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Microbial electrochemical Cr(VI) reduction in a soil continuous flow system

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EDITOR'S NOTE:

This article is part of the special series “Remtech Europe 2022: Integrated Approaches for Risk Management and Remediation.” The series documents and advances the current state of practice with respect to the sustainable management of contaminated sites, high-resolution techniques for characterization, disrupting technologies for remediation of soil and groundwater, and risk assessment frameworks.

Abstract

Microbial electrochemical technologies represent innovative approaches to contaminated soil and groundwater remediation and provide a flexible framework for removing organic and inorganic contaminants by integrating electrochemical and biological techniques. To simulate in situ microbial electrochemical treatment of groundwater plumes, this study investigates Cr(VI) reduction within a bioelectrochemical continuous flow (BECF) system equipped with soil-buried electrodes, comparing it to abiotic and open-circuit controls. Continuous-flow systems were tested with two chromium-contaminated solutions (20–50 mg Cr(VI)/L). Additional nutrients, buffers, or organic substrates were introduced during the tests in the systems. With an initial Cr(VI) concentration of 20 mg/L, 1.00 mg Cr(VI)/(L day) bioelectrochemical removal rate in the BECF system was observed, corresponding to 99.5% removal within nine days. At the end of the test with 50 mg Cr(VI)/L (156 days), the residual Cr(VI) dissolved concentration was two orders of magnitude lower than that in the open circuit control, achieving 99.9% bioelectrochemical removal in the BECF. Bacteria belonging to the orders *Solirubrobacterales*, *Gaiellales*, *Bacillales*, *Gemmatimonadales*, and *Propionibacterales* characterized the bacterial communities identified in soil samples; differently, *Burkholderiales*, *Mycobacteriales*, *Cytophagales*, *Rhizobiales*, and *Caulobacterales* characterized the planktonic bacterial communities. The complexity of the microbial community structure suggests the involvement of different microorganisms and strategies in the bioelectrochemical removal of chromium. In the absence of organic carbon, microbial electrochemical removal of hexavalent chromium was found to be the most efficient way to remove Cr(VI), and it may represent an innovative and sustainable approach for soil and groundwater remediation. *Integr Environ Assess Manag* 2024;00:1–17. © 2024 The Author(s). *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Bioelectrochemical systems; Hexavalent chromium; Innovative soil remediation technology; Microbial electrochemical remediation; Sustainable soil bioremediation

INTRODUCTION

The widespread occurrence of Cr(VI) in soil and groundwater stems from industrial processes, mining activities, and

improper waste disposal (Kiliç et al., 2010; Yang, Zhang, et al., 2021) and poses a significant threat to human health and ecosystem integrity worldwide (Kanagaraj & Elango, 2019). Traditional methods rely on chemical reductants, such as ferrous sulfate (FeSO₄), sodium sulfide (Na₂S), and calcium polysulfide (CPS), to convert Cr(VI) to Cr(III) (Di Palma et al., 2015; Hu et al., 2021; Yuan et al., 2018), potentially altering soil properties. Bioremediation strategies, including bio-sorption and biotransformation, aim to mitigate contamination; however, their efficacy may diminish with increasing Cr(VI) concentrations (Ahluwalia & Goyal, 2007; Das & Mishra, 2010; Ksheminska et al., 2008; Oves et al., 2017).

This article contains online-only Supporting Information.

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Among the diverse array of remediation techniques, bioelectrochemical systems (BES) have emerged as promising candidates for in situ treatment of Cr(VI)-contaminated soil and groundwater plumes. By harnessing the redox reactions mediated by microorganisms, BES can facilitate the reduction of Cr(VI) to less toxic and immobile trivalent chromium (Cr(III)) species under environmentally relevant conditions.

Several researchers have investigated Cr(VI)-containing wastewater treatment within BES combined with energy recovery in microbial fuel cells (MFCs) (Wang, Cui, et al., 2020; Wang et al., 2015, 2021, 2023; Zhao, Liu, et al., 2018). Such systems use Cr(VI) either at the abiotic or biocathode as an effective electron acceptor of the electrons resulting from the oxidation of organic substances at the anode (Beretta et al., 2019; Gangadharan & Nambi, 2015; Sophia & Saikant, 2016; Wu et al., 2015).

High efficiency in Cr(VI) reduction in groundwater has recently been reported in potentiostatically controlled or power-supply operated biocathodes without the addition of any organic substrate or in co-contamination with chlorinated solvents (Beretta et al., 2020; Lai et al., 2021; Matturo et al., 2022).

Wang et al. set up different dual chamber MFCs with red clay soil and fluvo-aquic soil spiked with Cr(VI) (up to 550 mg Cr(VI)/kg soil) at the cathode and bioanode in a buffer medium with acetate. After 16 days of operation, they observed removal efficiencies in the range of 50%–99%, depending on the soil type, availability of other electron acceptors competing with Cr(VI), and external resistance applied to the MFC (Wang et al., 2016, 2021).

Plant microbial fuel cells (PMFC) were also tested with Cr(VI)-contaminated saturated soil showing the potential of integrated systems combining plants, microbes, and electrochemical elements for treating Cr(VI)-contaminated soils.

Guan et al. (2019) examined various batch setup conditions, with initial Cr(VI) soil concentrations between 200 and 500 mg/kg, different plant species, and electrode materials, to assess electricity generation and chromium removal. After 96 days of operation, the PMFC systems achieved 99% Cr(VI) removal (Guan et al., 2019). Similarly, Habibul et al. (2016) observed Cr(VI) reduction efficiencies above 90% in batch PMFCs with two different initial Cr(VI) concentrations (9.5 and 19 mg/L), using acetate (0.5–0.55 g/L) as the primary carbon source. Long-term operation tests (65–100 days) with 10 mg Cr(VI)/L, without acetate supplementation, revealed that plants could serve as a carbon source for chromium-reducing bacteria, maintaining high stable removal efficiency even without any external supply of organic carbon (Habibul et al., 2016).

In another study, Wang et al. investigated the remediation of soil contaminated by cadmium and chromium using two-chamber air-cathode MFCs equipped with bipolar membranes. In 50 days of operation, they observed that metal removal efficiency could be affected by the electrical resistance of the soil (Wang, Zhang, et al., 2020).

Mohan and coworkers have investigated the effectiveness of BES in the remediation of soils co-contaminated by BTEX and Cr(VI) using a pure culture of *Pseudomonas putida*

YNS1. The experiments investigated different BTEX initial concentrations (50–400 mg/L), a 4–10 pH range, and a set of applied potential voltages (from 0.4 to 1.2 V). At 10 mg/L initial Cr(VI) concentration and 200 mg/L BTEX at pH 7.0 and 0.8 V applied potential, Cr(VI) removal reached 90% in five days of the test, alongside BTEX simultaneous degradation (Mohan et al., 2020).

Despite the growing interest in Cr(VI) BES-mediated remediation, previous studies have focused on ex situ approaches involving contaminated media excavation or extraction for their treatment. Conversely, this study investigates bioelectrochemical Cr(VI) reduction in a continuous-flow saturated soil column (BECF) with buried electrodes to simulate in situ treatment taking place directly within the Cr(VI)-contaminated aquifer.

The Cr(VI) removal, Coulombic efficiencies (CEs), and kinetics in the BECF system at different initial Cr(VI) concentrations were investigated. The microbial community structure involved in chromium reduction processes was also explored. The results of this study offer preliminary insight into microbial electrochemical remediation of Cr(VI)-contaminated aquifers, contributing to the development of effective and sustainable in situ BES-based treatment strategies.

MATERIALS AND METHODS

Experimental soil

The main characteristics of the sandy loam topsoil used in this study were pH 6.8, 2.58 mS/cm electrical conductivity (EC), 15.38 cmol/kg cation exchange capacity, with 11.3% of carbonates (% CaCO₃ eq), and organic matter content equal to 3.83 g/kg. Other soil characteristics, such as particle size distribution, and measurement methods of EC and cation exchange capacity (CEC) are reported in Supporting Information S1.

