condition.

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Combination of electrochemical and biological mechanisms, limited amount of energy requirements that are sufficient to induce otherwise non-spontaneous reactions, make these systems more convenient than those requiring the full energy input for equivalent reactions. Given the peculiarity of each site's condition, a broader analysis, taking into consideration all the possible effects of bioelectroremediation on the surrounding environment, should always be conducted.

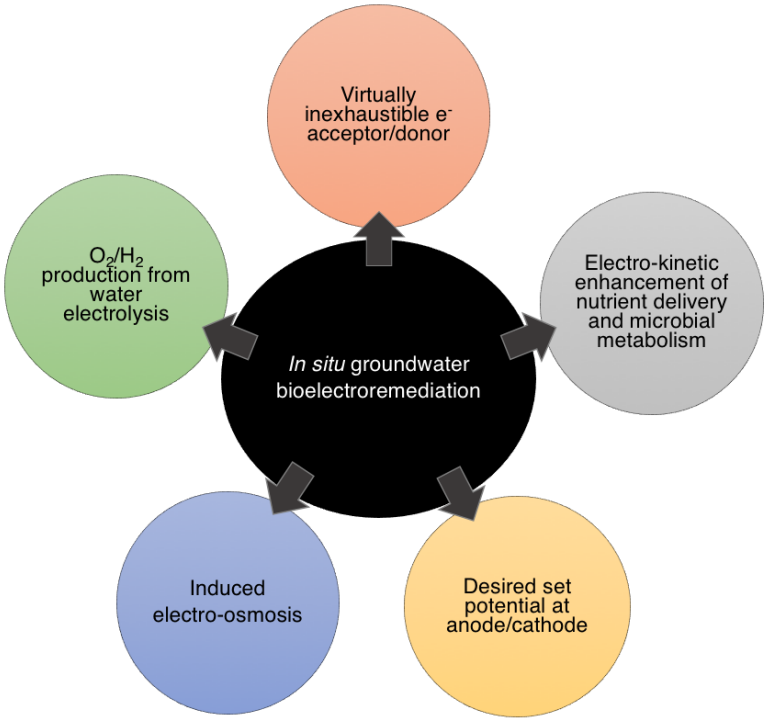

Figure 1: Main advantages of *in situ* bioelectroremediation.

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

Due to the multidisciplinary and faceted nature of BESs, different setups based on this technology have been proposed or developed in the last decade. Most applications have focused on GW denitrification and removal of petroleum hydrocarbons (as seen in Table 1). Petroleum hydrocarbons are usually removed in BESs by anodic oxidation; NO_3^- is reduced 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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147 **Table 3**: Specifications of BES performing *in situ* GW treatment. All experiments performed in batch.

Target	Name	Removal pathway(s)	Volume (mL)	Applied potential/voltage/driving force	Initial conc.	Rem. rate	η	Inoculum	Prevalent microbial species	Ref.
Nitrate	BES	Anodic heterotrophic denitrification	90[A], 160[C]	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	18	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	500[A]	0.8 V (between electrodes)	21.4 mgNO_3^--N L^{-1}	-	55% in 17 hrs	Anaerobic sludge	-	Tong and He (2014)
Nitrate	Biocathode buried in simulated aquifer	Cathodic autotrophic denitrification	350[C]	-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	Cathodic autotro	110[C]	-0.303 V vs SHE	30 mg NO_3^--N L^{-1}	35.35 mgNO_3^--N	97%	Parent biocathode	-	Ceccone et al.

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	in sand or gravel	phic denitrification				m^{-2} d^{-1}				(2019 a)
			110 C	1.0 V (between anode and cathode	30 mg NO_3^--N L^{-1}	36.23 mgN O_3^--N m^{-2} d^{-1}	100%	Parent biocathode	-	
Nitrate	SMFC-BER	Cathodic autotrophic denitrification	250 (BER)	0.27 mA, powered by a SMFC	30 mg NO_3^--N L^{-1}	3.87 mgN L^{-1} h^{-1}	-	Groundwater	*Hyphomicrobium, Terrimicrobium, Teridiphaera, Prosthecobacter*	Liu et al. (2019)
Phenantrene and benzene	MFC	Anodic oxidation	500 A, 300 C	MFC setup	100 ppm (phenantrene), 2000 ppm (benzene)	-	>80% (phenantrene, >90% (benzene)	Parent MFC	-	Adelaja et al. (2017)
Phenol	Bioelectric well	Anodic phenol oxidation	250	+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. (2018 a)
Toluene	Bioelectric well	Anodic toluene oxidation	250	+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. (2018 b)
Benzene, toluene, ethyl-benzene, xylene	Bioelectric well	Anodic oxidation	250	+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	-	Refinery wastewater	*Geobacter*	Palma et al. (2019)

