

Review

# Bioelectrochemical Systems for Removal of Selected Metals and Perchlorate from Groundwater: A Review

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**Abstract:** Groundwater contamination is a major issue for human health, due to its largely diffused exploitation for water supply. Several pollutants have been detected in groundwater; amongst them arsenic, cadmium, chromium, vanadium, and perchlorate. Various technologies have been applied for groundwater remediation, involving physical, chemical, and biological processes. Bioelectrochemical systems (BES) have emerged over the last 15 years as an alternative to conventional treatments for a wide variety of wastewater, and have been proposed as a feasible option for groundwater remediation due to the nature of the technology: the presence of two different redox environments, the use of electrodes as virtually inexhaustible electron acceptor/donor (anode and cathode, respectively), and the possibility of microbial catalysis enhance their possibility to achieve complete remediation of contaminants, even in combination. Arsenic and organic matter can be oxidized at the bioanode, while vanadium, perchlorate, chromium, and cadmium can be reduced at the cathode, which can be biotic or abiotic. Additionally, BES has been shown to produce bioenergy while performing organic contaminants removal, lowering the overall energy balance. This review examines the application of BES for groundwater remediation of arsenic, cadmium, chromium, vanadium, and perchlorate, focusing also on the perspectives of the technology in the groundwater treatment field.

**Keywords:** groundwater; bioelectrochemical systems; microbial fuel cell; microbial electrolysis cell; biocathode; arsenic; cadmium; vanadium; chromium; perchlorate

## 1. Introduction

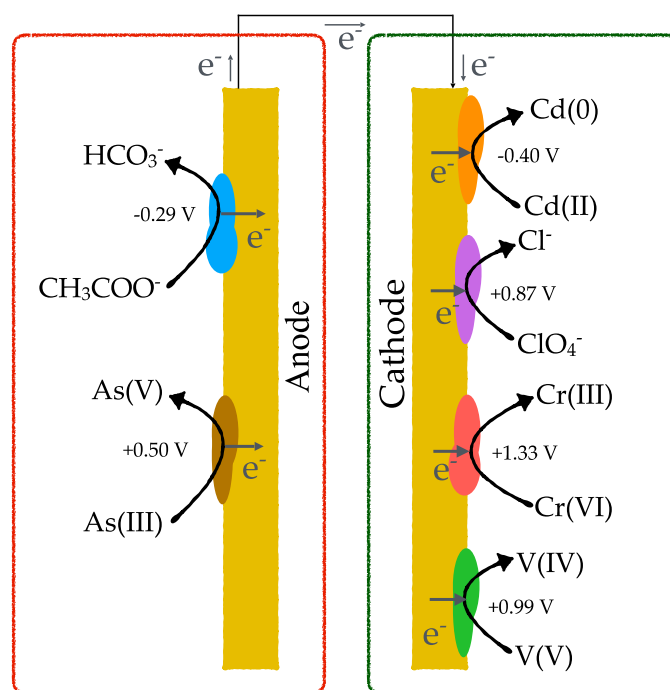
Groundwater contamination is a highly important issue, due to the exploitation of this resource for water supply (drinking, irrigation, industrial process water). Several contaminants can be detected in groundwater and consequently limit its use: nitrate [1], perchlorate [2,3], arsenic [4,5], chromium [6], cadmium [4,7], and vanadium [8] are widely diffused. Those contaminants can be naturally occurring or the consequence of anthropic activities [9].

To perform groundwater remediation of the abovementioned contaminants, several technologies can be applied, namely chemical, biological, biochemical, biosorptive and physico-chemical [10]. Besides conventional and well established approaches, novel technologies are being developed and investigated to increase remediation effectiveness and sustainability. Amongst these, bioelectrochemical systems (BES) have remarkably emerged in the last fifteen years. BESs can be defined as electrochemical systems in which electrochemically active microorganisms act as catalyzers for anode and/or cathode reactions [11]. Research in the BES field initially focused on the production of electric energy from the degradation of organic matter at the anode of microbial fuel cells (MFC). Simple organic compounds such as acetate [12], methanol [13], and glucose [14] have been successfully used as the organic matter source in anolytes. Additionally, MFCs were reported as being able to produce energy from more complex

substrates such as domestic and industrial wastewater: dairy [15–18], food-processing [19], leachate [20,21], pharmaceutical [22], brewery [23,24], winery [25], oil [26] and petroleum refinery wastewater [27] are amongst the principal examples.

After the initial exclusive interest as possible net energy producers from organic matter degradation, which had somehow disappointed researchers' initial development expectations [28–32], BES technology has been used as a flexible platform for fulfilling several other tasks: brackish water desalination in microbial desalination cells (MDC) [33,34], hydrogen production in the microbial electrolysis cell (MEC) setup [35,36], microbial electrosynthesis (MES) of valuable chemicals and commodities [37,38], power-to-gas energy storage [39], nutrient recovery [40,41], and biosensing [42,43] are some notable examples.

Due to the intrinsic characteristics of the technology, BES has been identified as a promising technology for groundwater bioremediation [44]. In BESs, both oxidation and reduction reactions can occur, respectively at the anode and at the cathode [45–47], and thus oxidized contaminants such as nitrate, vanadium, perchlorate or chromium can be reduced in the cathodic environment, while arsenic and/or organic matter can be oxidized in the anodic environment (Figure 1), with possible complete groundwater remediation due to the integration in a single treatment sequence.



**Figure 1.** Scheme of the bioelectrochemical reactions involving the considered contaminants and their redox potentials. In the figure, microorganisms catalyze the reactions at both anode and cathode; cathodic reaction may also occur at an abiotic cathode. The redox potentials ( $E^0$ ) in the figure are under standard conditions and are referred to the standard hydrogen electrode (SHE); the sources for the values are listed below:  $\text{CH}_3\text{COO}^-/\text{HCO}_3^-$ : reference [48];  $\text{As(III)}/\text{As(V)}$ : references [49,50];  $\text{ClO}_4^-/\text{Cl}^-$ : reference [51];  $\text{Cr(III)}/\text{Cr(VI)}$ : reference [52];  $\text{V(V)}/\text{V(IV)}$ : reference [53];  $\text{Cd(II)}/\text{Cd(0)}$ : reference [54].

In addition, BES application for in situ treatment has been proposed; in conventional bioremediation, a continuous addition of chemical amendments ( $\text{O}_2$ ,  $\text{H}_2$ , nutrients, organic matter) is necessary to increase the naturally occurring microbial removal activity [44], and this factor may limit the diffusion and applicability of the process due to connected costs and practical issues [55]. On the other hand, BES may overcome these limitations due to the possible use of anode and cathode as virtually inexhaustible electron acceptor and donor [44,56], avoiding (or drastically lowering) the

amount of chemicals added in the matrix; moreover, the electrodes may serve as physical support for microorganisms' growth [44].