Experimental system

Setup of continuous flow systems. For the continuous flow systems, three identical 260 mL transparent plastic columns, 3.8 cm internal diameter and 25.5 cm long, were used.

The three columns were arranged vertically and set up as follows:

- The abiotic control (AC) system was filled up to a height of 6 cm with glass spheres (3 mm diameter); above this layer, a graphite electrode, another 11 cm layer of glass spheres, and a second graphite electrode were inserted. The remaining space was filled with other glass spheres;
- The bioelectrochemical continuous flow (BECF) system and open circuit control (OCC) systems were filled, from the base onward, with a 4 cm layer of glass spheres, 2 cm of clean sand, a graphite electrode (serving as the anode), and 11 cm layer of Cr(VI)-contaminated soil. A second graphite electrode (the cathode) was placed at the top of the soil layer, and the remaining space was filled with glass spheres. In the latter two systems, the

glass spheres and clean sand layers at the bottom helped to ensure a uniform inlet flow distribution, preventing the formation of preferential water pathways.

Each column was then connected to a water-pumping system to initiate the upflow water movement. Before the final setup, some tests with clean water were performed on the columns to evaluate the pumping flow rates and obtain seepage velocities in the columns of the same order of magnitude as a real aquifer ($\approx 1\text{--}10$ m/day) (Accoto et al., 2016; Hudak, 2005). A peristaltic pump (Watson-Marlow 313S) was connected to the BECF and OCC systems. The AC column, instead, was connected to an electric diaphragm metering pump (TELAB BF 414). By setting the pumps, a water seepage velocity equal to 5.8 m/day in each column was obtained.

The graphite electrodes were created by cutting circular pieces of graphite felt (RVG-2000) of the same diameter as the columns; then, a stainless-steel mesh was inserted between a pair of felts, and the felts were sewn together. One end of a titanium wire was welded to the stainless-steel mesh, the other end was bent to create a small loop, and the remaining wire was covered with a heat-shrink casing.

For the BECF and OCC systems setup, the volume between the graphite electrodes was filled with Cr(VI)-contaminated soil from two of the batch soil microbial fuel cells (SMFCs) described in the Supporting Information. In addition, to enhance the EC of the system, a bit of the granular graphite of these SMFCs was inserted above the lower graphite felt and below the higher one (to be in contact with either the electrodes and the Cr(VI)-contaminated soil layer). Soil was added to the columns and completely saturated with tap water.

To generate a flow of the electrons from the anode (the graphite felt at the bottom of the column) toward the cathode (the top graphite felt), 0.6 V was constantly applied among the electrodes of both the BECF and AC systems for the entire duration of the experiment, using a DC power supply (DC Power Supply ARL300 3D) with the negative pole connected to the anodes and the positive pole connected to the cathodes through electrical wires linked to the titanium wire connected to the electrodes. The 0.6 V potential difference was chosen according to previous experiences in heavy metal bioelectrochemical treatment from the literature. For instance, Li and colleagues imposed 0.2–0.8 V to stimulate electron migration for the treatment of heavy metal-polluted wastewater (Li et al., 2021). Furthermore, values lower than 1.2 V, the voltage required for water electrolysis, should be selected to avoid the effects associated with the production of hydrogen and oxygen gases at the electrodes (first, the risk of reducing the overall EC of the system due to the gas bubbles).

Throughout the test, the circulating currents in the BECF system were monitored using a recording digital multimeter (Iso-Tech IDM-8344, UT61E Interface Program Ver 4.01 software tool), which measured the voltage drop across a $10\ \Omega$ resistance inserted between the cathode of the BECF system and the power supply. The voltage drop can be easily converted into current values using the first Ohm's law.

A photograph of the setup and a schematic overview of the continuous flow systems and sampling points are shown in Figure 1. The experimental results are summarized in Table 1.

Cr(VI) contaminated solution. Two different runs at different initial concentrations of Cr(VI) in the feeding solution

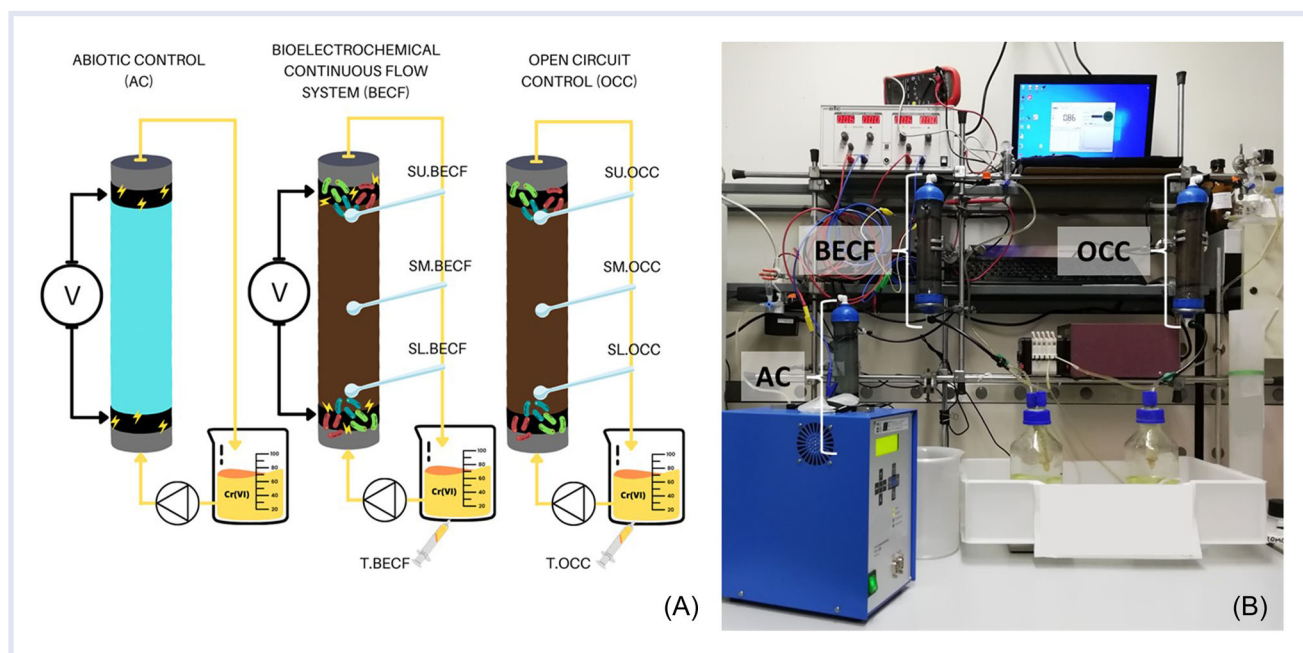


FIGURE 1 (A) Schematic overview of the continuous flow systems (abiotic control [AC], bioelectrochemical continuous flow [BECF], and open circuit control [OCC]) and sampling points for microbiological analyses (white spoon for soils and syringe for liquid) and (B) photo of the experimental setup with continuous flow systems, peristaltic pumps, power supply and data acquisition systems.

