Bioelectrochemical Chlorinated Aliphatic Hydrocarbons Reduction in Synthetic and Real Contaminated Groundwaters

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The widespread contamination of chlorinated aliphatic hydrocarbons (CAHs) as Perchloroethylene (PCE) and Trichloroethylene (TCE) over the past recent years and their uncorrected disposal and storing brought these substances to become one of the most common contaminants of subsoils and groundwater in the world. In recent years, more sustainable remediation and cost-effective technologies involving groundwater's indigenous microorganism such as the dehalorespiring microorganisms. Dehalorespiring microorganisms can reduce PCE and TCE via reductive dechlorination (RD) while aerobic dechlorinating microorganisms oxidized low chlorinated compound such as cis-dichloroethylene (cDCE) and vinyl chloride (VC) into non harmful products. The integration of reductive dechlorination and aerobic dechlorination results in an efficient approach for the complete mineralization of high chlorinated compounds, which usually led to a build-up of VC. Bioelectrochemical systems, which exploit the capability of microorganisms to interact with a polarized electrode, provide an effective strategy to promote reductive and oxidative environments by the regulation of the applied potentials. Indeed, the complete mineralization of high chlorinated CAHs, can be obtained by a sequential reductive/oxidative bioelectrochemical process which allows for the optimization of the reductive and oxidative dechlorinating conditions. In this study the performances of the reductive reactor, devoted to the reductive dechlorination has been presented with three different contaminated feeding solutions. The three different feeding solutions included an optimized mineral medium, a synthetic groundwater (constituted by tap water added with nitrate and sulphate) and a real contaminated groundwater. Moreover, different operating conditions like hydraulic retention time (HRT) and applied cathodic potential have been investigated to assess the performance of the reductive dechlorination and on side reactions. The analysis of the coulombic efficiencies for the reductive dechlorination in the reductive reactor showed an important effect of the feeding solution composition and operating conditions (applied potential and HRT), namely strongly decreasing under when using real contaminated groundwater. Despite the progressive decrease of the coulombic efficiency obtained using more complex matrixes, the CAHs removal rates along with the energetic consumption of the process showed an advantageous perspective in the adoption of the bioelectrochemical process for the stimulation of the reductive dechlorination reaction.

1. Introduction

Chlorinated Aliphatic Hydrocarbons (CAHs) such as Perchloroethylene (PCE) and Trichloroethylene (TCE) are organic compounds in which chlorine atoms are directly linked to the carbon skeleton of the molecule. Due to their peculiar physical-chemical properties, the chlorinated solvents were widely used for many industrial and civil activities. The massive utilization and improper storage or disposal have made the CAHs one of the most common and ubiquitous contaminants of many matrices. Nowadays the contaminated matrices were often remediate using technologies that are based on the CAHs chemical-physical properties (Casasso et al. 2020) but to develop more sustainable and low costs technologies (Rossi et al. 2021), the remediation intervention that exploit indigenous microbial communities are gaining the interest of the scientific community. The Reductive Dechlorination reaction (RD) is a biological step happening reaction in which for every step the molecule loose a chlorine atom and gain a hydrogen atom that came from the molecular hydrogen oxidation (Matturro et al

2018). In the field condition is difficult providing the redox condition for reaching the total removal of CAHs, and this led to a possible Vinyl Chloride accumulation (the most toxic and cancerogenic RD intermediate). To stimulate the biological reductive dechlorination, during the remediation activities, is often performed the direct injection of fermentable organic matter that provides the necessary hydrogen for the dechlorinating microbial communities. Although this type of stimulation can establish competition for reducing power between organohalide respiring bacteria and other microorganism as sulphate and nitrate reductor. Moreover, the direct push of organic substances as Volatile fatty acids can generate the fracture of the subsoil and due to their low pH can leach metal species as Fe, Cr, Sb that can led to a secondary contamination. An innovative approach is to provide the hydrogen thanks to bioelectrochemical systems (BES), systems in which peculiar electroactive microorganism interact with solid states electrodes (Rosembaum et al 2011). The microbial electrolysis cell can stimulate selectively the activity of the microorganism able to perform the reductive dechlorination reaction controlling the cathode potential or the flowing current. The necessary presence of both a cathode and an anode can also generate a sequence of anaerobic and aerobic environment in which different type of dechlorination reaction can occur (Zhu et al 2022). This study reports the results obtained in a tubular bioelectrochemical reactor with an innovative membrane-less internal counterelectrode configuration for CAHs removal in different experimental conditions and with different contaminated feeding solutions.

