CHEMICAL ENGINEERING TRANSACTIONS
VOL. 99, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Flavio Manenti

ISBN 978-88-95608-98-3; **ISSN** 2283-9216
DOI: 10.3303/CET2399118

Sequential Reductive/Oxidative Bioelectrochemical Process for Chlorinated Aliphatic Hydrocarbons Removal in Contaminated Groundwaters: Fluid Dynamic Characterization of the Scaled-Up Field Test

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Chlorinated Aliphatic Hydrocarbons (CAHs) as Perchloroethylene (PCE) and Trichloroethylene (TCE) are worldwide contaminants due to their uncorrected disposal and storage in the past years. An effective remediation strategy for CAHs contaminated groundwaters is the stimulation of dechlorinating microorganisms which can carry out reductive and oxidative reactions that allowed for the complete mineralization of CAHs. More in detail, dehalorespiring microorganisms can reduce PCE and TCE throughout reductive dechlorination reaction (RD) a step happening reaction that remove a chlorine atom from the carbon skeleton of the molecule and replaces it with a hydrogen ion. Hence, aerobic dechlorinating microorganisms oxidize low chlorinated compounds such as cis-dichloroethylene (cDCE) and vinyl chloride (VC) into CO_2 using enzymes, such as monooxygenases, to produce instable molecules with oxygen atom like epoxides. The combination of reductive and oxidative dechlorination could maximize the microbial activities allowing to work on the preferred substrates and can be easily tuned by the adoption of bioelectrochemical systems. In these electrochemical devices, an electrodic material interact with so-called electroactive microorganisms, acting like electron acceptor or donor of the microbial metabolism. In this study, a sequential reductive/oxidative bioelectrochemical process developed by the combination in series of two membrane-less microbial electrolysis cells (MECs) has been applied for the treatment of a CAHs contaminated groundwater coming from a polluted site in northern Italy. More in detail, the study presents the development and the validation of the sequential bioelectrochemical process under laboratory conditions and the and subsequent scale-up of the process for a field. The investigation of the laboratory scale performance was conducted by synthetic and real contaminated groundwater while the design and the characterization of the scaled-up process have been obtained with real contaminated in a field test. The scale-up allowed to increase the reactor volume 42 times (from 10 L to 420 L) dividing the reductive and the oxidative sections into 4 different columns with a volume of 105 L (Figure 1).
The field test of the bioelectrochemical technology represents the most important scaled-up application in a bioelectrochemical system devoted to the remediation of CAHs contaminated groundwater, thus, it shows an effective solution for the stimulation of microbial activity without the utilization of any chemical in a real environment.

1. Introduction

Chlorinated Aliphatic hydrocarbons, i.e. Tetrachloroethane (TeCA), Trichloroethylene (TCE), and Perchloroethylene (PCE), are harmful and worldwide spread contaminants (USEPA, 2004). Due to their peculiar chemical and physical properties and extremely low threshold contamination concentrations, chlorinated aliphatic hydrocarbon removal from contaminated groundwater is particularly difficult (Casasso et al., 2020).

Paper Received: 2 March 2023; Revised: 3 April 2023; Accepted: 12 May 2023
Please cite this article as: Zeppilli M., Dell'Armi E., Palumbo M.T., Petrangeli Papini M., 2023, Sequential Reductive/Oxidative Bioelectrochemical Process for Chlorinated Aliphatic Hydrocarbons Removal in Contaminated Groundwaters: Fluid Dynamic Characterization of the Scaled-Up Field Test, Chemical Engineering Transactions, 99, 703-708 DOI:10.3303/CET2399118