TABLE 1 Summary of the experimental work

| Work phase | Description | Acronym | Carbon source | Hexavalent chromium | Microbial characterization | | |
|---|---|---------|------------------------|-------------------------------|----------------------------|----------------------------|---------|
| | | | | | Matrix sampled | Sampling point | Acronym |
| Electroactive bacteria (EAB) enrichment | Soil microbial fuel cell | SMFC | Acetate | $K_2Cr_2O_7$ (3.2 mg/kg soil) | Soil | - | - |
| In situ Cr(VI) removal tests | Bioelectrochemical continuous flow system | BECF | No carbon source added | $K_2Cr_2O_7$ (20–50 mg/L) | Soil | Upper part of soil column | SU.BECF |
| | | | | | | Middle part of soil column | SM.BECF |
| | | | | | | Lower part of soil column | SL.BECF |
| | | | | | Water | Cr(VI) solution tank | T.BECF |
| | Open circuit control | OCC | No carbon source added | $K_2Cr_2O_7$ (20–50 mg/L) | Soil | Upper part of soil column | SU.OCC |
| | | | | | | Middle part of soil column | SM.OCC |
| | | | | | | Lower part of soil column | SL.OCC |
| | | | | | Water | Cr(VI) solution tank | T.OCC |
| | Abiotic control | AC | No carbon source added | $K_2Cr_2O_7$ (20–50 mg/L) | - | - | - |

Note: The work phases, acronyms, and descriptions of tests, carbon sources, the initial hexavalent chromium concentrations, and microbial characterization (matrix sampled, sampling points and sample acronyms) are described in this table.

(20 and 50 mg/L) were carried out to evaluate the effects of Cr levels on the efficiency of its bioelectrochemical reduction.

Cr(VI)-containing tap water was fed into the system at the bottom of the column through the anode compartment at a flow rate of 665 $\mu\text{L}/\text{min}$ (39.9 mL/h), passed through the soil (BECF and OCC) or through the glass spheres (AC) and then through the cathode compartment, and finally flowed out the columns and continuously recirculated to the Cr(VI) solution tank. The reduction of Cr(VI) with time was assessed by taking solution samples at the outlet section of each system to analyze the residual Cr(VI) concentration.

The residual Cr(VI) concentrations measured on the last day of the first run (20 mg/L) (Supporting Information: Table S2) were then used to calculate the volume of concentrated $\text{K}_2\text{Cr}_2\text{O}_7$ solution added to the systems to reach an initial concentration of 50 mg/L for the second test run.

Before both runs, the solution was circulated in the systems for 24 h to ensure uniform initial conditions in the columns.

From the 42nd day after the beginning of the second test run, in addition to Cr(VI) concentration, the pH, EC, and redox potential of the systems outlet solution samples were monitored with a pH meter, conductivity meter, and oxidation-reduction potential (ORP) meter.

Analytical methods and data processing

The samples periodically collected from the three systems were analyzed for Cr(VI) concentration according to a previously reported method (Beretta et al., 2020). Dissolved trivalent chromium species were not monitored as being far less soluble than Cr(VI) at neutral pH, as in all the systems. The circulating currents in BECF and AC and the CE of the BECF system were calculated as reported by Beretta et al. (2020). The calculations are reported in Supporting Information SI (paragraph 1.3).

To characterize the microbial communities, samples of soils have been collected at three different heights, in the low portion (SL.BECF, SL.OCC), in the middle portion (SM.BECF, SM.OCC), and in the upper portion (SU.BECF, SU.OCC), from the columns BECF and OCC. Other details regarding the soil collection are provided in Supporting Information: Figure S3. Water samples from hexavalent chromium solution tanks were also collected and filtered through 0.45 μm sterile paper filters (T.BECF and T.OCC) to characterize planktonic microbial communities in the systems.

Genomic DNA was extracted from the samples following the method described in a previous study by Beretta and colleagues (Beretta et al., 2020). The sequencing was conducted at Nuova Genetica Italiana SRL (Monza-Brianza, Italy). For the elaboration on forward and reverse reads, as well as the singleton sequences, the UPARSE pipeline (<https://www.drive5.com>) was used, as reported in a previous work by Tartari and colleagues (Tartari et al., 2021). The operational taxonomic units (OTUs) and the abundance of each of them as well as the classification of the representative sequences of each OTU, were defined following

the method reported by Federici and colleagues in previous work (Federici et al., 2018; Wang et al., 2007). Further details about DNA analysis methods and data processing are reported in Supporting Information SI (paragraph 1.4).

A principal component analysis (PCA) on Hellinger-transformed community data (Daghio et al., 2016) was performed in R version 4.2.3 and vegan package (Oksanen et al., 2015) to visualize the changes in the continuous flow systems (BECF systems) versus OCC in soil and water.

RESULTS AND DISCUSSION

Cr(VI) trends in continuous flow systems

During the first 20 days of operation, in the first test run, the systems were subjected to an initial concentration of 20 mg Cr(VI)/L. In contrast, in the second test run, the initial Cr(VI) concentration was raised to 50 mg/L (Beretta et al., 2022).

First run: 20 mg Cr(VI)/L. During the first run, the effluents from all systems were regularly sampled and analyzed for dissolved Cr(VI), as shown in Figure 2A and Supporting Information: Table S2.

A reduction in hexavalent chromium concentrations of more than 80% of the initial concentrations was observed in all the systems, with dissolved residual Cr(VI) concentrations at the end of the test of 2.66 ± 0.13 , 0.10 ± 0.01 , and 1.37 ± 0.07 mg/L, corresponding to removals of 86.7%, 99.5%, and 93.2% in the AC system, BECF system, and OCC, respectively. The trend in time of dissolved Cr(VI) concentrations was similar in the various systems, as it tended asymptotically to a minimum value (Figure 2). Notably, the BECF demonstrated remarkable efficiency, exhibiting a 99.4% reduction on the ninth day of testing, outperforming both control systems. Chromium removal rates in the AC (electrochemical removal), BECF (voltage-aided biological reduction), and OCC (biological reduction) were 1.32, 1.73, and 1.48 mg/(L day), respectively, nine days after the test's start. At the end of the test, the chromium removal rates in the AC, the BECF, and the OCC were 0.87, 1.00, and 0.93 mg/(L day), respectively. Therefore, according to the test results, the bioelectrochemical process showed better performance for the reduction of Cr(VI) in the contaminated soil-water system.

Second run: 50 mg Cr(VI)/L. Before the second test run, a Cr(VI) solution was dosed in all systems to obtain an initial concentration of 50 mg/L. Concentration monitoring performed 24 hours following the addition of chromium revealed an unexpectedly low concentration in the abiotic system in comparison to the BECF and OCC systems, where Cr(VI) concentrations were comparable to the initial value. This discrepancy was likely due to the initial fast, but, at neutral pH, short-lasting electrochemical Cr(VI) reduction, as already observed in previous studies (Beretta et al., 2020; Li et al., 2008; Molokwane et al., 2008).