2. Materials and Methods

The reductive reactor is made by a tubular glass reactor with a volume of 8.24L, the working electrode is constituted by a granular graphite bed which ensure the dechlorinating biofilm formation on the electrodic material. The counter electrode is internal and is also made by granular graphite, the separation between the internal counterelectrode chamber and the external working electrode chamber is ensured by a structure made by a plastic grid and a non-woven membrane. Three different feeding solutions were utilized in the reductive reactor:

- A Mineral Medium (MM) made by 1 g/L of NaCl, 0.5 g/L of $MgCl*6H_2O$, 0.2 g/L KH_2PO_4, 0.3 g/L NH_4Cl, 0.3 KCl, 0.015 $CaCl_2*2H_2O$, 0.05 g/L Na_2S, 2.5 g/L $NaHCO_3$, 10 mL/L of vitamin solution and 1 mL/L of metal solution (Dell'Armi et al. 2021b).
- A Synthetic groundwater solution made by tap water as matrix and 460 mg/L of $NaSO_4$ and 20 mg/L of $NaNO_3$ (Dell'Armi et al 2021a).
- A real contaminated groundwater from a contaminated site in northern Italy.

The first two synthetic solution were contaminated with a PCE theoretical concentration of 100 µmol/L.

The polarization of the bioelectrochemical reactor was performed by a VSP potentiostat (Biologic®) which allowed the utilization of a three-electrode polarization by the utilization of an Ag/AgCl electrode (3M KCl+0.199 V vs SHE). The different experimental setups are reported in table 1.

Table 1: Principal explored condition in the reductive reactor.

	Reductive Reactor							
Feeding Solution	Mineral Medium			Synthetic Groundwater				Real Groundwater
Applied Potential (mV vs SHE)	-450	-350	-550	-350	-450		-650	-450
Hydraulic Retention Time, HRT (d)	4.1			1.8	4.1	1.8	1.2	1.8	1.8

2.1 Analytical Methods

The chlorinated aliphatic hydrocarbons as perchloroethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (cDCE) and vinyl chloride (VC) together with methane ethylene and ethane were quantified with a gas cromatograph Dani-Master equipped with a flame ionization detector for the periods with the synthetic feeding solutions. Due the extremely low concentration of the CAHs in the real groundwater for the determination is used a gas chromatograph (DANI Instruments, Contone, Switzerland) with Head Space autosampler equipped with an FID (Flame Ionization Detector). The sulphate and nitrate were quantified with an ion cromatograph (Dionex ICS-1000 IC, Sunnyvale, California) equipped with a conductivity detector and the Fe^{3+} was quantified with a Nanocolor® colorimetric kit with a concentration range of 0.02-3.00 mg/L Fe and was then analyzed on a Shimadzu spectrophotometer with a wavelength set at 540.

2.2 Calculation

The most important process parameters were calculated using the equations reported in table 2. The F represent the Faraday Constant (96485 C/mole$^-$) while 86400 are the seconds in one day, Q is the flow rate of the feeding solution in litre per day.

Table 2: Fundamental reactor parameter and equation for reductive reactor

Parameter	Equation
CAHs Removal Rate (μeq/Ld)	[CAHs]in -[CAHs]out * $Q/V_{reductive}$
RD rate (μeq/Ld)	$Q/V_{reductive}$*[TCE]*2+[cisDCE]*4+[VC]*6+[Eth]*8+[Eta]*10
RD rate (mA)	RD (μeq/Ld) *$V_{reductive}$*F/86400/1000
CH$_4$ production rate (μeq/Ld)	RCH$_4$ (μeq/Ld) = Q/V_r*[CH$_4$]*8
CH$_4$ production rate (mA)	RCH$_4$ (μeq/Ld) *V_r*F/86400/1000
Sulphate Reduction rate (meq/Ld)	Q/V_r*[SO$_4^{2-}$]$_{removed}$*8
SR rate (mA)	RS (μeq/Ld) *V_r*F/86400
Nitrate Reduction rate (meq/Ld)	Q/V_r*[NO$_3^-$]$_{removed}$*5
NR rate (mA)	RN (μeq/Ld) *V_r*F/86400
Fe^{3+} Reduction Rate (meq/Ld)	Q/V_r*[Fe^{3+}]$_{removed}$*1
Fe^{3+} Rate (mA)	RFe^{3+} (μeq/Ld) *V_r*F/86400
Coulombic Efficiency RD (CE$_{RD}$ %)	RD (mA) /i (mA) *100
CE$_{CH_4}$ (%)	RN (mA) /i (mA) *100
CE$_{SR}$ (%)	RS (mA) /i (mA) *100
CE$_{NR}$ (%)	RCH$_4$ (mA) /i (mA) *100
CE$_{Fe^{3+}}$ (%)	RFe^{3+} (mA) /i (mA) *100