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						.2 mg L^{-1} d^{-1} (xylene)				
Benzene	t-MFC	Anodic oxidation	3300[A]	MFC setup	60 mg L^{-1}	-	100% in 12 d	Selectively enriched mixed microflora	-	Liu et al. (2018)
Light PAHs	GAC-BES	Anodic oxidation and adsorption on GAC	80.46	MFC setup	1546 mg L^{-1}	-	99%	Contaminated groundwater	*Beta-proteobacteria* (in particular *Pseudomanadaceae*)	Kirmizakis et al. (2019)

[A]: net volume anodic chamber; [C]: net volume cathodic chamber

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Tong and He (2013) developed an *in situ* laboratory BES, placed in aquifer medium, that attracted NO_3^- into the anode chamber, removing it by heterotrophic denitrification (Figure 2A). This system was tested with both synthetic and real GW. Anode and cathode chambers consisted of separated porous tubes wrapped by anionic (AEM) and cationic (CEM) exchange membranes, respectively. The anode was fed with GW medium while the cathode with buffer solution. The system was operated in both MFC and MEC modes; application of 0.8 V potential between anode and cathode in MEC mode 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 ion migration was observed; an open circuit NO_3^- removal rate of 158.2± 4.2 $gNO_3^-N\ m^{-3}\ d^{-1}$ was reported, caused by the sole ion exchange. In closed circuit conditions, electricity generation prevented undesired ions migration into the GW by inhibition of ion exchange. Higher current densities were generated when the system was operated with real GW due to the natural presence of ions that would enhance charged particles' general movement and favor electricity generation (Tong and He, 2013). This phenomenon should encourage the experimental application of BER in field-scale applications. In a follow-up study by the same researchers (Tong and He, 2014), the current generated by a tubular BES induced NO_3^- migration out of groundwater, with accumulation in a concentration chamber. This BES setup was similar to 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 by the CEM, preventing their intrusion into the anode chamber. In this case, rather than biological denitrification, NO_3^- removal from GW was due mainly to physical migration induced by electric current (Tong and He, 2014).. Subsequent denitrifying treatment of the concentrated solution (brine) would then be necessary to achieve final removal of nitrate.

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 it was transferred to the cathode chamber, where it was reduced *via* autotrophic denitrification (Figure 2B). NO_3^- removal efficiency of 90.5% was obtained with 12 hours HRT, the ionic strength of GW being a limiting factor for NO_3^- removal. Addition

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of a nitrification step in the anode to cathode NO_3^- transferring loop was beneficial to both bioelectricity production and NO_3^- attraction, removing ammonia (NH_3/NH_4^+) that appeared in the anode chamber due to anoxic conditions. This 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). For bioelectricity generation, Tong and He (2013, 2014) and Zhang and Angelidaki (2014) used synthetic or real wastewater as anode feed in their systems. While this increased the energy sustainability of treatment, the use of wastewater as anolyte was not always be practically feasible and represented additional concerns due to possible leakages contaminating GW both in terms of organic matter and microbial contamination.

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

The influence of local recirculation was discussed by Jain and He (2018), where, in order to achieve better BES performances, proper liquid recirculation was indicated as essential to promote contact between substrate and biomass and decrease overpotentials. This required, however, stirring, and its energy contribution in small reactors (possibly pumping in the bigger ones) cannot be neglected, and may massively affect the overall energy balance of an application (Jacobson et al., 2015; Zou and He, 2018). Recently, Cecconet et al. (2019a) confirmed the decrease in NO_3^- removal rates previously reported by Nguyen et al. (2016a) by operating buried biocathodes completely immersed in sand and gravel, assisted by potentiostat or power supply. Biocathodes operated in gravel achieved better results due to a greater degree of water movement, compared to those in 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

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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 and interaction, substrate gradients, ~~and cross-influences~~ that allow 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 insertion of electrodes in a porous medium, even though feasible and simple, presents severe limitations that should be eliminated with a dedicated design (Figure 2D). Both studies were performed in lab-scale H-cells; in a field application contribution of GW advective flow should be properly assessed, as it would favor contact between substrate and biomass, and may reduce the drawbacks mentioned above.

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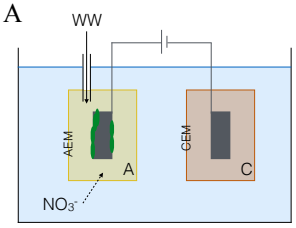
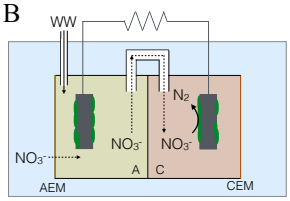
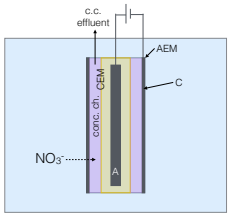
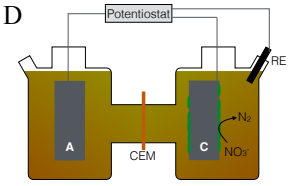
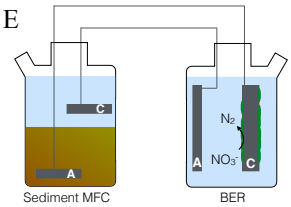
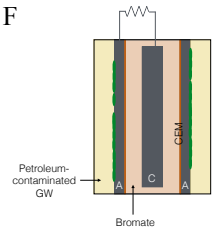
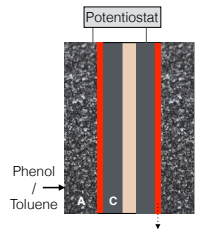
Target	Setup	Advantages	Drawbacks	Ref.
NO_3^-	A 	Heterotrophic denitrification (higher kinetics compared to autotrophic)	Necessity of power supply despite OM oxidation; wastewater as anolyte may contaminate the aquifer	Tong and He (2013)
NO_3^-	B 	Versatile	Use of wastewater as anolyte may contaminate 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)