The aim of this review is to illustrate and discuss known applications of BES for groundwater remediation of several pollutants: arsenic, chromium, vanadium, cadmium, and perchlorate. The removal of nitrate is not discussed in this review, as it has been extensively scrutinized and analyzed in recently published reviews [51,56,57].

## 2. Groundwater Contamination Issues

Arsenic is a contaminant known for its toxicity and carcinogenicity [58]. Exposure to arsenic-contaminated groundwater can lead, over the long period, to development of kidney, lung, bladder, and skin cancer and to other severe pathologies [59–61]. It is naturally occurring in the environment in different oxidation states: As(V), As(III), As(0), and As(-III). In water, its most common valences are As(V) (arsenate), stable in aerobic surface waters, and As(III) (arsenite), stable in anaerobic groundwater [62]. Biologically, As(III) is about 60 times more toxic than As(V) [63]. The presence of arsenic in groundwater is related to anthropic activities (mainly agricultural or industrial practices) [64,65] or to the leaching from rocks and sediments [66]. In the former case, the cause of the contamination may lie in the use (or overuse) of As-containing materials (dyes, wood preservatives, pesticides, pharmaceutical substances, additives) [67] that may also accumulate in groundwater, sediments, and surface water [68–70]. In the latter case, rocks may naturally contain As and cause its dissolution in groundwater [70]. Arsenic poisoning is widespread in Asia, Africa, and South America, however its occurrence in groundwater has also been reported worldwide and is not unknown in developed countries either, including Canada [71], Italy [72] and USA [73,74]. The World Health Organization (WHO) identified a guideline value for arsenic presence in drinking water of  $10 \mu\text{g L}^{-1}$ ; this value is adopted as the limit in different areas of the world (Table 1).

**Table 1.** Standards in drinking water prescribed by national/regional regulations and international guidelines for the contaminants considered in the review.

| Contaminant | Limit/Guideline Value ( $\mu\text{g L}^{-1}$ ) | Country/Organization                        |
|-------------|------------------------------------------------|---------------------------------------------|
| Arsenic     | 10                                             | USA [75], WHO [76], EU [77], China [78]     |
| Chromium    | 100                                            | USA [75]                                    |
|             | 50                                             | EU [77], WHO [76], China [78]               |
| Cadmium     | 5                                              | EU [77], USA [75], China [79]               |
|             | 3                                              | WHO [76]                                    |
| Vanadium    | 140                                            | Italy [80]                                  |
|             | 100                                            | Ukraine [81]                                |
|             | 5                                              | Bosnia and Herzegovina, Croatia, FYROM [81] |
|             | 1                                              | Serbia [81]                                 |
| Perchlorate | 70                                             | WHO [76], China [78]                        |
|             | 15                                             | USA [82]                                    |
|             | 6                                              | California (USA) [82]                       |
|             | 2                                              | Massachusetts (USA) [82]                    |

Hexavalent chromium (Cr(VI)) is a toxic heavy metal, found in effluents from industries such as electroplating, steel and metal alloys production, leather tanning, cement, dye/pigment manufacturing, mining, photographic materials, paints, and fungicide production [6,83]. Its accumulation in the environment is a serious threat since Cr(VI) is a known mutagen, teratogen, and carcinogen, besides being also highly corrosive [84,85]. Its high solubility makes it a highly mobile element in the environment. Different limits for Cr(VI) concentration in drinking water have been issued by national authorities (Table 1).

Exposure to cadmium, a heavy metal, has been correlated to several pathologies: high blood pressure, cancer, diabetes, DNA hypomethylation, cardiovascular diseases, and other health issues [86–89]. Cadmium presence in groundwater is due mainly to anthropogenic activity, such as industrial and mining processes [90,91]; a recently-identified source of cadmium in groundwater is the informal recycling process

of e-wastes, a growing problem in China and India, other than in the African continent [92]. The WHO recommends a guideline value for cadmium in drinking water of  $3 \mu\text{g L}^{-1}$  [76], while a higher value of  $5 \mu\text{g L}^{-1}$  is prescribed in the European Union [77] and in China [79] (Table 1).

Vanadium is a naturally occurring element in nature, and can be detected in different types of rock [93]. In addition, it can be easily located in water originating from volcanic springs [8,94,95]. Additional anthropogenic sources of vanadium in groundwater are metallurgic, mining, and the chemical and polymer industries [93]; vanadium contamination of groundwater from the deposition of ashes produced from crude oil or coal burning is still controversial [96,97]. Vanadium is an essential element for human life, and its consumption in a low dose may have a positive effect on human health [98]; yet, acute vanadium poisoning may result in several disorders, including palpitations, coronary insufficiency, and reduced neurobehavioral activities [99,100]. Due to its toxicity, the threshold for vanadium's concentration in drinking water has been set at  $140 \mu\text{g L}^{-1}$  by Italian law [80]; lower values are prescribed in some Balkan countries [81] (Table 1).

Perchlorate contamination in groundwater is mainly attributed to human activity: it is widely used in the production of rocket propellers, fireworks, and ammunitions, and the related industries can be identified as the major contributors in the anthropogenic perchlorate contamination of groundwater [101,102]. Nevertheless, there is some evidence of the presence of natural perchlorate deposits [103], frequently associated with the occurrence of natural nitrate deposits [104]. The perchlorate consumption in drinking water, even in low concentration, is linked to alterations in thyroid hormone levels, that may negatively affect fetal neurodevelopment outcome [105,106]. U.S. EPA set the perchlorate standard in drinking water at  $15 \mu\text{g L}^{-1}$ , with lower standards existing in Massachusetts and California ( $2$  and  $6 \mu\text{g L}^{-1}$ , respectively) [82]; a higher standard ( $70 \mu\text{g L}^{-1}$ ) has been set by the Chinese government [78] and by the WHO [76] (Table 1).

### 3. Contaminants Removal from Groundwater Using BES

#### 3.1. Arsenic

As stated in Section 2, due to a predominantly reducing environment in groundwater, arsenic is generally present in the As(III) form, less soluble and more toxic than As(V); in addition As(V) has been reported as being easier to remove in physical processes [107–110]. Therefore, a common strategy for As(III) removal from groundwater is the application of microbially-catalyzed oxidation of As(III) to obtain As(V), which is then usually physically removed, e.g., by adsorption on a variety of adsorbents [111–113].

