

# Control of Sulfate and Nitrate Reduction by Setting Hydraulic Retention Time and Applied Potential on a Membraneless Microbial Electrolysis Cell for Perchloroethylene Removal

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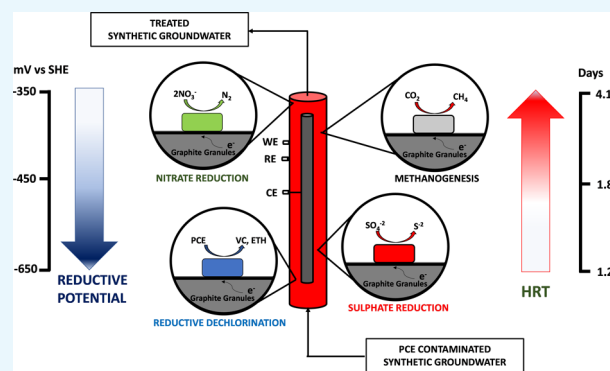
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**ABSTRACT:** A membraneless microbial electrolysis cell (MEC) has been developed for perchloroethylene (PCE) removal through the reductive dechlorination reaction. The MEC consists of a tubular reactor of 8.24 L equipped with a graphite-granule working electrode which stimulates dechlorinating microorganisms while a graphite-granule cylindrical envelopment contained in a plastic mesh constituted the counter electrode of the MEC. Synthetic PCE-contaminated groundwater has been used as the feeding solution to test the nitrate and sulfate reduction reactions on the MEC performance at different hydraulic retention times (HRTs) (4.1, 1.8, and 1.2) and different cathodic potentials [−350, −450, and −650 mV vs standard hydrogen electrode (SHE)]. The HRT decrease from 4.1 to 1.8 d promoted a considerable increase in sulfate removal from  $38 \pm 11$  to  $113 \pm 26$  mg/Ld with a consequent current increase, while a shorter HRT of 1.2 d caused a partial inhibition of sulfate reduction with a consequent current decrease from  $-99 \pm 3$  to  $-52 \pm 6$  mA. Similarly, the cathodic potential investigation showed a direct correlation of current generation and sulfate removal in which the utilization of a cathodic potential of −350 mV versus SHE allowed for an 80% decrease in the sulfate removal rate with a consequent current decrease from  $-163 \pm 7$  to  $41 \pm 5$  mA. The study showed the possibility to mitigate the energy consumption of the process by avoiding side reactions and current generation, through the selection of an appropriate HRT and applied cathodic potential.



## 1. INTRODUCTION

The wide diffusion of chlorinated aliphatic hydrocarbons (CAHs) as perchloroethylene (PCE) and trichloroethylene (TCE) over the past years and their incorrect disposal and storage made these substances become one of the most common contaminants of both subsoil and groundwater in the world.<sup>1–3</sup> These compounds can be naturally degraded directly in the contaminated matrix by various species of microorganisms; in case of anaerobic conditions, the reaction is known by the name of organohalide respiration or reductive dechlorination (RD).<sup>4,5</sup> This microbial consortium can couple growth with dehalogenation, but only *Dehalococcoides mccartyi* can degrade PCE to a harmless product, ethene.<sup>6–9</sup> Indeed, the RD reaction usually promotes the accumulation of less toxic chlorinated byproducts like vinyl chloride (VC). Enhanced in situ bioremediation (EISBR) consists of the stimulation of dechlorinating microorganisms by adding organic fermentable compounds to the contaminated aquifer,<sup>10–12</sup> which allows slow H<sub>2</sub> release. EISBR represents an effective strategy for CAH remediation,<sup>13,14</sup> particularly when sustainable fermentable byproducts are used.<sup>15–18</sup> An innovative approach used for the control of microbial activity is offered by a

bioelectrochemical system (BES) in which the microbial metabolism is stimulated by the presence of a polarized electrode. During the years, many environmental applications of the BES have been developed;<sup>19–22</sup> indeed, microbial electrolysis cells (MECs)<sup>23,24</sup> have been used for remediation applications of contaminants including CAHs and heavy metals.<sup>25–28</sup> Recently, a new membraneless MEC configuration has been successfully adopted for the complete mineralization of PCE through a sequential reductive/oxidative step. The introduction of synthetic groundwater, prepared according to a real groundwater composition, introduced sulfate and nitrate in the reductive reactor, which were responsible for the current increase due to the establishment of sulfate and nitrate bioelectrochemical reduction. Iron, sulfate, and nitrate reductions<sup>29,30</sup> usually compete with CAH RD,