Figure 2: Advantages and disadvantages of different BES setups for *in situ* GW denitrification. OM: organic matter; WW: wastewater; CEM: cation exchange membrane; AEM: anion exchange membrane;

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BTEX: benzene, toluene, ethylbenzene, xylene; PAH: polycyclic aromatic hydrocarbons; MFC: microbial fuel cell; BER: bioelectrochemical reactor.

A BES setup, known as "bioelectric well", was proposed for *in situ* remediation of hydrocarbon contaminated GW (Palma et al., 2018b) (Figure 2G). The setup consisted of a granular graphite anode and a stainless steel mesh cathode, physically separated by a polyethylene mesh, which maintained hydraulic continuity. The system, operated at a 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 for inoculum. In both cases, *Geobacter* species were predominant in 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 a 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 GW (Palma et al., 2019). Compared to previous applications, the bioelectric well, due to its vertical design, has the advantage of being easily adaptable for placement in existing groundwater wells. In addition, the setup may be easily scaled-up and configured to include internal recirculation; the lack of membranes increases its economic sustainability. However, the use of granular graphite as electrode material might require some special attention due to its non-scalable properties (Rozendal et al., 2008; Zhou et al., 2011) and the tendency to internally form dead volumes with resulting performance loss (Cecconet et al., 2018b). Therefore, the application of other 3-D, scalable electrode materials (e.g., carbon or graphite foam) should be further investigated. At the moment, the

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bioelectric well is the most advanced BES for *in situ* bioelectroremediation, showing potential to remove different contaminants with excellent rates. However, its ability to reduce oxidized contaminants has yet to be tested, as well as the ability of biomass to exert anocathophilic abilities.

Kirmizakis et al. (2019) proposed a BES designed with a graphite electrode chamber (in place of conventional non-conductive material) coupled with granular activated carbon (GAC) to increase available anode surface area, for gasworks GW *in situ* remediation. A latex membrane was used to divide 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 GW (Kirmizakis et al., 2019).

In situ treatment of phenanthrene and benzene contaminated GW with MFC was reported by Adelaja et al. (2017), where a tubular MFC with carbon felt anode was exposed to contaminated GW and tested for long term operation (155 days) (Figure 2F). This system removed 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) organic C (≃ 1500 ppm benzene and 100 ppm phenanthrene) and oligotrophic (low concentration) organic C (≃ 50 ppb for both 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 consistently high (higher than 80% for benzene and phenanthrene 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 GW was reported (Butler et al., 2005), mainly as a byproduct of potabilization processes (Butler et al., 2006). *Ex situ* treatments would allow a combined treatment of both contaminants, maintaining separate streams.

A small scale tubular BES composed of three air-cathode MFC connected in series was proposed for GW benzene removal. The tubular shape allows displacement in wells, and air was insufflated to

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ensure the presence of oxygen at the cathode (Liu et al., 2018). Effects of the necessary insufflation of air should be further investigated, as this might induce air sparging, with additional sideway stripping of volatile compounds.

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 observed denitrification rate of 3.7 mg N L^{-1} h^{-1}. These results were achieved in both simulated GW and, at higher levels, in real GW. The presence of microcurrent positively influenced the establishment of naturally occurring GW denitrifying microorganisms (Liu et al., 2019). From a sustainability point of view, the approach followed by Liu et al. (2019) is of particular interest due to the use of sediment as a source of organic matter for GW denitrification. This setup needs further testing at a larger scale to demonstrate operational feasibility in practical GW remediation cases.

Based on existing literature analysis, the main characteristics of an optimal BES for *in situ* GW treatment can be identified, as shown in Figure 3. These include the possibility to be positioned in existing wells or trenches, avoiding additional expensive excavations, ability to passively intercept GW flow, lack of membranes to reduce costs and maintenance, internal recirculation to allow proper intensive contact between biomass and substrate, large electrodes' surface to allow ample biofilm growth, use of sustainable-source power supply or potentiostat to set the desired work potential and avoid limitations linked to anodic organic matter oxidation rate, ease of scalability, modular design setup or both.