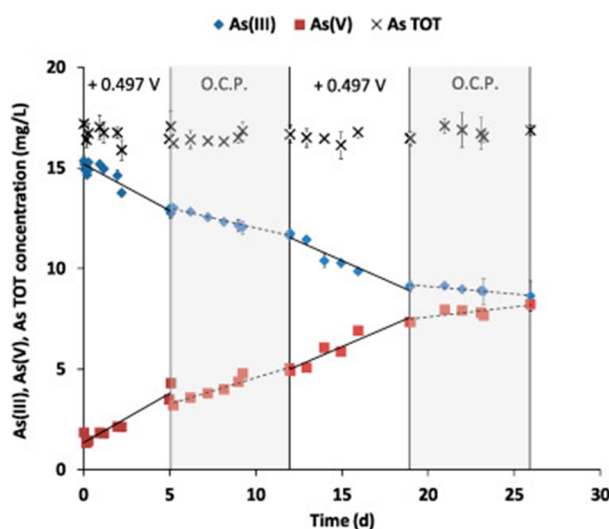
The application of BES in this field is mostly connected to the first phase of arsenic removal, the biological oxidation of As(III) to As(V), using the electrode as a virtually unlimited electron acceptor [50,56]. Some notable examples of application of BES technology for As(III) oxidation are reported in Table 2.

**Table 2.** Arsenic removal using bioelectrochemical systems (BES).

| BES Type                        | Electrode(s) Type                                       | Applied Potential/Voltage | As (III) Removal Rate                     | Energy Production                        | Ref.  |
|---------------------------------|---------------------------------------------------------|---------------------------|-------------------------------------------|------------------------------------------|-------|
| Polarized bioanode              | Graphite rod                                            | +0.497 V vs. SHE          | $0.42 \text{ mg L}^{-1} \text{ day}^{-1}$ | -                                        | [49]  |
| MFC                             | Carbon-fiber felt (anode), plain carbon paper (cathode) | -                         | n.a. <sup>a</sup>                         | $752.6 \pm 17 \text{ mW m}^{-2\text{b}}$ | [114] |
| MFC                             | Carbon paper                                            | -                         | $13.2 \text{ mg L}^{-1} \text{ day}^{-1}$ | $1\text{--}3 \text{ mV}^{\text{c}}$      | [115] |
| Polarized bioanode <sup>d</sup> | Carbon paper                                            | +0.500 V vs. SHE          | $29.6 \text{ mg L}^{-1} \text{ day}^{-1}$ | -                                        | [115] |
| Polarized bioanode <sup>e</sup> | Carbon paper                                            | 1 V                       | $29.6 \text{ mg L}^{-1} \text{ day}^{-1}$ | -                                        | [115] |
| MDC                             | Carbon brush                                            | -                         | n.a.                                      | $7.67 \pm 0.71 \text{ mA}^{\text{f}}$    | [116] |

BES: bioelectrochemical system. MFC: microbial fuel cell. MDC: microbial desalination cell. SHE: standard hydrogen electrode. n.a.: data not available. <sup>a</sup> Removal efficiency was reported being similar to ref. [49]. <sup>b</sup> Maximum current density. <sup>c</sup> Voltage. <sup>d</sup> The bioanode was polarized using a potentiostat and coupled with a denitrifying biocathode. <sup>e</sup> The bioanode was polarized using a DC supply and coupled with a denitrifying biocathode. <sup>f</sup> Peak current.

Bioelectrochemical As(III) oxidation was firstly demonstrated by Pous et al. [49]: a polarized graphite electrode was used as electron acceptor for As(III)-oxidizing microorganisms in an anaerobic BES; the potential was chosen based on the formal potential for NT-26 autotrophic bacteria As(III) oxidase (+0.497 V vs. Standard Hydrogen Electrode, SHE) reported by Bernhardt and Santini [117]. The BES showed an almost identical rate of As(III) removal and As(V) formation ( $420 \pm 38$  and  $428 \pm 59 \mu\text{g L}^{-1} \text{ day}^{-1}$ , respectively); the decrease in As(III) concentration was linear in the presence of electrode polarization (Figure 2).



**Figure 2.** Evolution of As(III), As(V) and As<sub>TOT</sub> concentration during batch tests with the polarized electrode described in Pous et al. [49]. Black lines represent the As(III) removal rate, and the As(V) formation rate. Error bars represent the standard deviation of replicated analytical measurements. Reprinted from Pous et al. [49] with permission from Elsevier.

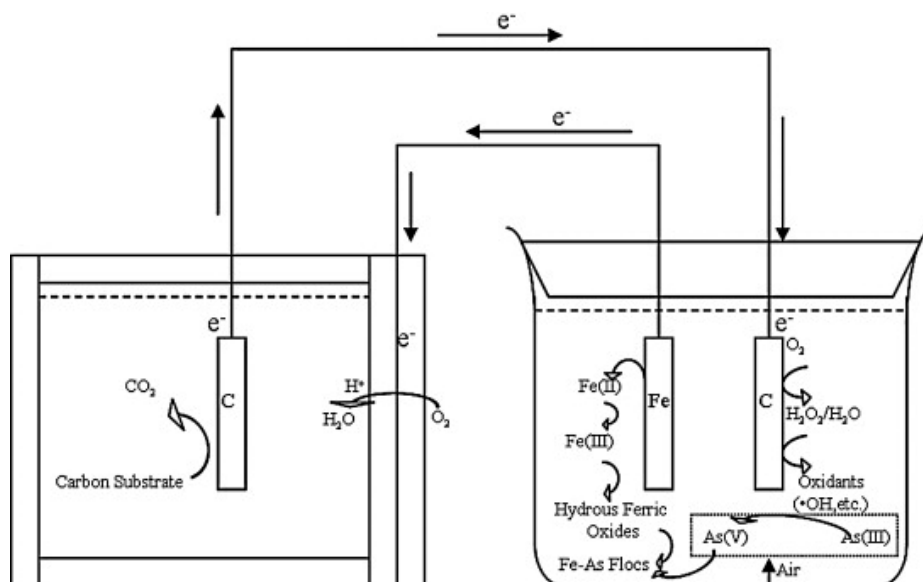
No phenomena of adsorption on the electrode or precipitation were reported, as the concentration of total As remained constant. The application of cyclic voltammetry highlighted the absence of peaks related to redox mediators' occurrence, suggesting a direct extracellular electron transfer; As(III) oxidation potential was measured at +0.500 V vs. SHE, very close to the cathodic poised potential. The dominant population at the anode was composed of *gamma-proteobacteria* [49].