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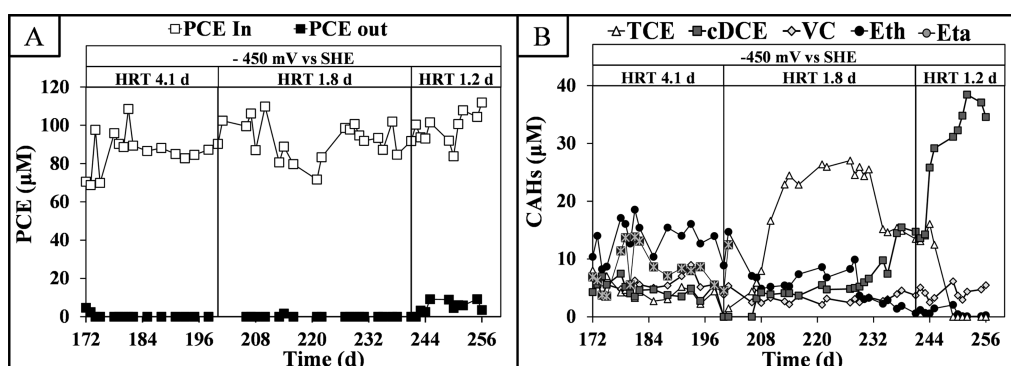


Figure 1. PCE removal (A) and CAH RD byproducts (B) during the three operating periods at different HRTs.

being reducing-power consuming reactions; moreover, various studies indicate similar  $H_2$  threshold concentrations for dechlorinating and sulfate-reducing microorganisms.<sup>31–34</sup>

Sulfate and nitrate reduction reactions under bioelectrochemical conditions have been widely described by several authors.<sup>35,36</sup> Under potentiostatic conditions, the establishment of these additional power consumption reactions, along with bioelectromethanogenesis, promotes a current increase which is directly linked to an increase in power consumption. In order to control the sulfate and nitrate reduction reactions under the adopted operating conditions, hydraulic retention time (HRT) and cathodic potential ( $E_{\text{cath}}$ ) effects have been explored by using synthetic groundwater containing sulfate and nitrate anions. Furthermore, three different HRTs (4.1 d, 1.8 d, and 1.2 d) and three different  $E_{\text{cath}}$  [−450, −650, and −350 mV vs standard hydrogen electrode (SHE)] have been adopted for the membraneless reductive reactor to allow the optimization of PCE RD in terms of the dechlorination rate, Coulombic efficiency, and energy consumption.

## 2. RESULTS AND DISCUSSION

**2.1. Effect of HRT on Reductive Reactor Performances.** The reductive reactor feeding solution, composed of PCE-contaminated synthetic groundwater, was acclimated to nitrate and sulfate presence in a previous study, in which the effects on bioelectrochemical performance of the synthetic groundwater were highlighted.<sup>37</sup> To investigate more in detail the effects of operating conditions on the RD reaction, the reductive reactor has been separated from the sequential bioelectrochemical process to characterize the HRT and applied cathodic potential effects.<sup>39</sup> The first operating condition explored was the HRT which was decreased from 4.1 to 1.8 and 1.2 days by increasing the synthetic groundwater flow rate from 2.0 to 4.5 and 7 L/d (i.e. empty volume of the reductive reactor is 8.24 L). During the HRT effect investigation, the cathodic chamber of the reductive reactor was polarized at −450 mV versus SHE. As reported in Figure 1A, under the first operating condition, at 4.1 days, a complete PCE removal was obtained, with PCE not being present in the outlet of the reductive reactor. The subsequent HRT decrease from 4.1 to 1.8 days allowed for the maintenance of complete PCE removal from the synthetic groundwater, with an average PCE removal efficiency of  $100 \pm 3\%$ ; however, a further HRT decrease from 1.8 to 1.2 caused the partial loss of the PCE removal capacity with a decrease in the PCE removal efficiency to  $95 \pm 6\%$ . Even if the HRT of 1.2 days promoted a slight decrease in PCE removal efficiency, as summarized in Table 1, the PCE removal rate increased from  $22 \pm 3$  to  $74 \pm 13$   $\mu\text{mol}/$