The common remediation approach was usually based on contamination containment by pumping wells coupled with an on-site physio-chemical chemical treatment based on stripping and adsorption on granular activated carbon. In recent years, the development of innovative site characterization tools coupled with geology-related factors control (Ciampi et al., 2019) promote the use of more specific approaches focused on the secondary contamination source aggression to avoid the contamination migration to susceptible receptors.
Among the available remediation techniques, in-situ remediation technologies that involve the indigenous microorganisms present in the contaminated matrices seem to be the most costs effective and promising to be used in a treatment train to achieve clean-up goals (Dell'Armi et al, 2022a). Specialized microorganisms, known as dechlorinating microorganisms are able to remove chlorine atoms from the carbon backbone of the molecule using metabolic and co-metabolic pathways under anaerobic or aerobic conditions.
Two major types of dechlorinating reactions are known: the reductive dechlorination reaction, which occurs in anaerobic environments, and the oxidative dechlorination which takes place in the aerobic ones. Reductive dechlorination is a sequential-step reaction in which chlorinated compounds are reduced as a consequence of the substitution of a chlorine atom with a hydrogen atom that came from the reduction of the molecular hydrogen. Only one kind of microorganism can reduce the PCE to ethylene which is the only non-toxic backbone daughter product, and it is the Dehaloccoides McCartyii. Often, due to the lack of the proper redox condition and electron donor quantity, the reductive dechlorination led to the accumulation of cis-Dichloroethylene and Vinyl Chloride. In particular, the VC is the only cancerogenic compound in the RD pathway. However, oxidative dechlorination which is a co-metabolic reaction that produces carbon dioxide, cannot dechlorinate high-chlorinated compounds due to electronegativity issues. For these reasons, a combination of reduction and oxidation seems to be a promising way to fully mineralize the starting CAHs (M. Zeppilli et al., 2019).
In the last twenty years bioelectrochemical systems (Rosembaum et al., 2011), electrochemical technology that involves the interaction between solid-state electrodes and microorganisms, has been studied for several purposes from the treatment of wastewaters to the production of valuable synthesis intermediates clarifying the mechanisms of the interactions between several microbial consortia and electrodes. In particular, two types of mechanisms have been identified: the direct mechanisms in which electrons and microorganisms' proteins, such as cytochromes, can directly exchange electrons; and the undirect mechanisms or mediated in which electrons shuttles molecules or exo/endogenous redox mediator can transport the electrons into a more easily metabolizable form to the microbial community (Rossi et al., 2022). For remediation purposes due to their capability to easily generate sequential reductive/oxidative environments and the low operational energy requirements. In this paper, the fluidynamic characterization of reductive and oxidative upscaled units is reported. After a laboratory-scale validation period (Dell'Armi et al., 2022b) the configuration of the reactor has been scaled up to prove the capability of BESs for groundwater remediation possibility on a field test. Tracer tests and Reynolds number determination were adopted to describe the results of the scale-up procedure.

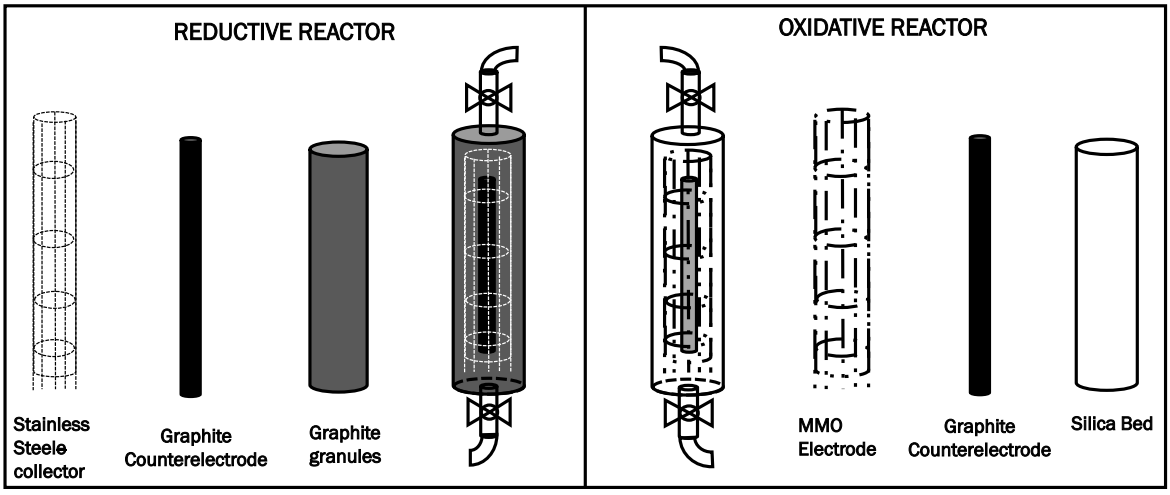

Figure 1. Schematic representation of the reductive and oxidative scaled up bioelectrochemical units.