The spontaneous As(III) oxidation at the anode of single-cell MFCs, with carbon-fiber felt anode and plain carbon paper cathode was investigated by Li et al. [114]: As(III) was almost completely removed in 7 days; electrochemical oxidation of As(III) was excluded, as the control abiotic fuel cells achieved practically no removal. The addition of As(III) led to a modification in the MFC's microbial composition, with the appearance of *Actinobacteria* and the increase of *Chlorobi* and *Firmicutes*. Glucose was used as organic carbon source, and removal efficiency was similar to that obtained by the poised bioanode reported by Pous et al. [49], with the advantage of a spontaneous process. Nevertheless, due to the general lack of organic matter in groundwater, glucose or another organic carbon source should be dosed carefully, in order not to create an additional groundwater contamination.

Nguyen et al. [115] demonstrated the feasibility of coupling As(III) oxidation at the bioanode and  $\text{NO}_3^-$  reduction at the biocathode of a BES, proving that anaerobic oxidation of As(III) can provide electrons for biocathodic denitrification; the application of a DC supply (operated at 1 V) or the use of a potentiostat (to poise the anode potential at +0.5 V vs. SHE) were necessary to achieve complete bioelectrochemical oxidation of As(III), which was only incomplete in MFC mode. The higher density of the microbial species and electrode surface were deemed responsible for the higher removal rates compared to that reported by Pous et al. [49] ( $29.6$  and  $0.42 \text{ mg L}^{-1} \text{ day}^{-1}$ , respectively). While no differences were noticed in As(III) anodic oxidation using DC supply and the

potentiostat, an accumulation of nitrite was reported at the DC supply-operated cathode due to the less stable potential [115].

While the described works dealt with the biological oxidation of As(III), the chemical oxidation of As(III) was obtained by a hybrid system composed by an MFC coupled with a zero valent iron process (ZVI) (Figure 3) [118].



**Figure 3.** Schematic of the MFC–ZVI (microbial fuel cell–zero valent iron) process. Reprinted from Xue et al. [118] with permission from Elsevier.

In the ZVI process strong oxidants (hydroxide  $\text{H}_2\text{O}_2$  and hydroxyl radical  $\bullet\text{OH}$ ) are produced via a sacrificial corrosion process releasing Fe(II), oxidized to Fe(III): the oxidants are then able to oxidize As(III) to As(V). A current flowing in the electrolyte of the system is necessary to control the corrosion process, and avoid the consumption of  $\text{H}_2\text{O}_2$  by Fe(II). In the MFC–ZVI system, the bioelectricity generated by the MFC was used for this purpose, and As(III) was removed by the associated ZVI system, obtaining better results than the conventional ZVI process [118].

As(III) removal can be achieved also using another technology in the BES family: Brastad and He [116] showed that arsenic, due to its charge, can be parenthetically removed from the influent during a hardness-removal treatment using a microbial desalination cell (MDC), obtaining an 89% removal.

A growing field for BES applications is their use as biosensors for contaminant monitoring [119–122]; Rasmussen and Minteer [123] reported the use of an MFC inoculated with *Enterobacter cloacae* for arsenic monitoring: the MFC was able to quantify both As(III) and As(V) with low detection limits (4.4  $\mu\text{M}$  for As(III) and 46  $\mu\text{M}$  for As(V)), showing a decrease in power output in the presence of inorganic arsenic. A BES-based arsenic specific biosensor was developed by Webster et al. [124] by genetically modifying the component of the metal reduction pathway of *Shewanella oneidensis* and placing it under the control of an arsenic sensitive promoter, obtaining an As(III) detection limit of 40  $\mu\text{M}$ , and a linear range up to 100  $\mu\text{M}$ .

As shown in the applications above, the use of BES for bio(electro)remediation of As-contaminated groundwater is extremely interesting, due to several factors. The introduction of electrodes in an aquifer (similarly to permeable reactive barriers) could allow development of localized in situ treatment zones, allowing the oxidation of As(III) to As(V). The necessity of a sole polarized electrode with no need for chemicals is particularly attractive from a sustainability-related viewpoint; the electrons harvested in the As(III) oxidation process can be used for the reduction of other groundwater contaminants (e.g., nitrate) in the biocathode. With apposite adsorbing material next to the anode, a complete treatment train would be achieved. In addition, cathodic polarization could reduce the corrosion process of

adsorbents (usually metal oxides or conductive metals), allowing an extension of their lifetime and increasing the sustainability of the process. As alternative, an ex situ treatment can be achieved, which is usually easier to implement, even though it may be more energy-expensive [57].

### 3.2. Chromium

Cr(VI) is an excellent terminal electron acceptor, due to its half-cell reduction reaction potential of +1.33 V vs. SHE, higher than that of O<sub>2</sub> (+1.23 V vs. SHE) [52,125]. Therefore, two main options for Cr(VI) reduction to Cr(III) are available using BES technology: the use of an abiotic cathode or a biocathode (Table 3).