Table 1. PCE Removal and RD Rate under the Three Operating Conditions at Different HRTs

HRT (d)	4.1	1.8	1.2
PCE removal rate ( $\mu\text{mol}/\text{Ld}$ )	$22 \pm 5$	$52 \pm 9$	$74 \pm 13$
PCE removal efficiency (%)	$99 \pm 3$	$100 \pm 3$	$95 \pm 6$
RD rate ( $\mu\text{eq}/\text{Ld}$ )	$61 \pm 3$	$80 \pm 7$	$134 \pm 11$
$\text{CE}_{\text{RD}}$ (%)	$0.8 \pm 0.1$	$0.7 \pm 0.2$	$2.1 \pm 0.5$

Ld according to the HRT decrease. As reported in Figure 1B, the RD byproduct composition remained stable during the operating periods of 4.1 and 1.8 days, with a predominance of medium–low chlorinated RD byproducts such as cisDCE and VC present at an average concentration of 5 and 4  $\mu\text{mol}/\text{L}$ , respectively. Moreover, by the adoption of an HRT of 1.2 days, a considerable increase in cisDCE was observed, reaching a concentration around 35  $\mu\text{mol}/\text{L}$  (Figure 1B). As shown in Figure 1B, the adoption of different HRTs influenced the byproduct composition, that is, the HRT decrease promoted the production of medium and high chlorinated PCE byproducts, showing the possible correlation of the HRT with the activity of the specific reductive dehalogenase enzymes involved in each dechlorination step.<sup>37</sup> Despite the predominance of medium chlorinated RD byproducts, the HRT decrease promoted an increase in terms of reducing equivalents involved in the RD reaction, which increased from  $61 \pm 3$  to  $134 \pm 11$   $\mu\text{eq}/\text{Ld}$ .

The principal effect of the HRT decrease detected during the reductive reactor operation was the current profile generated by the cathodic reactions, as shown in Figure 2. Indeed, while the average current increased from  $-65 \pm 3$  to  $-99 \pm 3$  with the decrease in HRT from 4.1 to 1.8 days, a further HRT decrease to 1.2 days caused a current decrease

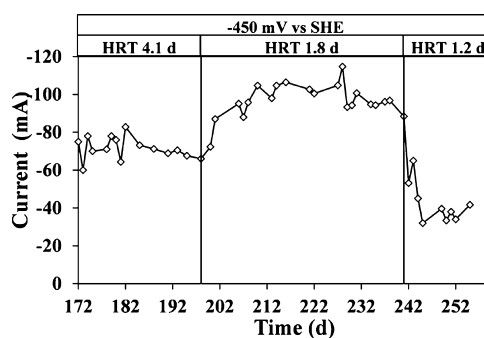
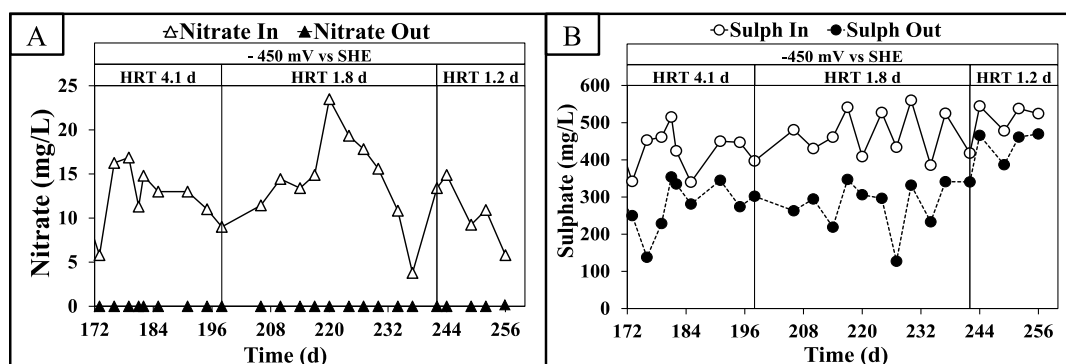