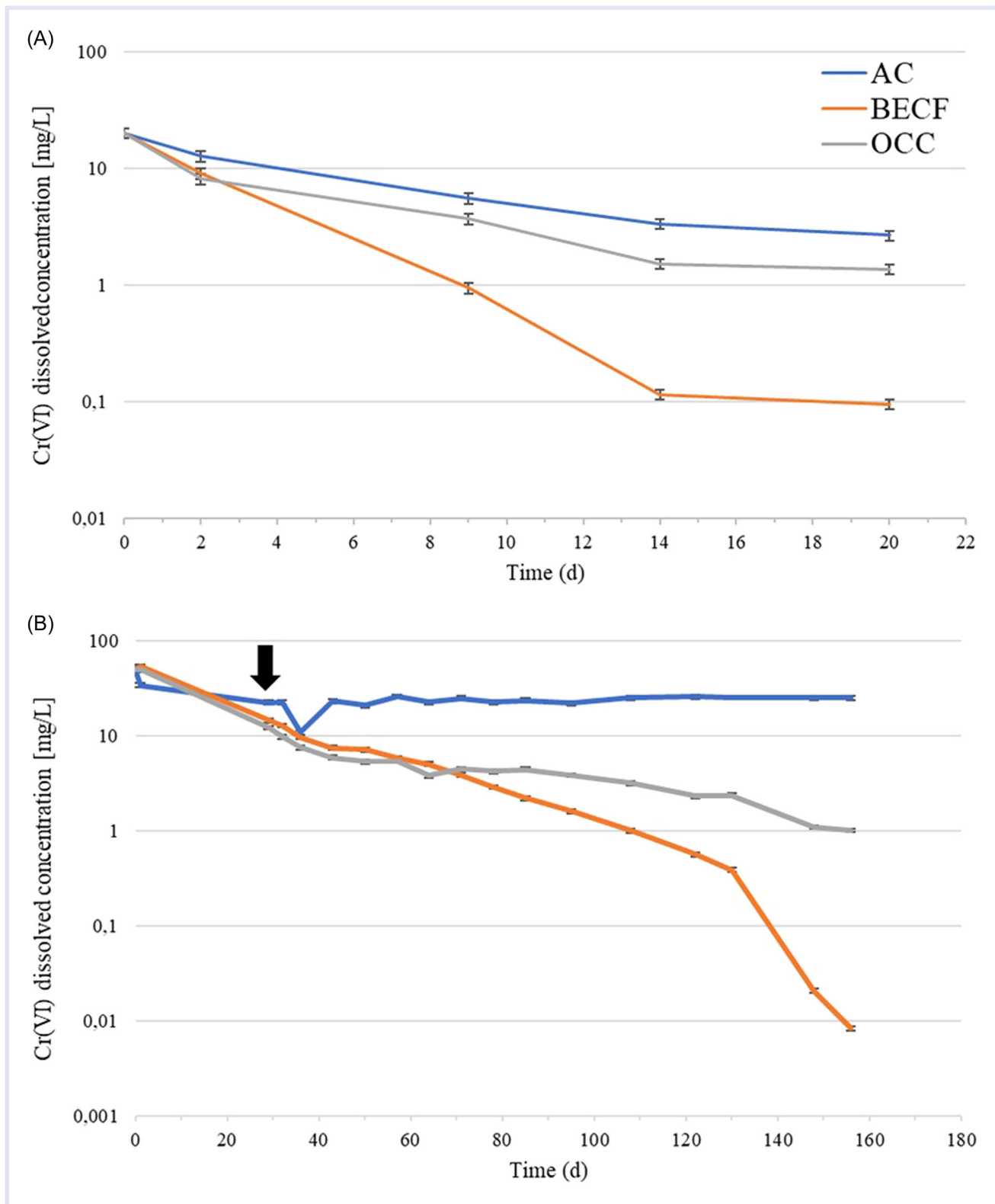


FIGURE 2 Cr(VI) dissolved concentration in the effluent of abiotic control (AC) (blue line), open circuit control (OCC) (gray line), and bioelectrochemical continuous flow (BECF) (orange line) with time, in the first run, with 20 mg Cr(VI)/L as the initial concentration. For acronyms, see Table 1 (A). Cr(VI) dissolved concentrations with time in the effluents of the second run with 50 mg Cr(VI)/L as the initial concentration; AC (blue line), OCC (gray line), and BECF system (orange line). The black arrow indicates the reactivation of continuous flow conditions and power supply.

At the end of the first day, due to electrical power supply issues in the laboratory, the three systems were switched off and kept unpowered in batch conditions for 28 days. After this period, all feeding pumps were reactivated, and the AC and BECF systems were reconnected to the power supply to ensure 0.6 V between the electrodes. From this moment until the end of the test, periodic monitoring of Cr(VI) in the effluents was performed, as summarized in Figure 2B and Supporting Information: Table S3.

During the first 28 days of the test, the biotic systems BECF and OCC actually run in the same batch unpowered conditions, which explains the similar trends in chromium concentrations observed up to about the 70th day of the test. At that time, both biotic systems showed over 90% Cr(VI) reduction (93% in BECF and 91% in OCC), in comparison to approximately 34% reduction in Cr(VI) observed in the AC.

In the long period, a divergence in the trend of the concentrations in BECF and OCC was observed. After 108 days of operation, the residual dissolved Cr(VI) concentration in the BECF system was equal to 0.99 ± 0.05 mg/L; instead, in the OCC system, the same value was reached only at the end of the test, 48 days later (Figure 2B). In contrast, after the first drop, Cr(VI) concentrations in the AC remained steady, ranging between 20 and 25 mg/L, until the completion of the trial.

At the end of the experiment, the systems' dissolved chromium concentrations were 24.80 ± 1.24 , 0.01 , and 1.01 ± 0.05 mg/L in the AC, BECF, and OCC systems, respectively, corresponding to 26.6%, >99.9%, and 97.0% reductions. In comparison to the OCC, the residual dissolved Cr(VI) concentration in BECF was two orders of magnitude lower. Overall chromium removal rates in BECF and OCC were determined to be 0.32 and 0.31 mg/(L day), respectively, with bioelectrochemical Cr(VI) reduction proving to be quite an

effective technique for removing Cr(VI) from polluted soil-water systems. From the 42nd day after the beginning of the experiment, in addition to Cr(VI) concentration, pH, EC, and redox potential of the systems outlet solution were monitored, as reported in Table 2 and Supporting Information: Figure S4. The pH trends in the three systems were similar, with values ranging between 7.69 and 8.35. The lowest values, on average, were observed in AC (7.77–8.18); instead, the highest ones were observed in BECF (7.9–8.35). No significant variations of pH and EC AC were usually higher than $850 \mu\text{S}/\text{cm}$ and showed a clear increase from approximately 870 to $962 \mu\text{S}/\text{cm}$ in the final measurements.

The data acquisition system, except for a period of about 20 days (from the 32nd to the 52nd day of the test) and a few other malfunction episodes, allowed us to record the trend of the currents flowing through the cathode in the BECF system (soil and/or interstitial solution and microorganisms) throughout the test. Outages in the data recording did not affect the operational conditions of the BECF system.

The values of the circulating currents ranged from -0.60 to -1.08 mA during the test (Figure 3), with fluctuations likely due to daily variations in the room temperature (22 ± 5 °C) and a slight and constant increase with time. On the 73rd day, the systems required short maintenance, which involved switching off the power supply and pausing the data recording. This explains the drop of about 0.1 mA in the current values and their subsequent gradual increase to the preintervention level in less than a week.

Based on the measured Cr(VI) concentrations in the effluent from the BECF system and the current data at the same time, it was possible to calculate the Coulombic efficiency (CE) of the Cr(VI) bioelectrochemical removal process (see Supporting Information SI (paragraph 1.3)). The calculated CE showed an increase with time, from 29% at the beginning of

TABLE 2 pH, ORP (mV), and EC ($\mu\text{S}/\text{cm}$) values in the effluents of the systems during the experimental period (43th–85th days)

| Day | pH | | | ORP (mV) | | | EC ($\mu\text{S}/\text{cm}$) | | |
|-----|------|------|------|----------|------|-----|--------------------------------|------|-----|
| | AC | BECF | OCC | AC | BECF | OCC | AC | BECF | OCC |
| 43 | 7.81 | 7.92 | 7.69 | −45 | −55 | −44 | 873 | 732 | 835 |
| 45 | 8.05 | 8.18 | 8.11 | −37 | −49 | −44 | 887 | 734 | 809 |
| 57 | 8.12 | 8.34 | 8.21 | −44 | −56 | −50 | 871 | 692 | 702 |
| 64 | 8.18 | 8.30 | 8.18 | −46 | −55 | −48 | 839 | 693 | 712 |
| 71 | 8.10 | 8.35 | 8.20 | −37 | −37 | −51 | 851 | 691 | 712 |
| 78 | 8.01 | 8.22 | 8.09 | −37 | −51 | −44 | 855 | 685 | 720 |
| 85 | 8.12 | 8.27 | 7.96 | −43 | −53 | −47 | 871 | 760 | 776 |
| 95 | 7.77 | 8.09 | 7.97 | −36 | −49 | −50 | 857 | 700 | 759 |
| 122 | 7.98 | 8.19 | 8.07 | −38 | −50 | −43 | 901 | 756 | 846 |
| 130 | 8.14 | 8.08 | 8.27 | −46 | −43 | −53 | 962 | 631 | 713 |
| 148 | - | 8.01 | 8.00 | - | −41 | −40 | - | 646 | 826 |

Abbreviations: AC, abiotic control; BECF, bioelectrochemical continuous flow; EC, electrical conductivity; OCC, open circuit control; ORP, oxidation-reduction potential.