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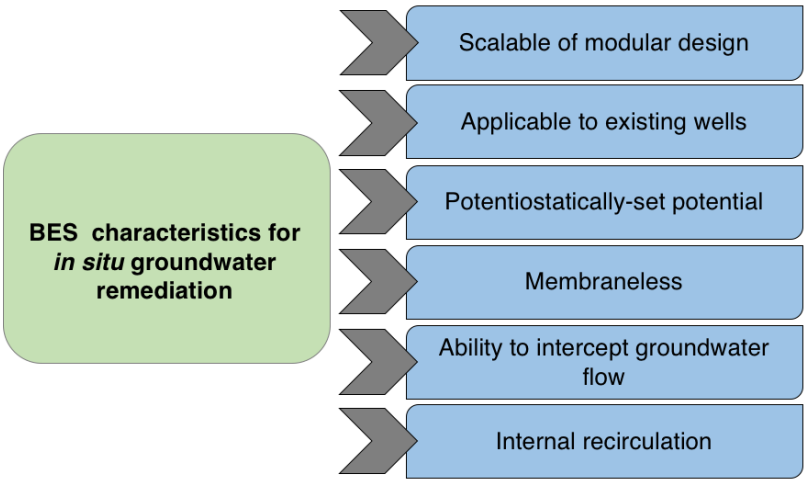

284

285 **Figure 3:** Optimal BES characteristics for *in situ* bioelectroremediation

286

287 **4. Discussion**

288 Based on sections 2 and 3, different issues involving *in situ* GW BES have been identified; their current
289 status and present gaps are discussed in the following subsections.

290

291 **4.1. Evolution of permeable reactive barriers: a future for BES development?**

292 Among the options for remediation of contaminated GW plumes, the use of permeable reactive barriers
293 (PRBs), and in particular of their biological declination, has been advocated and applied widely. A PRB
294 consists of a trench or a series of injection wells through which a reactive medium is introduced in the
295 soil matrix orthogonally to the flowpath of a contaminated GW plume. The latter, driven by the natural
296 hydraulic gradient, passively migrates through the barrier, allowing the contact of solute contaminants
297 with the reactive material, leading to their fixation, transformation, or precipitation to a neutral or less
298 environmentally harmful form (Obiri-Nyarko et al., 2014).

299 Combination of PRBs with microbial metabolism will constitute so-called “biobarriers”, or bio-
300 PRBs. These are built with the same technologies used for conventional PRBs, but consist of materials
301 that enhance, support and stimulate microbial metabolism, allowing *in situ* bioremediation of
302 contaminated GW (Obiri-Nyarko et al., 2014). Microbial populations, necessary for the degradation of

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target compounds, are usually already present in a contaminated area (Careghini et al., 2013) and, to maximize their growth and metabolic action, they may need supplemental nutrients or oxygen –supplied through the barrier filling material-. In the absence of strains not adapted to the specific contaminants, the barrier can be initially used to introduce properly enriched, pre-adapted bacterial species to speed up and promote efficacy of the remediation process (Sarkar et al., 2017).

Several examples of contaminants removed through biobarriers are reported in recent literature: reduced compounds, such as petroleum hydrocarbons, were removed by direct oxygen (terminal electron acceptor) addition via air sparging, or indirectly by addition of oxygen-releasing compounds, such as CaO_2, MgO_2, H_2O_2, in the barrier filling (Careghini et al., 2013). Oxidized compounds instead, were removed by the addition of low-cost, recycled organic matter of plant or anthropic origin, such as wood chips, alfalfa waste, leaves, sawdust, mulch, composted municipal sewage sludge, acting as an electron donor (Zhang et al., 2018).

Advantages of using PRBs and bio-PRBs are many and include the passive nature of the technology, which does not require constant energy input, the possibility of combining multiple selective barriers to sequentially remove a series of contaminants in a plume, the avoidance of GW extraction and high related energy consumption, the possibility of using the above-ground areas in the remediation site for other purposes (Obiri-Nyarco et al., 2014; Careghini et al., 2013). Conversely, one disadvantage, maybe the need for periodical removal/replacement of reactive materials for continuous, long-time operation.

Integration of BESs with PRBs has been proposed by Palma et al. (2018b) as a possible practical application of their bioelectric well (Figure 4A). Such setup could provide efficient GW treatment and save pumping energy by using natural flow to achieve contact between substrate and bioelectrodes. Aquifer natural flow may also (completely or partially) substitute internal recirculation needs, with an additional decrease in the overall system energy demand.

3-D electrodes assembled with innovative materials, such as carbon foam or granular graphite, could constitute a good candidate for these applications, as they have a porous medium structure that