Figure 2. Average current flow in the reductive reactor during the three operating periods at different HRTs.



**Figure 3.** Nitrate (A) and sulfate (B) removal in the reductive reactor during the three operating periods at different HRTs.

from  $-99 \pm 3$  to  $-52 \pm 6$  mA. Under potentiostatic control of the process, the decrease in the generated current was directly correlated with the decrease in the reduction reaction rate in the reactor. The consequent Coulombic efficiency for the RD reaction ( $CE_{RD}$ ), that is, the amount of electricity involved in the PCE dechlorination, resulted in the range of  $0.8 \pm 0.1$  to  $2.1 \pm 0.1\%$ , as reported in Table 1.

As reported in a previous study,<sup>38</sup> most of the current produced in the reductive reactor under evaluation was derived from the establishment of nitrate and sulfate reduction reactions. The nitrate concentration in the inlet and outlet of the reductive reactor during the three different HRT operating periods is reported in Figure 3A; due to the low concentration of nitrate in synthetic groundwater (around 15 mg/L), under all the conditions explored, the nitrate was completely removed, indicating a complete reduction of the anion by the bioelectrochemical denitrification pathway. On the contrary, as reported in Figure 3B, sulfate removal increased from  $38 \pm 11$  to  $113 \pm 26$  mg/Ld by a HRT decrease from 4.1 to 1.8 days, while a further HRT decrease to 1.2 days caused a drastic sulfate removal rate decrease to  $60 \pm 9$  mg/Ld. The sulfate removal rate decrease was probably due to low HRT and the consequential low contact time between the species and the biofilm together with a high sulfate load reached by adopting a flow rate of 6.5 L/d (a theoretical sulfate load rate of  $393 \text{ mgSO}_4^{2-}/\text{Ld}$ ) in the reductive reactor. Interestingly, the sulfate removal rate correlated with the current–time course (Figure 2), indicating the current dependence of sulfate reduction. Indeed, as reported in Table 2, most of the current

**Table 2.** Sulfate and Nitrate Contribution to Current Generation under the Three Different Operating Conditions

HRT (d)	4.1	1.8	1.2
$\text{SO}_4^{2-}$ removal rate (mg/Ld)	$38 \pm 11$	$113 \pm 26$	$60 \pm 9$
$\text{NO}_3^-$ removal rate (mg/Ld)	$3 \pm 1$	$8 \pm 3$	$9 \pm 2$
current (mA)	$-65 \pm 3$	$-99 \pm 3$	$-52 \pm 6$
$CE_{RS}$ (%)	$45 \pm 5$	$88 \pm 13$	$89 \pm 7$
$CE_{RN}$ (%)	$4 \pm 2$	$6 \pm 1$	$12 \pm 4$

flowing in the reductive reactor was justified by the complete nitrate and sulfate reduction, which presented Coulombic efficiencies for the nitrate and sulfate reduction of  $6 \pm 1$  and  $88 \pm 13\%$ , respectively, under the 1.8-day HRT condition and  $12 \pm 4$  and  $89 \pm 7\%$  under the 1.2-day HRT condition.