2. Material and methods

2.1 Laboratory and pilot scale reactors configuration

The laboratory-scale sequential bioelectrochemical process consisted of a reductive and an oxidative reactor with an empty volume of 8.24 and 3.14 L (Dell'Armi et al., 2022c), respectively. The reductive reactor was a borosilicate glass column with a height of 100 cm and an internal diameter of 10 cm while the oxidative reactor was constructed with a borosilicate glass column with a height of 40 cm and an internal diameter of 10 cm. Both reactors were equipped with an internal counter electrode consisting of a tubular structure filled with graphite granules enveloped in a plastic material that avoided the shortcut of the circuit while allowing for electrolyte migration. The scale-up strategy adopted was the Geometric similarity approach which consists of the maintenance of a constant scale ratio between the volume of the laboratory scale and the scaled-up units. As reported in table 1, a constant scale factor of 13 was maintained for the scale-up of the working and counterelectrode volume (i.e. the external and the internal reactor body). Figure 1 shows the scheme of the reductive and oxidative bioelectrochemical units. The external module is made by a polyethylene pipe equipped with three lateral sections that allows the electric connection to a potentiostat; the top and the bottom of the units were closed throughout a flanged disk provided of a half and an inch hydraulic connection. The internal counterelectrode module was made by a common piezometer's polyvinylchloride pipe closed by two screw caps and wrapped with a geotextile membrane typically utilized for avoiding the blockage of fenestrated monitoring wells.

Table 1: Working volume of the laboratory and pilot scale bioelectrochemical units and the relative scale factor.

	LAB SCALE	PILOT SCALE	SCALE FACTOR
Working electrode volume (L)	6.54	82	12.5
Counter electrode volume (L)	1.70	23	13.5
Working/Counter Ratio	3.8	3.6	

Pilot scale units were realized with an external HDPE pipe with a diameter of 300 mm and a height a 1500 mm, while a PVC pipe with a diameter of 170 mm and an height of 1000 mm was used as internal body to realize the counterelectrode. The same packing materials were used in laboratory and pilot scale units consisting of graphite granules and gravel. Graphite granules were previously selected and washed with water using a vibrating screen, which allowed the selection of the granules with a diameter higher than 1 mm. With a similar approach, the gravel was washed and selected with a diameter higher than 1 mm. The average graphite granules diameter in the laboratory and pilot scale units, estimated by using a particle distribution size average was 2 mm while, a substantial difference, in the gravel average diameter was used in laboratory and pilot scale resulted 2 and 10 mm respectively. Static porosity determination by a cylinder test allowed for the determination of 0.336 and 0.472 for the graphite granules and gravel, respectively.
Borosilicate glass was used for the realization of the laboratory scale reactors while HDPE and PVC were used for the realization the external and internal chamber of the upscaled bioelectrochemical reactor. Graphite granules were adopted to set the different counterelectrodes in all the reactors explored, while in the laboratory scale configuration the graphite granules were enveloped in a tubular plastic grid, in the pilot scale reactor the graphite granules were inserted in a cracked PVC pipe covered by a geotextile HDPE membrane. Both laboratory and pilot scale reactors were assembled introducing the tubular counterelectrode in the inner body of the external chamber, in which the hydraulic connection for the influent and the effluent were present in the bottom and on the top of the cylindrical reactor.

2.2 Tracer test conduction on pilot scale units

The step tracer test (named F-test) consisted of the continuous feeding of the tracer solution in the inlet of each chamber at a constant flow rate of 1.4 L/min, while the pulse test (named C-test) consisted of the injection of 60 mL of the concentrated NaCl solution in the inlet of the RED 1 and OXI 2. Both tracer tests were performed by the continuous acquisition of the solution conductivity (χ) in the outlet of the respective reactor performed by a Handylab® 330 conductometer. (SI-analytics, Germany) The conductivity of the outlet solution was utilized to build an F-curve according to the following equations, and the first derivate method was then used for the flex point of the F-curve determination, which represented the experimental hydraulic retention time (HRT). In the step trace test, indicated also as F-test the conductivity (χ) continuously recorded in the outlet of the reactor was divided with the conductivity of the tracer's solution ($\chi 0$). In the pulse trace test, the net conductivity recorded (i.e. the conductivity recorded minus the water conductivity) in the outlet of the reactor, corresponded to the C-

curve. The graphical resolution of the F and C curve integral was used to evaluate the experimental HRT in the reactor, the experimental flow rate allowed for the determination of the effective free volume inside the reactors.

2.3 Data elaboration

Reynolds number determination was conducted by using the following equation:

$$Re = \frac{D_p\ \bar{v}\ \rho}{(1-\varepsilon)\mu}$$

In which D_p is the diameter of the section of the investigated reactor, $\bar{v}$ is the linear velocity, ρ and μ are the density and viscosity of the fluid and ε represent the porosity of the packed bed. The equation allows the determination of Re number in packed bed. Table 2 and Table 3 reports the different parameter utilized for Re determination in the laboratory and pilot scale reductive and oxidative units.

Table 2: Parameter of the laboratory and pilot scale reductive reactors.

	LAB SCALE	PILOT SCALE
Porosity ε	0.334	0.334
Particles average diameter (Dp)	2	2
Section Diameter (mm)	100	300

Table 3: Parameter of the laboratory and pilot scale oxidative reactors.