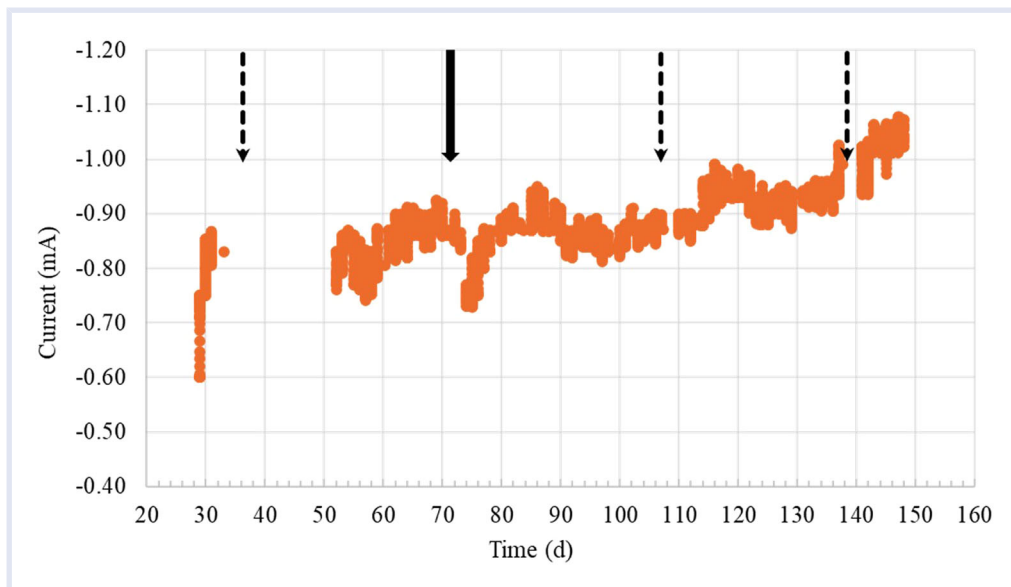


FIGURE 3 Reducing currents (mA) in the bioelectrochemical continuous flow system (mobile mean of 10 values—no outliers). The solid black arrow indicates maintenance involving a brief switch-off of the system. The dotted black arrows indicate outages in the data recording

the test (29nd–32nd day) up to 250% in the last period (between the 122nd–130nd day) (Figure 4, Supporting Information: Table S4). Therefore Cr(VI) reduction rate and CE were inversely proportional, with a decrease in the first one corresponding to an increase in the second one.

The decreasing trend of the Cr(VI) reduction rate could be related to the decrease in the dissolved Cr(VI) concentration in the BECF system. On the other hand, the increase in the CE likely indicates that part of the electrons from the cathode were used for other processes, either catalyzed by bacteria or not. The inhibitory effect of Cr(VI) on the development and metabolism of Cr(VI)-sensitive bacteria probably diminished with decreasing quantities of dissolved

Cr(VI). As a result, bacteria, including those with electroactive properties, previously constrained in their growth, could have utilized the presence of electron donors/acceptors to boost their metabolic activity. Coulombic efficiency values higher than 80%–100% might be ascribed to other electrochemical or bioelectrochemical processes not strictly related to Cr(VI) reduction.

Microbial communities

Here, below the sequencing results of the bacterial 16S rRNA gene at the order level on the sample taken from soil before the test (S.SMFC), the soil at the end of tests (SL.BECF, SL.OCC, SM.BECF, SM.OCC, SU.BECF, SU.OCC),

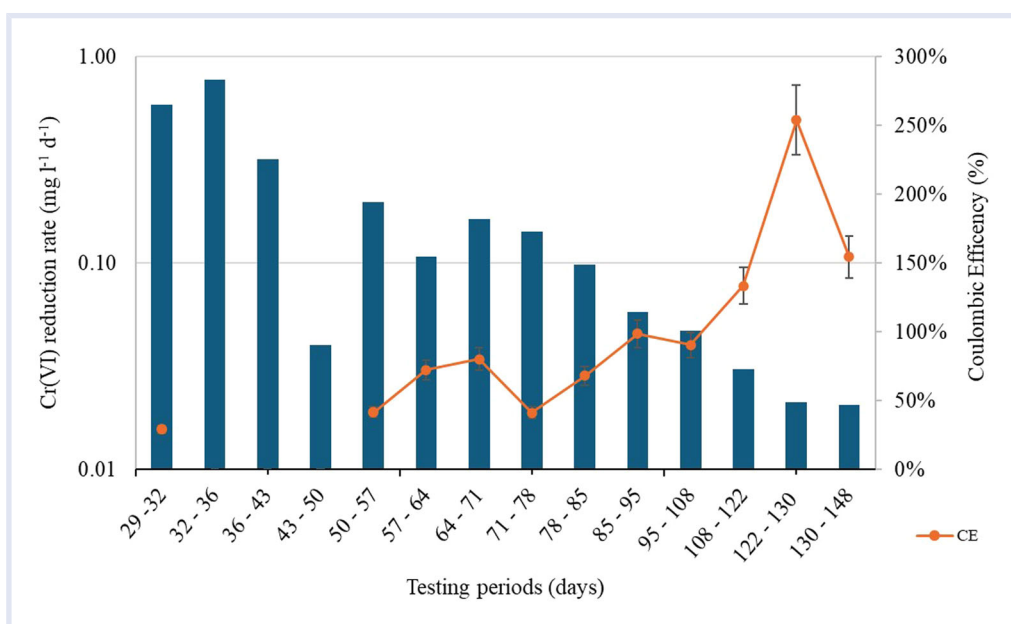


FIGURE 4 Cr(VI) reduction rate and Coulombic efficiency in the bioelectrochemical continuous flow system

and water samples from Cr(VI) contaminated water tanks (T.BECF, T.OCC) at the end of the tests are reported.

The results of microbiological analyses (Figure 5) showed a marked diversity between microbial community structure of soil samples (depicted as red points, including SL.BECF, SL.OCC, SM.BECF, SM.OCC, SU.BECF, and SU.OCC) and water samples collected from the columns feeding tanks

(represented as blue points, namely T.BECF and T.OCC). Water samples were very different depending on the type of system in which they were collected. Moreover, as reported in the PCA plot (Figure 6), samples from the BECF system (symbolized as squares) clustered together with the inoculum (denoted by red dots) and were separated from the OCC community (symbolized as triangles). This means that