**Table 3.** Chromium removal using BES.

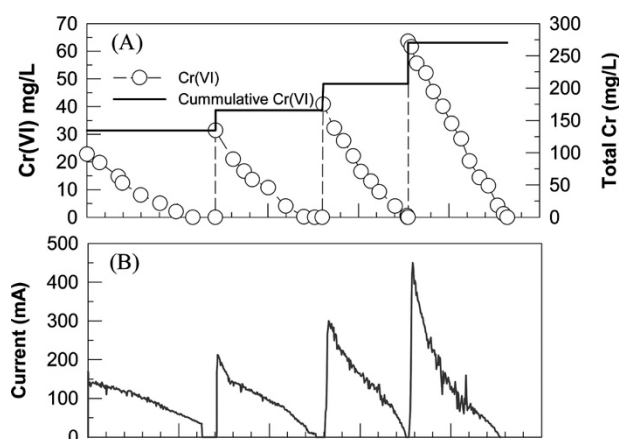
| BES Type | Cathode | Electrodes Material                                       | Cr(VI) Removal Rate                             | Maximum Power Density        | Maximum Current Density       | Ref.  |
|----------|---------|-----------------------------------------------------------|-------------------------------------------------|------------------------------|-------------------------------|-------|
| MFC      | Abiotic | Graphite plates                                           | n.a.                                            | 150 mW m <sup>-2</sup>       | 0.04 mA cm <sup>-2</sup>      | [52]  |
| MFC      | Abiotic | Carbon cloth                                              | n.a.                                            | 767.01 mW m <sup>-2</sup>    | 2.08 mA cm <sup>-2</sup>      | [126] |
| MFC      | Abiotic | Rutile-coated graphite plate (cat.), graphite plate (an.) | n.a.                                            | n.a.                         | n.a.                          | [127] |
| MFC      | Abiotic | Carbon brush (an.), carbon cloth (cat.)                   | n.a.                                            | 5367 mW m <sup>-2</sup>      | n.a.                          | [128] |
| MFC      | Abiotic | Graphite felt (an.), carbon rod (cat.)                    | 4.28 mg L <sup>-1</sup> h <sup>-1</sup>         | 3.3 W m <sup>-3</sup>        | 5.1 A m <sup>-3</sup>         | [129] |
| MFC      | Biotic  | Graphite plates                                           | 0.46 mg gVSS <sup>-1</sup> h <sup>-1</sup>      | 55.5 mW m <sup>-2</sup>      | 123.4 mA m <sup>-2</sup>      | [130] |
| MFC      | Biotic  | Graphite felt                                             | n.a.                                            | n.a.                         | 32.5 mA m <sup>-2</sup>       | [131] |
| MFC      | Biotic  | Graphite plate (an.), graphite plate and granules (cat.)  | 2.4 ± 0.2 mg gVSS <sup>-1</sup> h <sup>-1</sup> | 2.4 ± 0.1 W m <sup>-3</sup>  | 6.9 A m <sup>-3</sup>         | [132] |
| MFC      | Biotic  | Graphite felt                                             | 0.66 ± 0.01 mg L <sup>-1</sup> h <sup>-1</sup>  | 9.7 ± 0.4 mW m <sup>-2</sup> | 69.7 ± 1.4 mA m <sup>-2</sup> | [133] |
| MFC      | Biotic  | Graphite fiber                                            | 20.6 mg gVSS <sup>-1</sup> h <sup>-1</sup>      | 15 W m <sup>-3</sup>         | 48 A m <sup>-3</sup>          | [134] |
| MFC      | Biotic  | Graphite brush (an.), graphite felt (cat.)                | 1.24 ± 0.01 mg L <sup>-1</sup> h <sup>-1</sup>  | n.a. <sup>a</sup>            | n.a. <sup>b</sup>             | [135] |

<sup>a</sup> Power density not available. The reported maximum power is 48 μW. <sup>b</sup> Current density not available. The reported maximum current is 369 μA.

The first option was first explored by Wang et al. [52], who demonstrated the feasibility of cathodic reduction of Cr(VI) to Cr(III) using electrons harvested from a bioanode, simultaneously with energy production (0.04 mA cm<sup>-2</sup> as maximum current density). The best performances in terms of removal efficiency and speed (complete reduction of 100 mg L<sup>-1</sup> of Cr(VI) in 150 h) were obtained at pH = 2. The same value of pH was reported as being optimal for cathodic reduction by Gangadharan and Nambi [126], who obtained a complete reduction of Cr(VI) in 48 h and 99.85% removal of total chromium by precipitation on the electrode surface over 168 h. The low value of the pH was reported as increasing the Cr(VI) reduction due to the protons taking part in the reaction and increasing the reduction potential. The addition of a rutile coating to the cathode of an MFC to perform photoelectrocatalytic reduction of Cr(VI) was reported by Li et al. [127]: the coating enhanced the reduction speed by 1.6 times compared to the dark control where no photocatalysis was performed. No Cr(VI) removal was shown in the control cell with the sterile anode, meaning that the presence of the bioanode was crucial for the cathodic photocatalytic reduction. Even though the results using an abiotic cathode are interesting, their application for groundwater treatment is rather limited due to the sensibility of the cathodic reduction reaction to the pH: the use of pH = 2 is not feasible for any successive use of the groundwater (e.g., drinking water production or restitution to the aquifer) and would require a pH adjustment; the presence of higher values of pH would not prevent the reduction reaction occurring, but would need an excessive amount of time to complete the Cr(VI) reduction due to low proton presence (protons are necessary in the reduction reaction) and formation of a Cr(OH)<sub>3</sub> monolayer on the electrode surface [52,125].

Based on this premise, the application of biocathodes in which bacteria catalyze the desired Cr(VI) reduction to Cr(III) reaction using an electrode as electron donor have been explored parallel. The first

attempt to biologically reduce Cr(VI) in the biocathode of an MFC inoculated with a denitrifying mixed culture was reported by Tandukar et al. [130]: a control MFC equipped with an abiotic cathode showed slower removal rates (7–15% slower) than the MFC with biocathode. Direct relationships were detected between Cr(VI) concentration and the specific reduction rate, also affecting power generation (Figure 4): the maximum specific reduction rate recorded was  $0.46 \text{ mgCr(VI) gVSS}^{-1} \text{ h}^{-1}$  at initial Cr(VI) concentration of  $63 \text{ mg L}^{-1}$ , and no soluble chromium was detected in the effluent, meaning that it precipitated and/or was adsorbed on the biomass or on the electrode surface.



**Figure 4.** Four repetitive cycles of Cr(VI) addition and reduction (A), and the corresponding current production (B). Reprinted from Tandukar et al. [130]; Copyright 2009 American Chemical Society.

A microbial inhibition was shown at a  $80 \text{ mg L}^{-1}$  Cr(VI) concentration, with a decrease in reduction rates, meaning that a high concentration of Cr(VI) may slow down the desired reactions [130].

Other than the denitrifying mixed culture reported by Tandukar et al. [130], the use of other inocula have been reported: Xafenias et al. [131] obtained a biocathode using a *Shewanella oneidensis* MR-1 strain, while a chromate contaminated soil was used by Huang et al. [132]. The development of a Cr(VI)-reducing biocathode by the reversal of an anodic exoelectrogenic biofilm was reported by Wu et al. [133], who obtained a higher microbial density compared to a conventionally grown biocathode; the analysis of the microbial structure of the biofilm showed similar dominant bacteria species (*Gamma-proteobacteria* and *Bacteria*) in both biofilms. A similar procedure was applied by Beretta et al. [136], growing bioelectrodes in the anode of an MFC, and then transferring them to the cathode compartment of MEC reactors: the biocathode poised at  $-0.300 \text{ V vs. SHE}$  showed higher removal efficiency (93%) and rate compared to the biocathode poised at  $+0.700 \text{ V vs. SHE}$  and to the open circuit system's biocathode. This strategy is analogous to a procedure used for the development of denitrifying biocathodes [3,137]. Another option for the development of a Cr(VI) reducing biocathode is the application of a set potential of  $-0.3 \text{ V vs. SHE}$ : the start-up time of the system was reduced compared to a control MFC biocathode due to the applied selective pressure for microorganisms' adaptation, with an additional improvement in the Cr(VI) reduction rate [134].