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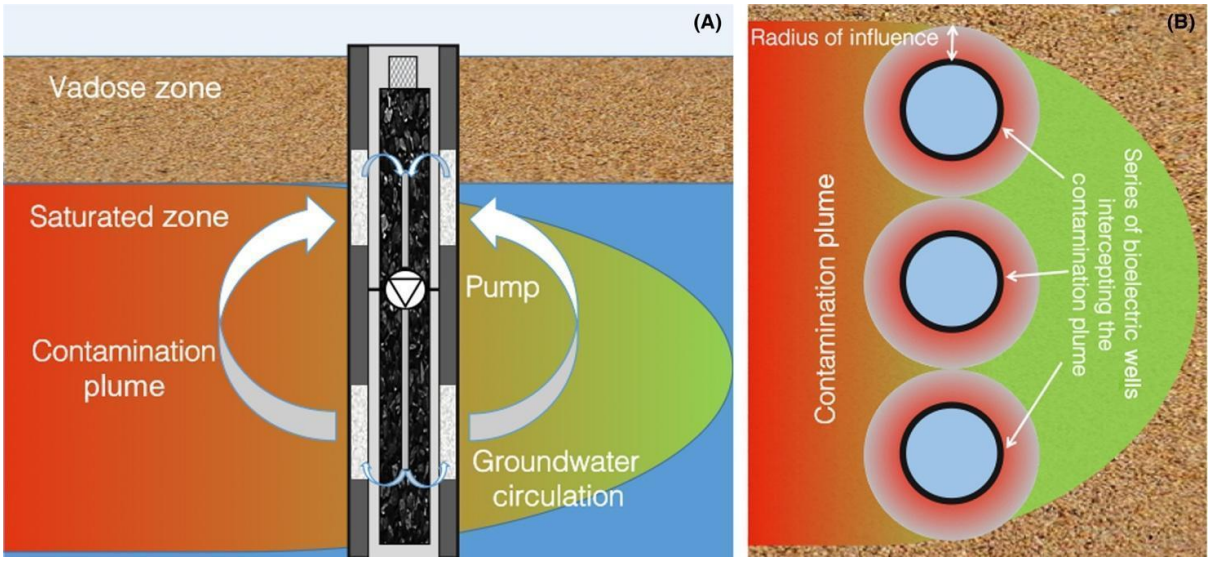
329 allows water to flow through freely, while still offering a large surface area for biofilm growth, combined
330 with excellent electrical conductivity. Microbial populations able to perform direct or indirect electron-
331 electrode transfer, necessary for BES establishment, have been already reported to naturally occur in
332 GW. These were used as indigenous inocula, meaning that the addition of exogenous bacteria may not
333 be necessary (Kirmizakis et al., 2019; Liu et al., 2019; Yang et al., 2015).
334



335

336 **Figure 4:** Scheme of the bioelectrochemical barriers proposed by Palma et al. (2018b).
337

338 One advantage of BES/PRB integration stems from both anode and cathode acting as virtually
339 inexhaustible electron sink and donor. Contrary to conventional PRBs, therefore, no replacement of
340 reactive materials or chemicals is needed. The build-up of thick biofilms could, however, modify the
341 original conductivity of the electrodes, and this may create the necessity of their periodical flushing or
342 replacement. On the other hand, Czurda and Haus (2002) reported that integration of electrochemical
343 processes in bio-PRBs might in fact reduce fouling induced by excessive microbial growth and remove
344 undesired biomolecules and precipitates. Based on this idea, existing permeable barriers may be
345 retrofitted and offer new possibilities of enhanced removal by oxidation/reduction of a variety of
346 contaminants.

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Palma et al. (2018a, 2018b) proposed the combined use of multiple units of tubular-designed bioelectric well. An evolution of this proposed system could be a setup similar to the common funnel-and-gate or open channel PRB design, able to intercept natural GW flow. (Fig. 4B). Addition of graphene oxide to enhance treatment performance of these systems was proposed by Camedda et al. (2019).

4.2. Complex, multi-contaminant groundwater matrix

Concomitant anthropic activities of different nature (i.e., agriculture, industry) may induce GW contamination with various pollutants (Bartzas et al., 2015; Han et al., 2016; Venkatramanan et al., 2016). Therefore, while focusing on single contaminants is useful to assess basic removal pathways and related kinetics for each solute, results achieved might not be of immediate use for real applications. This is mainly due to complex interactions that may occur between different contaminants, including conflicting redox conditions, which may require different remediation techniques. Earlier attempts of using BESs for the removal of multiple GW contaminants have been reported: Butler et al. (2010) first studied the interaction and competition of NO_3^- and perchlorate as terminal electron acceptors (often associated in groundwater) in a BES biocathode; Xie et al. (2014) showed inhibition of perchlorate reduction in the presence of 2.1 mM of NO_3^- and its slowed reduction at lower nitrate concentrations. Nguyen et al. (2016b) studied As oxidation at the anode and denitrification at the cathode of a BES, maintaining strict streams separation (i.e., anodic and cathodic influents). Competition between vanadium and chromium in BES cathodes was also investigated (Zhang et al., 2012), while Lai et al. (2015) performed reductive BES dechlorination of cis-dichloroethylene (cis-DCE) in NO_3^- and SO_4^{2-} contaminated real GW with simultaneous reduction of all three compounds. Chromium presence was reported to partially hinder NO_3^- removal in an MFC treating synthetic GW at the cathode and remediating sediment at the anode (Han et al., 2018). Interaction of chromium with other heavy metals during BER was recently reviewed by Beretta et al. (2019).