	LAB SCALE	PILOT SCALE
Porosity ε	0.400	0.472
Particles average diameter (Dp)	6	10
Section Diameter (mm)	100	300

3.Result and discussion

3.1 Tracer test results, volume determination of the two upscaled units

To evaluate the effective volume of each bioelectrochemical reactor, two different tracer tests were conducted in the RED 1 and OXI 2 unit, the tracer tests were conducted only in one reductive and oxidative unit assuming the similarity between the two reductive and oxidative units. A step mode and pulse mode tracer tests were performed by using a 2 g/L NaCl solution and a 20 g/L NaCl respectively. In the step trace, indicated also as F-test allowed the conductivity (χ) continuously recorded was divided with the conductivity of the tracer's solution (χ0) to obtain the F curve, reported in Figure 2 which was used for the determination of the effective hydraulic retention time (HRT). The resulting C-test curve, reported in Figure 2, shows the results of the pulse tracer test for the reductive and the oxidative bioelectrochemical reactor. By using curve elaboration, the effective HRT of the fluid particles has been determined, the results of the different curves are shown in Table 4.

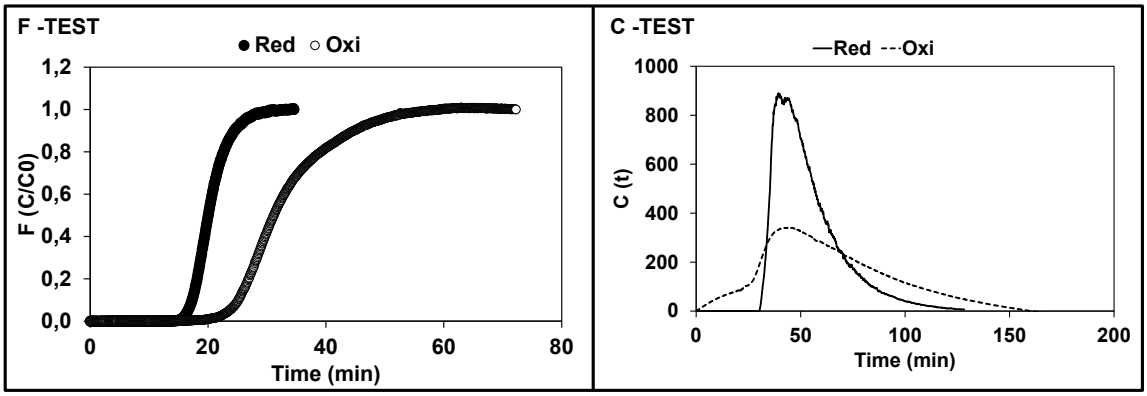

Figure 2. Tracer test results for the F-test and for the C-test.

As reported in Table 4 the F-test and the C-test results for the reductive reactor were more similar that the results for the oxidative reactor, which were significantly different. To assess the effectiveness of the tests, a separate determination of the porosity of each packing material (i.e. the graphite granules and the grave,) was performed using a graduated cylinder.

Table 4: F-test and the C-test results for the reductive and oxidative pilot reactors

	F -TEST	C -TEST
Reductive unit (L)	37	41
Oxidative unit (L)	45	64

As reported in Table 5, the resulting free volume of each unit, calculated by considering the geometric volume of the internal and external reactor body (82 and 23 litres), and the relative porosity (graphite granules 0.336 and 0.472 for the gravel) resulted in 35 and 46 L for the reductive and oxidative reactor. The correspondence with the F-test of the obtained results confirmed the contribution to the total volume of the reactor of the internal body of the reactor (i.e. the counterelectrode), which does not represent a dead zone of the reactor but is crossed by the liquid particles.

Table 5: Effective volume determination considering static and fluidynamic porosity.

	GEOMETRIC	POROSITY	F-TEST
Reductive unit (L)	37	35	37
Oxidative unit (L)	45	46	41

3.2 Fluidynamic similarity determination of the laboratory and pilot scale reactors

The fluidynamic similarity of the laboratory and pilot scale reactors has been determined as described in the previous section. The evaluation of the Re number has been conducted considering three different HRTs (i.e. different linear velocities) investigated in the laboratory condition (i.e. 4.1, 1.8 and 1.2 d) and projected for the pilot scale test (i.e. 1.3, 0.7 and 0.2 d). As reported in Table 6, which reports the Reynolds number obtained for the laboratory and pilot scale reactors, the fluidynamic similarity of the reductive units was maintained, indeed during the operation at similar HRTs of 1.2 and 1.3 days, the Reynolds number resulted 4.58 and 5.92 which means that the two scale of reactors were under full laminar regime. On the contrary, as reported in Table 7, the determination of the Re number for the oxidative unit at similar HRTs of 0.7 d showed a strong difference of the Reynolds number for the laboratory and the pilot scale reactors with 5.62 and 49.64, respectively. The main difference in Reynolds number can be easily explained by the significative difference in terms of average diameter of the gravel used as packing material in the lab and pilot scale reactor. Interestingly, during all the operational period of the operation of the reactors, the reductive reactors have been operated at full laminar regime while during the pilot test, the oxidative units resulted operated in the transient fluidynamic regime between laminar and turbulent.