### 3.3. Cadmium

In order to be removed/recovered from water, the reduction of Cd(II) to Cd(0), which is easier to be physically removed by precipitation and/or adsorption [54], is a common strategy. The first Cd bioelectrochemical recovery was achieved by Modin et al. [54], operating a BES with a biological anode to perform cathodic Cd recovery from a wastewater stream: the cathode potential was poised at  $-0.66 \text{ V}$ , with the necessity of an additional applied voltage of  $0.51 \text{ V}$  due to the low redox potential of Cd(II). Differently from other heavy metals (e.g., Cr(VI) or Cu(II), whose redox potentials are  $1.14 \text{ V vs. SHE}$  and  $0.34 \text{ V vs. SHE}$ , respectively), the low redox potential of Cd ( $-0.52 \text{ V vs. SHE}$ , lower than that of organic matter, ca.  $-0.30 \text{ V vs. SHE}$ ) cannot allow its spontaneous reduction in the cathode of

an MFC, and thus there is the need for additional energy to fulfill the task [135]. Cathodic reduction of Cd(II) was achieved using two MFCs connected in series in a double two-chamber MFC arrangement (d-MFC): this strategy allowed the power and voltage in excess produced by a Cr(VI) reducing MFC to sustain the cathodic reduction at neutral pH of Cd(II) in the second MFC. The system achieved Cd(II) reduction of  $89.73 \pm 0.28\%$ ,  $93.30 \pm 0.74\%$ , and  $93.43 \pm 0.17\%$  for  $200 \text{ mg L}^{-1}$ ,  $100 \text{ mg L}^{-1}$ , and  $50 \text{ mg L}^{-1}$  respectively [128]. A similar strategy was applied by Zhang et al. [129], that stacked a Cr(VI)-reducing MFC and a Cu(II)-reducing MFC to drive cathodic Cd(II) reduction in an MEC, obtaining a simultaneous recovery of Cd, Cr, and Cu. The possibility of a sequential treatment of Cu and Cd contaminated water was shown by Wang et al. [138], who demonstrated that the deposition of Cu in the first phase enhanced the Cd(II) reduction, and  $\text{H}_2$  production in the following stage MEC.

The feasibility of Cd(II) removal using the biocathode of a MEC was demonstrated by Huang et al. [135]: the biocathode was obtained by means of an adaptive acclimatization at a low concentration of a mixture of metals (starting from  $1.0 \text{ mg L}^{-1}$  Cd(II),  $1.0 \text{ mg L}^{-1}$  Cu(II),  $3.0 \text{ mg L}^{-1}$  Cr(VI) and up to  $5.0 \text{ mg L}^{-1}$  of each metal); the MEC scored a  $0.98 \text{ mg L}^{-1} \text{ h}^{-1}$  Cd(II) removal rate. Additional details on the above mentioned works are reported in Table 4.

**Table 4.** Cadmium removal using BES.

| BES type                                         | Cathode | Electrodes Material                           | Potential/Voltage Applied              | Cd removal Rate                                  | Ref.  |
|--------------------------------------------------|---------|-----------------------------------------------|----------------------------------------|--------------------------------------------------|-------|
| Bioanode + potentiostatically-controlled cathode | Abiotic | Carbon felt (an.),<br>Ti wire (cat.)          | $-0.66 \text{ V vs. SHE}$              | n.a.                                             | [54]  |
| Double MFC arrangement                           | Abiotic | Carbon brush (an.),<br>carbon cloth (cat.)    | Energy harvested from<br>upstream MFC  | n.a.                                             | [128] |
| MEC                                              | Abiotic | Graphite felt (an.),<br>Ti sheet (cat.)       | Energy harvested from<br>2 stacked MFC | n.a.                                             | [129] |
| MEC                                              | Abiotic | Graphite felt (an.),<br>carbon cloth (cat.)   | $0.7 \text{ V}$                        | $6.59 \text{ mg L}^{-1} \text{ h}^{-1}$          | [138] |
| MEC                                              | Biotic  | Graphite brush (an.),<br>graphite felt (cat.) | $0.5 \text{ V}$                        | $0.98 \pm 0.01 \text{ mg L}^{-1} \text{ h}^{-1}$ | [135] |

MEC: microbial electrolysis cell.

Neither of the described BES deals directly with groundwater but rather with heavy metal-contaminated wastewater; nevertheless, the lack of organic matter needed for the cathodic reduction suggests the suitability of these processes in a (biotic or abiotic) cathode, with the aid of a power supply or a potentiostat to overcome the limitation imposed by the Cd(II) low redox potential.

### 3.4. Vanadium

Vanadium may occur in two different forms in water: V(V), which is considered the most toxic form, and V(IV), less toxic and is characterized by insolubility at alkaline and neutral pH [125]. Therefore, a common strategy for V remediation in BES is the reduction of V(V) to V(IV) using V(V) as terminal electron acceptor. Some notable examples of application of BESs for V(V) reduction are reported in Table 5.

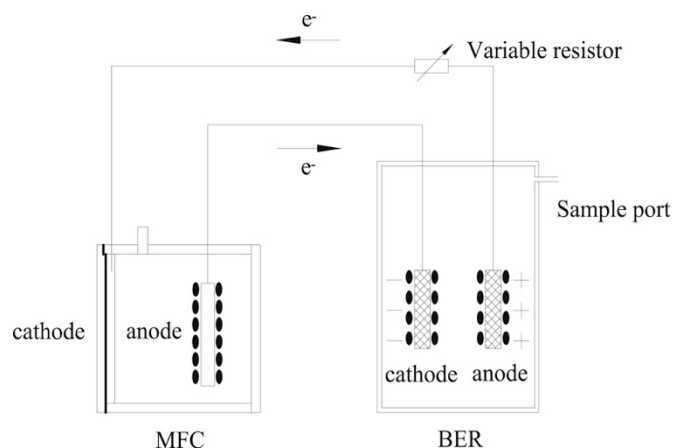
**Table 5.** Vanadium removal using BES.