In order to enhance GW treatment sustainability, multi-contaminant approaches could be of advantage, exploiting industry-originated organic carbon or organic contaminants sources that are

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commonly detected in GW (e.g., petroleum hydrocarbons); Liu et al. (2019) reported that anodic remediation of contaminated sediments, could be another feasible option as anodic electron source. Potential inhibition effects due to interaction of different contaminants should be assessed: application of BESs with separated chambers should be evaluated, as separation of reduced and oxidized contaminants in real conditions is not always feasible as in lab experiments. Flow-through systems, similar to the one described by Pous et al. (2017), may represent a valid option. The contaminated stream would first be exposed to the anode, performing oxidation, then to the cathode, where reduction would occur. Another option is the use anocathodophilic bacteria-based systems, employing electrodes as both electron acceptors and donors based on redox conditions. Examples in this direction 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).

4.3. 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 in GW worldwide: their presence was reported in Europe (Stuart et al., 2012), the 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 GW contamination due to wastewater infiltration and discharges (McCance et al., 2018). Most of the world population relies on GW use for drinking water supply, and given that CECs' regulations have not been officially issued at the present time in most countries, much debate on this sensitive issue is still ongoing (Lapworth et al., 2019).

BESs proved the capability to remove some CECs with high efficiency and in some cases higher than conventional water and wastewater treatments (e.g., biological process). Interesting results were obtained, particularly in the removal of recalcitrant contaminants with a combination of microbial

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399 metabolisms at different redox conditions offered by anode and cathode (Cecconet et al., 2017).
400 Investigation on CECs removal considering aquifer environment particularities and influence (general
401 low conductivity, and low concentration of nutrients and organic matter is quite active. Removal of
402 multiple contaminants in solution, especially when concentrations differ by orders of magnitude, as
403 discussed in section 4.2., is still an issue that needs great attention.
404
405 **4.4. Energy consumption: the stone guest**
406 Zou and He (2018) recently analyzed the energy sustainability of bioelectrochemical systems for
407 different applications (desalination, wastewater treatment, hydrogen production) considering additional
408 energy costs due to recirculation and feeding/extraction of influents/effluents. A similar analysis of *in*
409 and *ex situ* treatment with MFC and power supply-assisted biocathodes was conducted by Cecconet et
410 al. (2018d), showing that *in situ* denitrification using MFC can be energy-positive. Performances of
411 poised biocathodes were far higher than MFC's in terms of nitrogen removal rates (by approx. 30%).
412 Based on that estimate, it is possible to consider the use of MFC for long-term GW denitrification
413 applications (or biocathodic reduction of other chemicals). Electrons produced by anodic organic matter
414 oxidation could be used for cathodic reduction, and the limitation of achievable removal rates would be
415 acceptable for *in situ* treatment, where the spatial dimensions of contamination are large. One issue to be
416 addressed is the use of organic matter as anolyte and the need to avoid additional contamination. On the
417 other hand, in *ex situ* configurations, the use of a poised biocathode would benefit from higher removal
418 rates, ensuring higher flow rates. A more precise assessment of the real energy consumption of BESs,
419 taking into account all different aspects, such as recirculation, pumping, etc., could be achieved through
420 a specific life cycle assessment (LCA) of this technology.
421 Recently, microbial electrochemical snorkel emerged as a novel BES type (Figure 5). A snorkel
422 is basically a short-circuited MFC, where a microbial anode is directly coupled with a biotic or abiotic
423 cathode. The snorkel does not produce (or require) power but works continuously at the maximum
424 current sustainable by the system, and at the same time, performs at maximum electrochemical reaction

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rate (Hoareau et al., 2019). These systems are characterized by extreme constructive simplicity, as they may consist of a single rod of graphite, steel, or carbon, exposed to two different redox environments (Viggi et al., 2017, 2015). Snorkels have been used to degrade organic matter in wastewater (Aguirre-Sierra et al., 2016) and remove NO_3^- from low-organic wastewater, in addition to remediating hydrocarbon-contaminated sediments (Yang et al., 2015); promising results have been reported, showing removal up to 91% of COD removal and 98% of NO_3^- removal, respectively in Aguirre-Sierra et al. (2016) and Yang et al. (2015).

Snorkels application for GW remediation would allow treatment where no external energy is available or provided, and where simplicity could be the primary reason to suggest its use *in situ*. A snorkel is a relatively new type of BESs, and some of its operational challenges are still unsolved, such as the inability of fully controlling electrode potential, the lack of accurate delimitation of anodic and cathodic zones, and the possible presence of oxygen in the anodic zone. Some solutions, contemplating system's numerical and mathematical modeling and the use of anocathodophilic biofilms, have been proposed (Hoareau et al., 2019).