Table 6: Reductive units Reynolds number comparison.

	LAB SCALE			PILOT SCALE		
HRT (d)	4.1	1.8	1.2	1.3	0.7	0.2
Re	1.34	3.05	4.58	5.92	11.84	44.26

Table 7: Oxidative units Reynolds number comparison

	LAB SCALE			PILOT SCALE		
HRT (d)	1.6	0.7	0.5	1.3	0.7	0.2
Re	2.47	5.62	8.44	24.82	49.64	185.54

4. Conclusions

The correspondence with the F-test of the obtained results confirmed the contribution to the total volume of the reactor of the internal body of the reactor (i.e. the counterelectrode), which does not represent a dead zone of the reactor but is crossed by the liquid particles. The fluidynamic similarity is obtained for the reductive unit due to the utilization of the granular electrodic material, On the contrary, due to the different average diameter of the packing material the fluidynamic similarity of the oxidative units is not maintained. This not significant difference, anyway, should not lead to changes in the performances of the oxidative units.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 826244-ELECTRA.
Prof. Mauro Majone is acknowledged for helpful support and discussion during the experimental activity.

References

Casasso A., T. Tosco, C. Bianco, A. Bucci, R. Sethi, How can we make pump and treat systems more energetically sustainable? Water (Switzerland). 12 (2020). https://doi.org/10.3390/w12010067.

Ciampi A., C. Esposito, P. Viotti, J. Boaga, G. Cassiani, M.P. Papini, An integrated approach supporting remediation of an aquifer contaminated with chlorinated solvents by a combination of adsorption and biodegradation, Appl. Sci. 9 (2019). https://doi.org/10.3390/app9204318.

Dell'Armi E., M.M. Rossi, L. Taverna, M.P. Papini, M. Zeppilli Evaluation of the Bioelectrochemical Approach and Different Electron Donors for Biological Trichloroethylene Reductive Dechlorination, Toxics. 10 (2022)a 37. https://doi.org3390/toxics10010037.

Dell'Armi E., M. Zeppilli, M.L. Di Franca, B. Matturro, V. Feigl, M. Molnár, Z. Berkl, I. Németh, H. Yaqoubi, S. Rossetti, M.P. Papini, M. Majone, Evaluation of a bioelectrochemical reductive/oxidative sequential process for chlorinated aliphatic hydrocarbons (CAHs) removal from a real contaminated groundwater, J. Water Process Eng. 49 (2022)b 103101. https://doi.org/10.1016/J.JWPE.2022.103101.

Dell'Armi E., M.M. Rossi, M. Zeppilli, M. Petrangeli Papini, M. Majone, Bioelectrochemical Chlorinated Aliphatic Hydrocarbons Reduction in Synthetic and Real Contaminated Groundwaters, Chemical Engineering Transactions, 93 (2022)c, 217-222.

Rossi M.M., E. Dell'Armi, L. Lorini, N. Amanat, M. Zeppilli, M. Villano, M. Petrangeli Papini, Combined Strategies to Prompt the Biological Reduction of Chlorinated Aliphatic Hydrocarbons: New Sustainable Options for Bioremediation Application, Bioengineering. 8 (2021) 109. https://doi.org/10.3390/bioengineering8080109.

Rosenbaum M., F. Aulenta, M. Villano, L.T. Angenent, Cathodes as electron donors for microbial metabolism: Which extracellular electron transfer mechanisms are involved?, Bioresour. Technol. 102 (2011) 324–333. https://doi.org/10.1016/j.biortech.2010.07.008.

USEPA (U.S. Environmental Protection Agency), Cleaning Up the Nation's Waste Sites: Markets and Technology Trends., (2004).

Zeppilli M., E. Dell'Armi, L. Cristiani, M. Petrangeli Papini, M. Majone, Reductive/Oxidative Sequential Bioelectrochemical Process for Perchloroethylene Removal, Water. 11 (2019) 2579. https://doi.org/10.3390/w11122579.