| BES Type | Cathode | Electrodes Material | V(V) Removal Rate | Maximum Power Density              | Maximum Current Density             | Reference |
|----------|---------|---------------------|-------------------|------------------------------------|-------------------------------------|-----------|
| MFC      | Abiotic | Carbon fiber felt   | n.a.              | $572.4 \pm 18.2 \text{ mW m}^{-2}$ | $1094.0 \pm 50.6 \text{ mA m}^{-2}$ | [139]     |
| MFC      | Abiotic | Carbon fiber felt   | n.a.              | $970.2 \pm 60.5 \text{ mW m}^{-2}$ | $2462.5 \pm 23.1 \text{ mA m}^{-2}$ | [53]      |
| MFC      | Biotic  | Carbon fiber felt   | n.a.              | $529 \pm 12 \text{ mW m}^{-2}$     | n.a.                                | [140]     |

The reduction of V(V) to V(IV) was obtained at the abiotic cathode of an MFC, using the oxidation of sulfide and glucose as source for the electrons, then used in the biocathodic V(V) reduction process; the MFC obtained a V(V) reduction rate of  $25.3 \pm 1.1\%$  [139]. Zhang et al. [53] investigated the simultaneous reduction of V(V) and Cr(VI) in the cathode of a MFC, obtaining a  $67.9 \pm 3.1\%$  and  $75.4 \pm 1.9\%$  removal, respectively; Cr(III) was deposited on the surface of the electrode, while V(IV) was precipitated by pH adjustment.

Even though good results were shown by Zhang et al. [53,139], their approach is difficult to apply for groundwater remediation: in both cases the pH at the cathode was set at pH 2 (to increase the electrochemical redox potential), which is far from usual groundwater pH, and then adjusted to pH 6 to allow the precipitation of V(IV). Therefore, the application of biological reduction that may operate at neutral pH values is desirable, and the use of a biocathode is a feasible option. Qiu et al. [140] succeeded in reducing V(V) at the biocathode of an MFC, obtaining a complete removal in 7 days starting from an initial concentration of  $200 \text{ mg L}^{-1}$ , and a maximum bioelectricity production of  $529 \pm 12 \text{ mW m}^{-2}$ ; the neutral pH was optimal for microbial activity and allowed the precipitation of V(IV) without the need of pH conditioning. *Dysgonomonas* was identified as responsible for V(V) reduction [140].

Other than biocathodes, BESs have been applied for V(V) reduction in hybrid schemes: bioelectricity produced in a single-chamber MFC was used to operate a bioelectrochemical reactor (BER) with the purpose of bioelectrochemically reducing V(V) to V(IV) contained in groundwater (Figure 5) [141]. The BER achieved the best results in vanadium reduction (93.6%) at the maximum power density produced by the MFC ( $543 \text{ mW m}^{-2}$ ), and the addition of organic matter had little effect on the reduction process; differently from Zhang et al. [53,139]—in this case the V(V) was reduced via the anaerobic microbial metabolism, with *Lactococcus* and *Enterobacter* reducing V(V) using products from fermentative *Macellibacteroides* [141].



**Figure 5.** Experimental apparatus employed by Hao et al. [141]. Reprinted from Hao et al. [141] with permission from Elsevier. BER: bioelectrochemical reactor.

### 3.5. Perchlorate

Perchlorate is an excellent electron acceptor for microbial reduction due to the high reduction potential of the  $\text{ClO}_4^-/\text{Cl}^-$  couple ( $0.87 \text{ V vs. SHE}$ ), close to that of the  $\text{NO}_3^-/\text{N}_2$  couple ( $0.75 \text{ V vs. SHE}$ ) [51]; this potential makes perchlorate suitable for reduction at the cathode of BES, as shown by examples in Table 6.

**Table 6.** Perchlorate removal using BES.

| BES Type | Cathode | Electrodes Material                                            | $\text{ClO}_4^-$ Removal Rate           | Potential/Voltage Applied | Power Density           | Current Density          | Ref.  |
|----------|---------|----------------------------------------------------------------|-----------------------------------------|---------------------------|-------------------------|--------------------------|-------|
| MFC      | Biotic  | Graphite granules                                              | $12 \text{ mg L}^{-1} \text{ day}^{-1}$ | -                         | n.a.                    | n.a. <sup>a</sup>        | [142] |
| MFC      | Biotic  | Graphite granules                                              | $24 \text{ mg L}^{-1} \text{ day}^{-1}$ | -                         | $0.3 \text{ mW m}^{-2}$ | $0.17 \text{ mA m}^{-2}$ | [143] |
| MEC      | Biotic  | Polyaniline modified graphite (cat.), graphite electrode (an.) | n.a.                                    | $-0.4 \text{ V vs. SCE}$  | -                       | -                        | [144] |
| MFC      | Biotic  | Carbon cloth (an.), Pt-coated carbon cloth (cat.)              | $25.0 \text{ mg L}^{-1} \text{ h}^{-1}$ | -                         | n.a. <sup>b</sup>       | n.a. <sup>b</sup>        | [145] |
| MFC      | Biotic  | Ti wire-carbon fiber brushes                                   | $2 \text{ mg m}^{-2} \text{ day}^{-1}$  | -                         | n.a.                    | n.a.                     | [146] |

SCE: saturated calomel electrode. <sup>a</sup> The average current at the reported maximum perchlorate removal was  $0.28 \text{ mA}$ .

<sup>b</sup> The maximum voltage reported was  $68 \text{ mV}$ .

Perchlorate reduction in an MFC biocathode was first reported by Shea et al. [142], showing the feasibility of the process in the absence of exogenous electron shuttles, as previously done in a half-cell by Thrasher et al. [147]. The development of a perchlorate-reducing biocathode was obtained from a denitrifying biocathode, by gradually increasing the perchlorate concentration (from 0.1 to 20 mg L<sup>-1</sup>) and simultaneously decreasing the nitrate concentration (from 20 to 1 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>) [142]. A similar strategy was used to obtain a perchlorate reducing biocathode by Butler et al. [143]: a maximum perchlorate removal of 24 mg L<sup>-1</sup> day<sup>-1</sup> coupled with an 84% cathodic conversion efficiency were obtained, with no need for fixing the cathode potential or adding exogenous electron shuttles. While the optimal pH value for bioelectrochemical cathodic denitrification was reported as being in the range 7–7.5 [148,149], a higher value (8.5) was shown to enhance biocathodic perchlorate reduction [143]. Perchlorate was reported to be reduced via autotrophic H<sub>2</sub> reduction in a biocathode [150]: the analysis of the biofilm revealed the presence of *Aureibacter tunicatorum*, *Fulvivirga kasyanovii*, *Thermotalea metallivorans*, *bacterium WHC2-6*, and *Thauera sp. Q20-C*. Perchlorate removal was affected by the current intensity applied to the biocathode, and its maximum (98.99%) was obtained at 60 mA; perchlorate reduction showed a zero-order kinetics [150]. The presence of biofilm on a polyaniline (PANI) modified graphite cathode of an MEC was responsible for an increase of 12% in perchlorate reduction compared to an identical abiotic cathode, showing also that the biofilm (composed of *Azospiraoryzae* strain DSM 13638 of the class *Proteobacteria*) was involved in facilitation of the electron transfer from the cathode to the electrolyte (using its pili-like structure) rather than in perchlorate reduction [144]. The addition of an external redox mediator (resazurin) in the biocathode of an MFC was shown to enhance the perchlorate reduction ratio up to 101.6% at a dosage of 9 µM of resazurin, compared to a mediator-less MFC, and to alter the microbial communities [145].