3. Results and Discussions

3.1 RD by-products speciation in the different experimental set-ups

In the different experimental explored conditions, the different performances have been compared by the reductive dechlorination rate, the by-products of reductive dechlorination and the side reactions which compete with the reducing power.

In the mineral medium period, the only RD by-products were ethylene and vinyl chloride which concentrations depends on the working electrode potential, much more the reductive power was high more reduced species has and higher concentration from 30 ± 2 µmol/L, 41 ± 7 µmol/L to 29 ± 4 µmol/L for VC and 13 ± 1 µmol/L, 19 ± 4 µmol/L to 35 ± 7 µmol/L for ethylene. Moving to the condition with the synthetic groundwater the spectrum changed as reported in figure1, this was probably due to the lack of necessary grow factors coupled with the large amount of sulphate and nitrate reduction reactions, however this type of feeding solution allow to produce a measurable concentration ethane, the final RD by-product. During the experimentations with different HRT and reductive potentials the RD reaction seems inhibited, and the cDCE was the principal RD by-product were most of the products in the reactor effluent. These experimentations were conducted to clarify the role of sulphate and nitrate reduction and to figure out the best operating conditions for promoting the RD reaction and minimize the anions reduction. With the real contaminated groundwater, the major issue was the extremely low concentration of CAHs typical of an aged contaminated site and the simultaneous presence of PCE, TCE, cDCE and Vinyl Chloride. Otherwise, the reductive reactor showed the capability to fully convert the high chlorinated compound in a mixture of vinyl chloride principally and cis Dichloroethylene (cDCE) reaching a higher mass recovery in respect of the previous periods analysed.

3.2 Reductive reaction comparison

In Figure 2 are reported the values for the PCE removal rate and for the RD reaction, as showed the PCE removal rate depends basically on the contaminant load (which is the reactor contaminant incoming mass per day). On the contrary the RD reaction rate is strictly correlated with the concentration of the low chlorinated RD backbone products. Indeed, even if in the real groundwater period only vinyl chloride were produced the RD reaction rate had an extremely low value due to the small inlet contaminant concentration. It is interesting to compare these values with the rate of the reductive power competitive reaction reported in figure 2. In the experimentations with mineral medium the only competitive reaction were methanogenesis and for this reason the RD reaction rate increase in the -550 mV vs SHE condition to 99 ± 5 µeq/Ld. With the synthetic groundwater

condition, the RD reaction rate has comparable values both in the various HRT experimentation and the various reductive potential. In the real groundwater period incoming sulphate and nitrate concentrations are lower than in the previous experimental periods and this coupled with the small amount of CAHs promotes only methanogenesis.
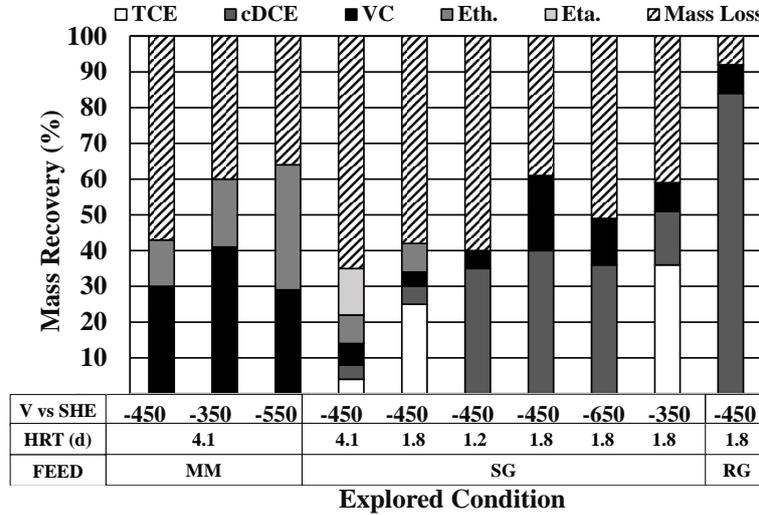