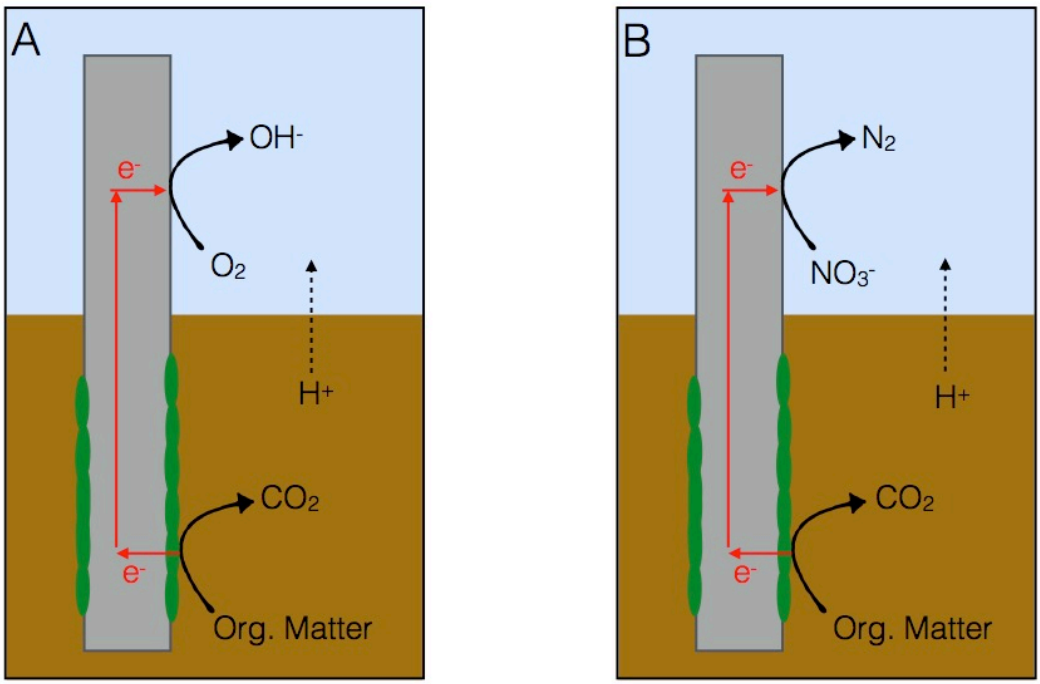

Figure 5: Microbial electrochemical snorkel. (A) Oxygen and (B) nitrate as electron acceptor.

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441

442 **4.5. Process modeling**

443 Modeling is an advantageous approach to assess and help understand the behavior of complex systems
444 in variable conditions. MFC operation and understanding have advanced extensively with the possibility
445 of predicting organic matter removal and energy production interactions (Capodaglio et al., 2017;
446 Gadkari et al., 2018; Pinto et al., 2010). MEC and MDC processes have also been successfully modeled
447 (Ping et al., 2014; Pinto et al., 2011). Latter models evaluated the effects of the integration of BESs with
448 membrane bioreactors and algal photobioreactors (Li and He, 2016; Luo et al., 2017). Statistical methods
449 have been applied to BES technology to improve operational knowledge (Cecconet et al., 2018a; Luo et
450 al., 2016).

451 To date, only limited modeling efforts were reported for BES-based GW remediation. Srinivasan
452 et al. (2016) developed a model for GW denitrification based on the one proposed by Pan et al. (2013),
453 which showed competition between NO_3^- and NO_2 for electrons in an MFC biocathode. Based on existing
454 models (Srinivasan et al., 2016; Pan et al., 2013), removal of target GW contaminants could be simulated,
455 taking into account competition effects between different electron acceptors.

456

457 **4.6. Scaling-up issues**

458 BES applications at full scale for wastewater treatment have been reported (Table 4), but no data are
459 available for full-scale applications for GW treatment, yet, as most results for such applications are still
460 at laboratory scale only. Recently, Wang and He (2019) discussed the required dimension BES systems
461 should reach in order to be considered "pilot scale", concluding that most examples of pilot scale reactors
462 cited in literature should not be considered as such, based on practical flow or hydraulic capacity. A pilot
463 reactor should, in fact, operate at between 0.1 and 5% of the related full scale application flow rate. This
464 concept is, however, difficult to apply for *in situ* GW bioelectroremediation since the estimation of a
465 proper reactor flow-rate is not feasible.

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Conversely, a range of flow rate values can be easily determined for *ex situ,* on-site applications. In 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 study was able to meet the 0.5-250 m^3 d^{-1} flow-rate required for pilot-scale classification. Different considerations emerge in case of decentralized applications: considering isolated dwellings housing four people, a daily water consumption of 400 L d^{-1} can be estimated based on World Health Organization (WHO) requirements of 100 L d^{-1} per capita as daily minimum water intake (Howard and Bartram, 2003). Therefore, a pilot scale BES reactor for such decentralized application should guarantee flow rates in the range of 0.4-20 L d^{-1}. This condition was met by BES performing GW denitrification treatment, with flow values exceeding 12 L d^{-1} described by Pous and co-workers (2017). It is possible, therefore, to state that BESs for GW treatment have reached pilot scale (limited to decentralized applications) and are no longer confined to laboratory settings.