An enrichment procedure for the development of perchlorate-reducing and nitrate-reducing precultures was proposed by Mieseler et al. [146], using a mixed culture sludge from a membrane bioreactor plant as inoculum and acetate as electron donor in the bioanode; the preculture was then used as inoculum for the biocathodes. The microbial community of the perchlorate-reducing biocathode was unique compared to the denitrifying biocathode community [146].

Other than having a similar redox potential, nitrate and perchlorate presence in water and groundwater are often concomitant, and thus the combination of perchlorate and nitrate reduction has been investigated. The interaction between the presence of perchlorate and nitrate acting as electron acceptors in a biocathode poised at −0.50 V vs. SCE (saturated calomel electrode) was investigated by Xie et al. [151], who reported a slowing effect in perchlorate reduction induced by the presence of nitrate even at low (0.07 mM) concentrations; a higher concentration (2.10 mM) completely inhibited the perchlorate reduction process. The analysis of the bacterial community revealed that the cathodic biofilm was composed of *Alfa-proteobacteria*, *Beta-proteobacteria*, *Gamma-proteobacteria*, *Bacilli*, and *Clostridia*, known denitrifiers, and this may have led to the preferred reduction of nitrate over perchlorate [151]; the decrease in the perchlorate reduction rate in the presence of NO<sub>3</sub><sup>-</sup> was also reported in a single-chamber MFC by Lian et al. [152]. The autotrophic reduction of nitrate and perchlorate in the biocathode of an MFC was investigated by Jiang et al. [153]: in the presence of the sole NO<sub>3</sub><sup>-</sup> and sole ClO<sub>4</sub><sup>-</sup> the MFCs obtained an excellent current density (1.52 mA m<sup>-3</sup> and 3.00 mA m<sup>-3</sup>, respectively) and substrate reduction (87.05% and 53.14%, respectively); the combined presence of NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> in a molar ratio of 1:1 led to the maximum current density (3.10 mA m<sup>-3</sup>) and to a 40.97% removal for ClO<sub>4</sub><sup>-</sup> 86.03% for NO<sub>3</sub><sup>-</sup>. The reduction of both contaminants was attributed to the autotrophic denitrifying biofilm, that showed a predominance of *Beta-proteobacteria*, known denitrifiers; cyclic voltammetry highlighted no evident distinctions in the curves of biofilm fed with NO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> [153].

#### 4. Perspectives

Several factors should be considered in the future development of BES research for the removal of the considered contaminants: the upscaling of the technology, the application of in situ treatment,

the simultaneous treatment of several contaminants, and the development of models to simulate the treatment of the considered contaminants.

The described applications are still at laboratory scale; some BES applications at full scale for wastewater treatment have been reported [154–156], but no data are available for full scale or pilot scale BES applications regarding groundwater treatment. Recently, the application of small scale BES in series has been proposed as an alternative to the increase in dimension for the upscaling of the technology [157]: the application of several small-scale BES in series may be a feasible option to both remove different contaminants (e.g., biocathodes poised at different potential focused each on a different contaminant, similar to the setup reported by Huang et al. [135]) and increase energy production. The engineering and optimization of novel high-performing electrodes should include both a porous structure and a highly conductive material to allow a vast microbially accessible specific surface area, and the development of high current areal densities [158]; the making of such electrodes would drastically help in the upscaling of the technology.

BESs have been proposed for in situ application due to the possibility of using the electrodes as virtually inexhaustible electron acceptor and donor, without the need to add expensive chemicals that may also further contaminate the water resource [44]; to do so, research should focus on the development of a specially designed BES setup. Some attempts in doing so have been reported for hydrocarbons [159] and nitrate [160–162] removal, but more research should be conducted to allow the presence of optimal conditions for bioelectroremediation (e.g., continuous contact between substrate and microorganisms, pH control).

More attention should also be focused on the treatment of a contaminants mixture: the competition between nitrate and perchlorate has been investigated [143,151], as the competition between vanadium and chromium in BES cathodes [53]. Arsenic and nitrate have been treated contemporarily in the anode and cathode of a BES [115], and shown that it is possible to simultaneously exploit the different available redox environment for groundwater remediation. This approach should be implemented, considering industry-originating organic carbon sources or organic contaminants commonly detected in groundwater (e.g., petroleum hydrocarbons) to enhance the sustainability of the treatment. Eventual inhibition effects due to the combination of different contaminants should also be assessed.

In the knowledge of the authors, no modeling attempts have been made to simulate the removal of the considered contaminants. Modeling of the MFC operation has reached good maturity, being able to predict both organic matter removal and energy production [163–165]. Also the MEC and MDC processes have been successfully modeled [166,167]. Statistical methods have been applied also to BES technology [168,169]. Based on existent models, the removal of the considered contaminants should be modeled, also taking into consideration the competition between the different electron acceptors, as performed for example for the biocathodic denitrification process [170].

## 5. Conclusions

BESs have been proposed, in recent years, as a feasible alternative for groundwater remediation: their ability in the removal of arsenic, cadmium, chromium, vanadium, and perchlorate has been described and discussed in this review. In the case of arsenic removal, BESs intervene to oxidize As(III) to As(V), which is then precipitated and/or adsorbed. In the case of the other considered contaminants, the treatment occurs at the cathode. Even though some of the applications involved the use of an abiotic cathode, biocathodes for contaminant removal have shown several advantages and higher applicability, due to the lack of requirement of chemical addition and the possibility of bacteria exploitation for microbial catalysis. It has to be highlighted that the totality of the considered studies dealt with ex situ applications, while more attention should be given to the development of in situ treatments, as is happening with the removal of other contaminants. In addition, neither modeling attempts nor full scale applications for the removal of the considered contaminants have been reported, showing a lack of research in these fields.

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