Figure 1: RD by products distribution and mass recovery in the reductive reactor
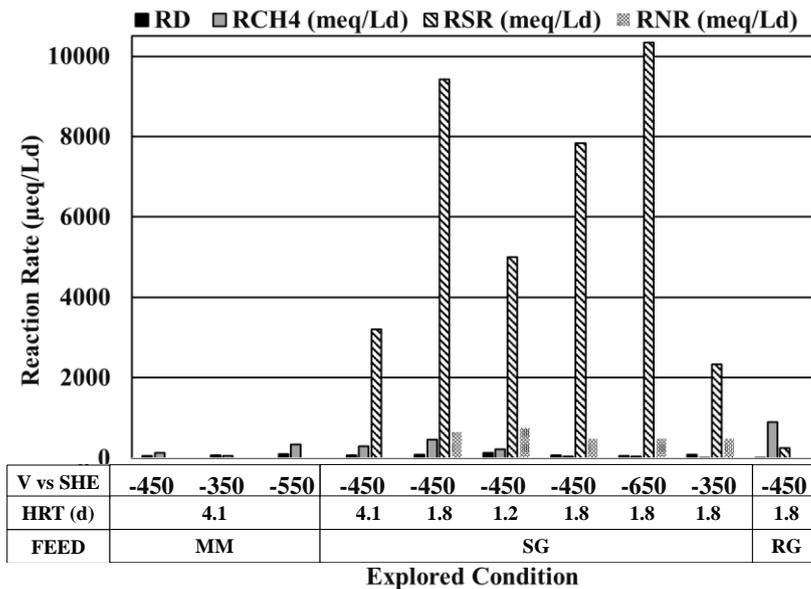

Figure 2: Reductive mechanism identified in the reductive reactor during the different operating condition explored

3.3 Coulombic Efficiency and Energy consumptions

During the operation with the mineral medium solution, the RD reached the highest values in terms of coulombic efficiency. Is interesting to see that the unrecovered current was similar in the three different working electrode reductive potentials 73% for -450 mV vs SHE, 70% for the -350 mV and 74 % for the -550 mV. This is probably due to the configuration of the reactor, in fact the lack of an ion exchange membrane between the external working electron chamber and the internal counter electrode chamber allow to some species as molecular hydrogen or, in the real groundwater period, Fe^{3+} to reach the counter electrode and be oxidized generating an electrons loop that increase the flowing current and consequentially the lost current. With the introduction of the

anions the flowing current is totally recovered in the period with the 1.2 d HRT and the working electrode set to -450 mV vs SHE potential. The increasing of competitive reaction probably limited the hydrogen migration to the counterelectrode and consequentially the electron loops mention above. With real groundwater period the lost current return like mineral medium experimentation but the RD utilized a very small amount of current for the reason already reported.
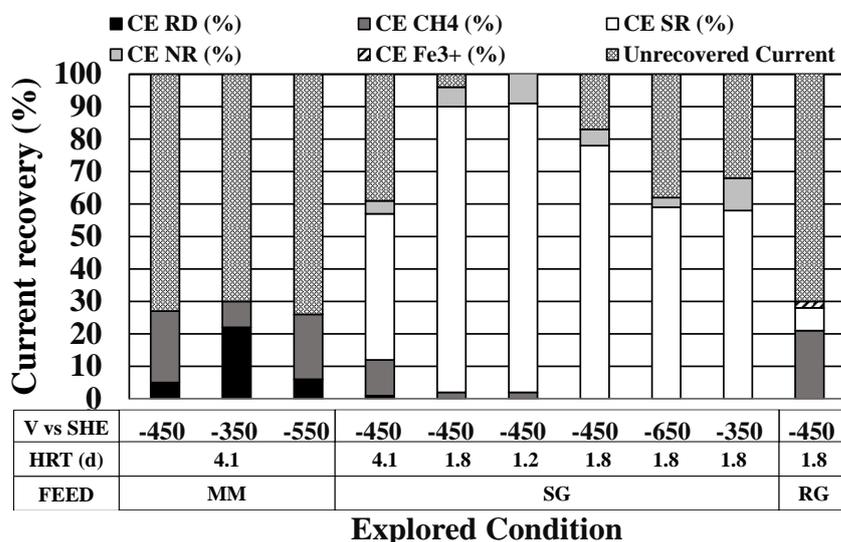