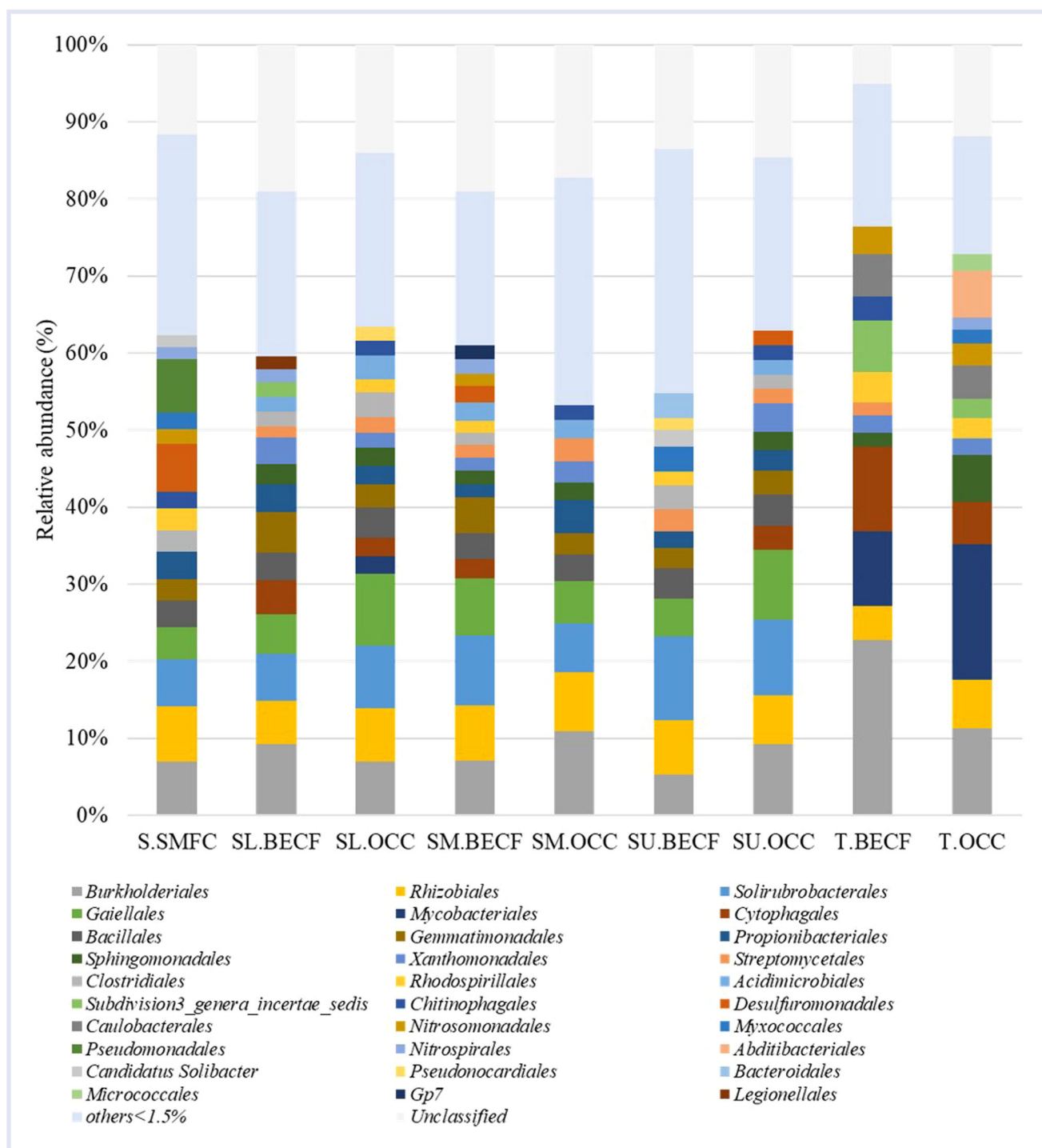


FIGURE 5 Bacterial community structures at order level of the samples taken at the beginning and at the end (156 days) of the test; S.SMFC represents the soil used in setting up the bioelectrochemical continuous flow (BECF) and open circuit control (OCC) systems; the suffix BECF or OCC indicates the system where the samples were collected from, whereas SL, SM., and SU. indicate soil samples from the lower, middle and upper portion of the columns, and T. water samples from the Cr(VI) contaminated water tanks. “others < 1.5%” indicated strains with abundance less than 1.5%.

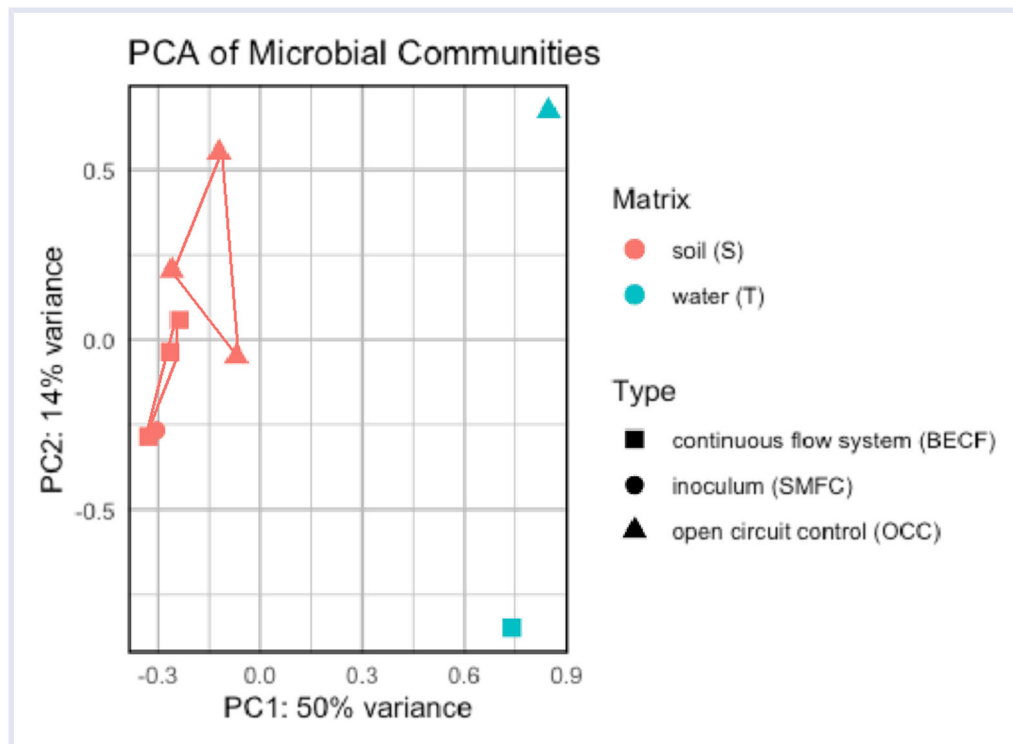


FIGURE 6 Principal component analysis (PCA) plot on Hellinger-transformed abundances of each operational taxonomic unit (OTU) of all the samples. Line colors denote the matrix of the samples (red for soil and blue for water), while symbols denote the type (squares = bioelectrochemical continuous flow [BECF] system, dots = inoculum [SMFC [soil microbial fuel cell]], triangles = open circuit control [OCC])

the inoculum, coming from Cr(VI)-contaminated soil batch microbial fuel cells (SMFCs) and enriched with an electrochemically active Cr(VI) resistant microbial community, maintained its structure in the BECF system. Finally, two distinct groups were observed between soil and water samples from the OCC and the BECF systems. This suggests that the microbial community changed open circuit conditions, where the electrodes did not serve as electron acceptor or donor. This difference was more evident in water samples (blue square and triangle, Figure 6), suggesting that the planktonic microbial community of BECF acquired characteristics very different from those of the OCC control.

From an initial analysis of the microbial communities, it was possible to observe the presence of bacteria belonging to the *Burkholderiales* and *Rhizobiales* orders in all the samples analyzed.

Planktonic microbial communities. Among the bacterial communities, the planktonic groups T.BECF and T.OCC exhibited a distinctive selection of bacterial populations. These two communities were characterized by the presence of bacteria belonging to the orders *Burkholderiales* (22.8%, 11.3%), *Mycobacteriales* (9.7%, 17.5%), *Cytophagales* (10.9%, 5.5%), *Rhizobiales* (4.4%, 6.4%), and *Caulobacteriales* (5.5%, 4.4%), in T.BECF and T.OCC, respectively. In particular, bacteria belonging to the order *Caulobacteriales* were exclusive to the two mentioned microbial communities. Furthermore, bacteria from the *Mycobacteriales* and *Cytophagales* orders were much more abundant in the planktonic communities than in those found in the soil samples.