**2.2. Effect of the Applied Potential on Reductive Reactor Performances.** The investigation of the effect of the

cathodic potential on the bioelectrochemical reactions has been performed by using a fixed HRT of 1.8 days, which represents a more realistic HRT for a full-scale application. Three different cathodic potentials have been adopted,  $-450$ ,  $-650$ , and  $-350$  mV versus SHE;  $-450$  mV versus SHE was replicated after the  $-450$  mV versus SHE condition operated with an HRT of 1.2 days to assess the capacity of the bioelectrochemical process in restoring a previous condition. As described in Figure 4A, the PCE removal was almost complete under the three explored conditions at different cathodic potentials; indeed, as also summarized in Table 3, the resultant PCE removal rates were  $28 \pm 8$ ,  $28 \pm 6$ , and  $43 \pm 11$   $\mu\text{mol}/\text{Ld}$ . Besides, the complete PCE removal was not influenced by the applied potential; as reported in Figure 5, a strong influence of the cathodic potential was observed with an average current flow in the reductive reactor. However, while the current increased from  $-93 \pm 3$  to  $-163 \pm 7$  mA at cathodic potentials of  $-450$  and  $-650$  mV versus SHE, a sharp current decrease from  $-163 \pm 7$  to  $-41 \pm 5$  mA was obtained using a cathodic potential of  $-350$  mV versus SHE.

The RD byproduct distribution during the three operating periods at the three different cathodic potentials was almost stable. The main RD byproducts consisted of a mixture of cis DCE and VC at an average concentration of  $20 \pm 5$  and  $5 \pm 1$   $\mu\text{mol}/\text{L}$ , respectively. Only during a cathodic potential of  $-350$  mV versus SHE, the less reductive explored condition, was TCE with an average concentration of  $6 \pm 1$   $\mu\text{mol}/\text{L}$  detected in the reductive reactor effluent. As reported in Table 2, the resultant RD rate was almost constant in the different operating periods with average values of  $73 \pm 5$ ,  $62 \pm 9$ , and  $84 \pm 7$   $\mu\text{eq}/\text{Ld}$  for the  $-450$ ,  $-650$ , and  $-350$  mV versus SHE conditions, respectively. Moreover, the less the reducing potential applied, the higher the RD Coulombic efficiency; that is, the Coulombic efficiency at  $-350$  mV versus SHE was 1.8 because of the current decrease promoted by the adoption of a less reductive potential.

The current profile correlated with the sulfate and nitrate removal as shown in Figure 6, which reports the influent and effluent anion concentrations in the reductive reactor. Although complete nitrate removal was obtained in all the three cathodic potentials explored (Figure 6A) due to the low concentration of nitrate in synthetic groundwater, sulfate reduction was mainly responsible for current generation under the different potentiostatic conditions explored (Figure 6B). As reported in Table 4, sulfate reduction Coulombic efficiency allowed for the justification of  $78 \pm 12$ ,  $59 \pm 10$ , and  $58 \pm 8\%$  of the flowing current under the different operating conditions. Furthermore, the utilization of  $-350$  mV versus SHE in the

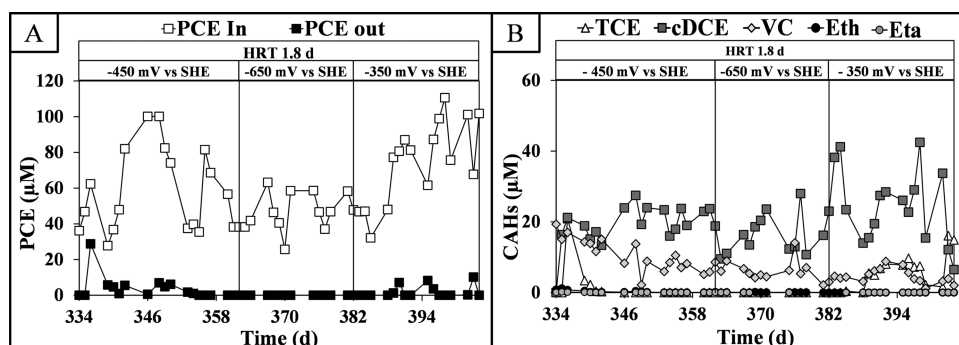


Figure 4. PCE removal (A) and CAH RD byproducts (B) during the three operating periods at different applied cathodic potentials.