Recently, the application of small scale BESs in series has been proposed as an alternative to sheer size increase for upscaling (Greenman and Ieropoulos, 2017). Serial application of multiple small-scale BESs may be a feasible option to both remove different contaminants, as in biocathodes poised at different potentials, each focusing on a specific contaminant, similar to what reported by Huang et al. (2015) and increase energy production. A comparable sequential approach was tested by Cecconet et al. (2019b) for GW denitrification. Sequential coupling of two denitrifying biocathodes showed to be particularly promising in terms of energy sustainability: the specific energy consumption (SEC) of the system decreased at the increase of the NO_3^- load, showing that such a system was more energy-efficient when operated at low HRTs, a highly advantageous aspect in full-scale facilities.

Electrical connection of two or more BES units, in series or parallel depending on the final goal, represents another aspect of the flexibility potential of this technology. Applications of stacked MFCs have been reported (Kim et al., 2017; Liu et al., 2018), as well as their application to supply sufficient voltage to MEC processes (Choi et al., 2014; Liu et al., 2016).

Table 4: Notable examples of full and pilot scale BES. WW: wastewater

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BES type	Size (L)	Influent	Modular	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)
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)

[1]The reactor indicated as Microbial Electrochemical System (MES), showed setup similar to an MFC.

Few examples of commercial applications of 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 construction materials (membrane and electrodes, 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 could be represented by the adoption 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 these considerations, major drops of the materials' costs (i.e., membranes) are needed in order to allow BES to become an established technology for GW denitrification.

4.7. Biosensing

Recently, much attention has been attracted by the development of BES-based biosensors for environmental monitoring (Capodaglio et al., 2016; Ivars-Barceló et al., 2018). Therefore, research has also addressed specific applications for contaminant detection and monitoring in GW. Velasquez-Orta et al. (2017) designed an MFC-based biosensor for the online monitoring of fecal and organic pollution in shallow wells, obtaining responsive increases in current output; the system was sensitive to temperature

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fluctuations but not to changes in salinity or modifications of external resistance (and longer wiring for electrodes' connections). Field tests highlighted the influence on measurements of water level oscillations in wells, causing air exposition at the cathode (Velasquez-Orta et al., 2017).

Organic matter presence in aquifers undergoing bioremediation was ascertained by an increase in current density in BES-based biosensors; current quickly dropped when organic matter presence ceased, suggesting that the system was able to monitor subsurface microbial activity during *in situ* bioremediation (Williams et al., 2010). Electrodes produced a detectable current, despite the long distance between anode and cathode (6 m), with electron transfer 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 the concentration of biogenic Fe(II), serving as an indicator. Fe(II) is a widely used chemical in GW remediation, and the system showed it could monitor its concentration in a reliable way (Feng et al., 2013). A BES-based arsenite (As) biosensor was developed by Webster et al. (2014) using an engineered *Shewanella oneidensis* strain. The sensor allowed an As detection limit of 40 µM and a linear range up to 100 µM. Another BES-based biosensor, able to monitor NO_3^- in real-time was proposed by Su et al. (2019); it was however designed for monitoring secondary WWTP effluents, hence requiring organic matter as the driving energy input. As such, this design could not be suitable for GW monitoring. Biosensors developed to monitor microbial activity in anoxic sediments (Wardman et al., 2014) could, however, with some setup modifications, be applied to GW 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 their suitability for *in situ* and on-site test monitoring, in addition to their faster response time and lack of advanced technological skills requirements, compared to conventional analytical techniques (Grattieri et al., 2017). BES-based biosensors could ideally complement any remediation processes, allowing low-cost, long-term monitoring of underground processes. Specifically, the applications developed by Williams et al. (2010) and Wardman et al. (2014) could properly assist *in situ* bioelectroremediation. Distance between

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electrodes would not be of concern, as it minimally, or not at all, affects sensing ability as reported in Velasquez-Orta et al. (2017) and Williams et al. (2010).

5. Conclusions

Among different technologies applicable for *in situ* treatment of contaminated GW, BESs showed to be a suitable and feasible option. Analysis of the different setups reported so far in literature highlighted the crucial need of robust and proper BES design for operation in a harsh and challenging environment such as an aquifer, and that simple adaptation of *ex situ* BES setups may not be sufficient to achieve the desired results.

Research in the field so far focused mainly on denitrification and hydrocarbons removal, showing excellent results due to the interaction of microbial metabolism and poised electrodes. In the near future there will likely be a shift of focus towards emerging topics such as interactions between multiple contaminants (both reduced and oxidized), accurate estimation of energy consumption for *in situ* BES remediation, development of reliable models to simulate and predict process behavior and the possible combination of BESs with PRBs for passive remediation of contaminated plumes. *In situ* process monitoring with biosensors is also emerging as an active investigation field. Integration of research gaps in existing BES technology could lead to the rapid development of reliable and resilient systems for *in situ* bioelectroremediation.

Acknowledgments

D.C. and F.S. wish to thank Dr. Shiqiang Zou (Stanford University, USA) for the fruitful discussion and the highly valuable comments; the authors would also like to thank Silvia Bolognesi (University of Pavia, Italy & University of Girona, Spain) for critically proofreading 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.

Peer-reviewed version available at Environment International 2020, 137; doi:10.1016/j.envint.2020.105550

Funding sources

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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