The relative abundance of bacteria belonging to the genus *Hydrogenophaga* (12.3%, 5.5%), order *Burkholderiales*, *Ohtaekwangia* (9.9%, 2.0%), order *Cytophagales*, *Blastomonas* (<1.5%, 5.3%), order *Sphingomonadales*, *Gordonia* (<1.5%, 16.2%), and *Mycobacterium* (7.9%, <1.5%), order *Mycobacteriales*, in T.BECF and T.OCC, respectively, highlights the main differences between the two planktonic bacterial communities.

Representative populations of the most abundant orders were identified with high relative abundance (Supporting Information: Table S5). Bacteria belonging to the genus *Hydrogenophaga* (order *Burkholderiales*) were reported to be hydrogenophilic, autotrophic bacteria using oxygen or nitrate as terminal electron acceptors (TEAs) (Song et al., 2020; Wang, Song, et al., 2022). *Hydrogenophaga* have also been reported to be responsible for cathodic Cr(VI) reduction (Wang, Song, et al., 2022; Liu, Lu, et al., 2022) and characterized by electrochemical activity (Chen et al., 2017; Kimura & Okabe, 2013), both in the anode (Kimura & Okabe, 2013) and cathode regions (Yu et al., 2022). Kimura and Okabe reported that a strain belonging to the *Hydrogenophaga* genus could secrete soluble electron carriers that might be involved in interspecific electron transfer (Kimura & Okabe, 2013). Several studies have also reported that the *Hydrogenophaga* genus comprises H₂-oxidizing bacteria that utilize hydrogen as the sole electron donor to reduce Cr(VI) directly (He et al., 2021; Huang et al., 2014). In our study, due to the low voltage applied and slightly reducing conditions in the BECF system, the hypothesis of H₂ electrogeneration was not considered. On the other hand, is

not possible to exclude the involvement of bacteria belonging to this genus with the increase in the reducing currents recorded in the BECF system and, consequently, the increase in Coulombic efficiency.

Ohtaekwangia was found in soils impacted by anthropogenic activity, such as acidic and heavy metal-contaminated soils (Bourceret et al., 2016; Kou et al., 2018). Bacteria belonging to the genus *Ohtaekwangia* exhibit tolerance to Cd(II) toxicity (Li et al., 2018). Furthermore, these bacteria have shown potential interactions with electroactive cathode biofilm for treating nitrate- and arsenite-polluted groundwater (Ceballos-Escalera et al., 2021; Yang, Zhan, et al., 2021). In addition, there were ecological relationships between *Ohtaekwangia* and cable bacteria during the degradation of organic pollutants (Huang et al., 2023). *Ohtaekwangia* spp. have been associated with the secretion of extracellular polymeric substances (EPS) (Lyu et al., 2021; Wang, Shen, et al., 2022). Although the precise role of *Ohtaekwangia* bacteria in a specific study might not be fully clarified, it is evident that they possess the ability to thrive in heavy metal-polluted soils and establish an ecological relationship with electroactive bacteria (EAB).

Several studies indicated that certain genera within the *Mycobacteriales* group exhibit resistance to Cu, Hg, and Zn. Metal ion efflux pumps have been identified as a shared mechanism for metal resistance (Johnson et al., 2020; Nies, 2003). *Mycobacterium* was also reported as a genus able to biosorb heavy metals, especially Cr(VI), with biosorption values over 30 mg_{Cr}/g dry biomass (Bennett et al., 2013; Chaturvedi et al., 2021; Srinath et al., 2002; Xing, 2011). *Mycobacterium* was studied as an efficient and economical biomass for the removal of chromium species from contaminated water (Aryal & Liakopoulou-Kyriakides, 2014) and also as one of the key role genera in a microbial community involved in the bioleaching of chromium from tannery sludge (Zeng et al., 2019). Some studies reported the ability of *Mycobacterium* to co-metabolize 1,4-dioxane in the presence of chromium at different concentrations (Johnson et al., 2020). In this study, the order *Mycobacteriales* was especially observed in the planktonic community (9.7% in T.BECF, 17.5% in T.OCC), whereas it was significantly less abundant in the soil sample bacterial community (2.3% in SL.OCC, <1.5% in other soil samples). The ability of bacteria belonging to *Mycobacteriales* to face Cr(VI) is well reported in the literature; therefore, it can be suggested that, in both OCC and BECF systems, they played an important role in the hexavalent chromium reduction processes. Despite some studies confirming *Mycobacterium* as an EAB capable of performing extracellular electron transfer (EET) (Abbas et al., 2022; Y. Chen et al., 2016; Su et al., 2022; Yang et al., 2022; Zhang et al., 2017), in this study, this genus was not detected in the soil samples collected close to the electrodes.

Some *Gordonia* strains (*Mycobacteriales*) were reported as capable of resisting different heavy metals (Berekaa et al., 2006; Gurbanov et al., 2019; Tishchenko et al., 2019). Mulla and colleagues identified *Gordonia* strains with a

minimum inhibitory concentration of Cr equal to 52 mg/L, suggesting that species belonging to these bacteria might be involved in the adsorption or reduction of Cr(VI) (Mulla et al., 2018). The ability of *Gordonia* to break down a variety of complex organic matter, such as humus or resistant organic pollutants, and their high relative abundance only in OCC (16.2% in T.OCC, >1.5% in all the other samples) could be linked. In line with the findings of Johnson and colleagues (Johnson et al., 2020), bacteria belonging to the *Gordonia* genus might utilize exopolymeric substances produced by other microorganisms as Cr(VI) defense mechanisms, as a growth source in organic substrate-limiting conditions, concurrently mitigating the presence of Cr(VI).

In planktonic bacterial communities, *Georgfuchsia* genera, detected in both T.BECF and T.OCC water samples, were reported by Weelink and colleagues as strictly anaerobic bacteria capable of degrading aromatic compounds with iron, manganese, or nitrate as electron-acceptors (Weelink et al., 2009). The flexibility to use Fe(III) and Mn(VI) as TEA confers *Georgfuchsia* the ability to adapt to different environmental redox conditions (Dorer et al., 2016; Ruiz-uriguén et al., 2018). In our study, the presence of this genus in the OCC and BECF systems could be the result of its adaptability and possible involvement in the Cr(VI) removal process.

Otherwise, *Tahibacter* and *Reyranella* genera were detected (relative abundance >1.5%) only in T.BECF, whereas bacteria belonging to the genera *Chryseotalea* and *Blastomonas* were detected (rel. abundance >1.5%) only in the T.OCC microbial community.

Bacteria belonging to the genus *Tahibacter* have been reported in previous studies to be resistant to Mn(II), Ni(II), and organic compounds (i.e., 4-fluoroaniline, 2,4-difluoroaniline) (Zhao et al., 2021). Some studies reported the presence of *Tahibacter* in BES applied for the removal of antibiotics (i.e., cephalosporin) (Guo et al., 2022). Xin et al. suggested that *Tahibacter* takes advantage of the soluble redox mediators present in the liquid of MFCs fed with waste-activated sludge (Xin et al., 2020).

Reyranella was widely isolated in soils and sediments and identified as Mn(II)-oxidizing, chromium-resistant bacteria (Kumar Pradhan et al., 2022; Marcus et al., 2017); its tolerance to other heavy metals (Cd, Fe, Cr, Ni, Al) was also reported (Chen et al., 2022; Duan et al., 2020; Taleski et al., 2020). Bacteria belonging to the genus *Reyranella* were found in electroactive biofilms or planktonic communities in several studies regarding the application of microbial electrochemical technologies (METs) (Abudurehman et al., 2023; Bardarov et al., 2018; Liu, Zhang, et al., 2022; Xue et al., 2022). According to Abudurehman and colleagues, electrical stimulation can encourage the development of these bacteria and their collaboration with EAB to break down complicated chemical substances (such as fluoroquinolones) (Abudurehman et al., 2023). In this study, the detection of bacteria belonging to the genera *Tahibacter* and *Reyranella* and their relative abundance only in the BECF system suggests that these microorganisms might have a role in the Cr(VI) bioelectrochemical removal process.