Figure 3: Coulombic efficiencies for the various reaction and unrecovered current in the different explored period
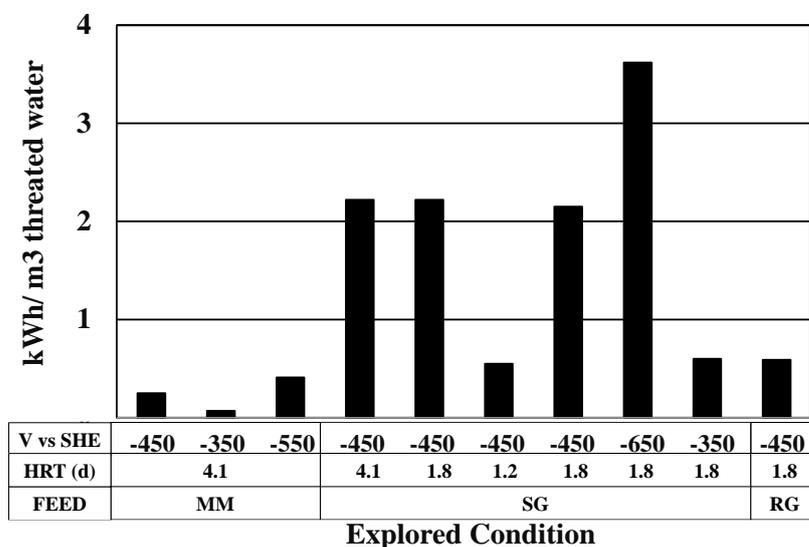

Figure 4: Energetic costs for the process in the different explored period

The energetic cost for the reductive reactor depends by the flowing current and the cell voltage applied to the bioelectrochemical reactor. The energy consumption expressed as kWh/m^3 of treated water resulted influenced by the applied cathodic potential during the operation of the reactor with mineral medium solution, i.e. a more reductive potential promote a higher energy consumption of the process. The utilization of synthetic groundwater increased remarkably the energetic cost probably due to the lower conductivity of the feeding solution and for the large amount of flowing current caused by the sulphate and nitrate reduction as shown in figure 4. The sulphate and nitrate reduction driven the current generation and or this reason the condition with the massive anion's reduction had double energetic consumption and reach the maximum of 3.62 kWh/m^3 in the -650 mV

vs SHE condition. The real groundwater instead gives promising results, i.e., the energetic consumptions turn out to be acceptable due to the small concentrations of anions in the matrix and the presence of nutrients typical of real matrices and comparable to other technologies.

4. Conclusions

The reductive reactor allows for the stimulation of the reductive dechlorination reaction of perchloroethylene and the other high chlorinated hydrocarbons, among the different explored operating condition, the dechlorination rate was influenced by the feeding solution composition, the adopted hydraulic retention time, and the applied cathodic potential. Reductive dechlorination rate and the consequent coulombic efficiency was influenced by the presence of side reductive reactions like nitrate and sulphate reduction. Energy consumption, as electric power, was mainly related to the operating conditions that stimulates side reactions with a consequent current increase. The analysis of the different operating conditions conducted in the presented study allowed for the bioelectrochemical technology validation, giving a comprehensive view of the dechlorination rate of the contaminants in presence of different side reactions. Future developments will aim to the test the system on field to prove the applicability in real remediation intervention

Nomenclature

PCE – Perchloroethylene
TCE – Trichloroethylene
cDCE – cis - Dichloroethylene
VC – Vinyl Chloride
Eth – Ethylene
Eta – Ethane
HRT – Hydraulic Retention Time
RD – Reductive Dechlorination

SHE – Standard Hydrogen Electrode
CE – Coulombic Efficiency
SR – Sulphate Reduction
NR – Nitrate Reduction
SG – Synthetic Groundwater
RG – Real Groundwater
MM – Mineral Medium

Acknowledgments

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