From the results of microbial characterization, we can conclude that the planktonic bacterial communities (T.BECF and T.OCC) are characterized by bacteria capable of different strategies (reduction, adsorption, etc.) to resist heavy metals and degrade organic substances, such as EPS produced by other bacteria, to minimize Cr(VI) toxicity. Furthermore, the T.BECF planktonic community showed the presence of bacteria able to create a network with electroactive species.

Soil microbial communities. Bacteria belonging to the orders *Solirubrobacteriales*, *Gaiellales*, *Bacillales*, *Gemmatimonadales*, and *Propionibacteriales* characterized the bacterial communities identified in soil samples (S.SMFC, SL.BECF, SM.BECF, SU.BECF, SL.OCC, SM.OCC, SU.OCC), differently from the planktonic bacterial communities (T.BECF, T.OCC). From the analysis of the bacterial communities identified in the soil samples, a similarity was observed between the initial bacterial community (S.SMFC) and those in the samples collected from the BECF (SL.BECF, SM.BECF, SU.BECF) at the end of the test. In contrast, a distinction was observed between these latter and the bacterial communities from the OCC (SL.OCC, SM.OCC, SU.OCC) system.

S.SMFC microbial community was characterized by the presence of bacteria belonging to the orders *Pseudomonadales* (6.9%) and *Desulfuromonadales* (6.3%). Instead, in the other soil samples, the relative abundance of bacteria belonging to the order *Desulfuromonadales* underwent a consistent reduction (from 6.3% to 2.1%, 1.9% in SM.BECF and SU.OCC, respectively), and the order *Pseudomonadales* was not observed in the OCC samples (Supporting Information: Table S5). In contrast, in BECF and OCC microbial communities, an average increase in the relative abundance of bacteria belonging to the *Gaiellales* orders (from 4.2% up to 7.3% and 9.3% in SM.BECF and in SL.OCC, respectively), *Burkholderiales* (from 7% up to 9.2% and 11.0% in SL.BECF and SM.OCC, respectively), and *Gemmatimonadales* (from 2.8% up to 5.3% and 3.0% in SL.BECF and SU.OCC, respectively) was observed (Supporting Information: Table S5).

The S.SMFC sample contained bacteria from the genera *Azotobacter* and *Pseudomonas*, which are facultative aerobic heterotrophs known to oxidize organic contaminants and use them as carbon sources (Sumbul et al., 2020). They are also resistant to heavy metal contamination (Chug et al., 2016; Ishibashi et al., 1990; Mohan et al., 2020; Oves et al., 2013) and can produce EPS (Joshi & Juwarkar, 2009; Rasulov et al., 2013). Furthermore, these bacteria interact with solid electron donors and/or acceptors, suggesting their involvement in EET processes (Lazzarini Behrmann et al., 2020; Li et al., 2021; Milton et al., 2017; Tandukar et al., 2009).

Bacteria belonging to the genus *Geobacter* (order *Desulfuromonadales*) present in the S.SMFC sample were widely described in the literature as EAB capable of oxidizing organic contaminants (Cai et al., 2020; Palma et al., 2018; Zhao, Li, et al., 2018) or reducing heavy metals (Bishop et al., 2014; Gregory & Lovley, 2005; Williams et al.,

2010; Zhao, Li, et al., 2018) in the presence of an organic carbon source (Lovley & Holmes, 2022; Speers & Reguera, 2012). The reduction of the relative abundance of these genera of bacteria in the microbial communities identified in the samples from the BECF and OCC systems can be ascribed to the absence, in the latter two systems, of an easily biodegradable organic carbon source (acetate was added only to the SMFC system, S.SMFC sample).

Bacteria belonging to the genus *Ramlibacter* (order *Burkholderiales*) were described in the literature for their resistance to heavy metals and their biotransformation and biosorption capabilities (Qu et al., 2022). Moreover, they were recently described as able to transfer electrons to a solid extracellular acceptor (oxidative EET) (Baker et al., 2022).

Bacteria belonging to the *Gaiellaceae* family (order *Gaiellales*) were identified in deep mineral waters under aerobic and low-mineral conditions (Albuquerque et al., 2011). More recently, *Gaiellaceae* have been observed within bacterial communities containing both iron-reducing and sulfate-reducing bacteria, and this family is recognized for its ability to break down a wide range of complex polysaccharides, including those originating from plant materials (Matsumoto et al., 2020; Zecchin et al., 2017).

Bacteria belonging to the genus *Gemmatirosa* (order *Gemmatimonadales*) are naturally present in natural, alkaline soils and have been described as predominant actors of the rhizospheres, involved in carbon fixation in soils contaminated by metals and metalloids (Hou et al., 2022; She et al., 2021).

In conclusion, bacterial communities in soil samples (SL, SU, and SM of both BECF and OCC reactors) presented different characteristics, such as the ability to deal with heavy-metal contamination, to weave networks of relationships with sulfate-reducing and iron-reducing bacteria to thrive in contaminated soil. Not least, in the BECF reactor, bacterial communities capable of exchanging electrons with the electrodes were also identified.

CONCLUSION

This research offers valuable insights that can contribute to advancing microbial electrochemical remediation systems designed to reduce Cr(VI) in water-saturated soils. This is especially noteworthy given the scarcity of studies in the existing literature that focus on the continuous bio-electrochemical removal of chromium. This configuration allowed simultaneously treating two contaminated matrices (soil and water) with significantly high removal efficiencies.

The substantial differences from the previously reported studies were as follows:

- acclimatization and/or adaptation of the electroactive bacterial community to Cr(VI) in preliminarily batch systems (SMFCs) and the subsequent transfer of the electroactive bacterial community on the electrode conductive material and in the soil of a BECF system;
- the BECF system does not require ion exchange membranes;

- contaminated tap water was used without any addition of buffer, nutrients, organic carbon source, or synthetic mineral media, which is typically used in bioelectrochemical laboratory tests.

All these elements made it possible to better simulate the real conditions of Cr(VI)-contaminated aquifers in terms of solid-to-liquid ratio, interactions among soil phases, and physicochemical parameters (pH and EC).

The outcomes achieved in the BECF system for Cr(VI) reduction in water-saturated soil can be viewed as a demonstration of the feasibility of employing MET for in situ treatment of Cr(VI) contaminated aquifers.

Moreover, the setup employed in this study may serve as a model for future research, the scale-up of this technology, and the development of in situ remediation schemes. In contrast to actual Cr(VI) bioremediation approaches, microbial electrochemical removal of Cr(VI) can take place without the need for external organic carbon substrates, with interesting implications in terms of both economic feasibility and reduced side effects in aquifers.

AUTHOR CONTRIBUTION

Gabriele Beretta: conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing—original draft, writing—review and editing. **Michela Sangalli:** conceptualization, formal analysis, investigation, writing—original draft. **Elena Sezenna:** conceptualization, data curation, methodology, supervision, visualization, writing—review and editing. **Anna Espinoza Tofalos:** data curation, formal analysis, methodology, writing—review and editing. **Andrea Franzetti:** funding acquisition, methodology, supervision. **Sabrina Saponaro:** funding acquisition, project administration, supervision.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data are available upon request by contacting the corresponding author Gabriele Beretta (gabriele.beretta@polimi.it).

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SUPPORTING INFORMATION

Soil microbial fuel cells description, soil characteristics, Coulombic efficiency calculations, and DNA analysis and data processing.

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