Table 3. PCE Removal and RD Rate under the Three Operating Conditions at Different Applied Cathodic Potentials

$E_{\text{cath}}$ (mV vs SHE)	-450	-650	-350
PCE removal rate ( $\mu\text{mol/Ld}$ )	$28 \pm 8$	$28 \pm 6$	$43 \pm 11$
PCE removal efficiency (%)	$96 \pm 4$	$100 \pm 2$	$98 \pm 4$
RD ( $\mu\text{eq/Ld}$ )	$73 \pm 5$	$62 \pm 9$	$84 \pm 7$
$\text{CE}_{\text{RD}}$ (%)	$0.7 \pm 0.2$	$0.4 \pm 0.1$	$1.8 \pm 0.4$

Table 4. Sulfate and Nitrate Contribution to Current Generation under the Three Different Operating Conditions at Different Applied Cathodic Potentials

$E_{\text{cath}}$ (mV vs SHE)	-450	-650	-350
$\text{SO}_4^{2-}$ removal rate (mg/Ld)	$94 \pm 8$	$124 \pm 9$	$28 \pm 4$
$\text{NO}_3^-$ removal rate (mg/Ld)	$6 \pm 2$	$6 \pm 3$	$6 \pm 2$
current (mA)	$-93 \pm 3$	$-163 \pm 7$	$-41 \pm 5$
$\text{CE}_{\text{RS}}$ (%)	$78 \pm 12$	$59 \pm 10$	$58 \pm 8$
$\text{CE}_{\text{RN}}$ (%)	$5 \pm 2$	$3 \pm 1$	$10 \pm 4$

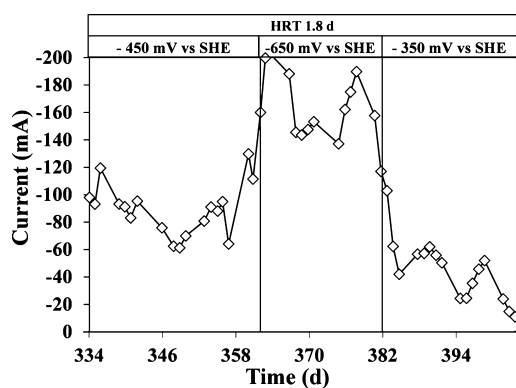


Figure 5. Average current flow in the reductive reactor during the three operating periods at different applied cathodic potentials.

reductive reactor caused a strong inhibition of sulfate reduction reaction which decreased from  $124 \pm 9$  mg $\text{SO}_4/\text{Ld}$  under the  $-650$  mV versus SHE condition to  $28 \pm 4$  mg/Ld at a cathodic potential of  $-350$  mV versus SHE. Probably, the less reducing power available for the reduction reaction promoted the sulfate-reducing microorganism activity due to the less

availability of reducing equivalents or molecular hydrogen concentration.

As reported in the literature, sulfate- and nitrate-reducing microorganisms have a similar hydrogen threshold value with respect to organohalide-respiring bacteria, that is, the microorganisms responsible for PCE RD. This similar hydrogen threshold value implies that at intermediate and more reducing potential values, the two types of reactions occur simultaneously, while under the lower reducing condition, the hydrogen production only sustained RD. Even though the dechlorinating microbial consortium resulted not inhibited by the less reductive condition, a partial PCE dechlorination with TCE production was observed, probably indicating the selection of different microbial species able to perform only the first step of the PCE dechlorination.<sup>37</sup>

**2.3. Methane Generation under the Explored Condition.** Bioelectromethanogenesis is a well-known scavenging reaction of reducing-power consumption, as already reported in previous studies;<sup>40</sup> bioelectromethanogenesis was responsible for the higher flowing current consumption. Under all the explored conditions, methane has been detected in the reductive reactor effluent mainly as a separated gaseous phase.

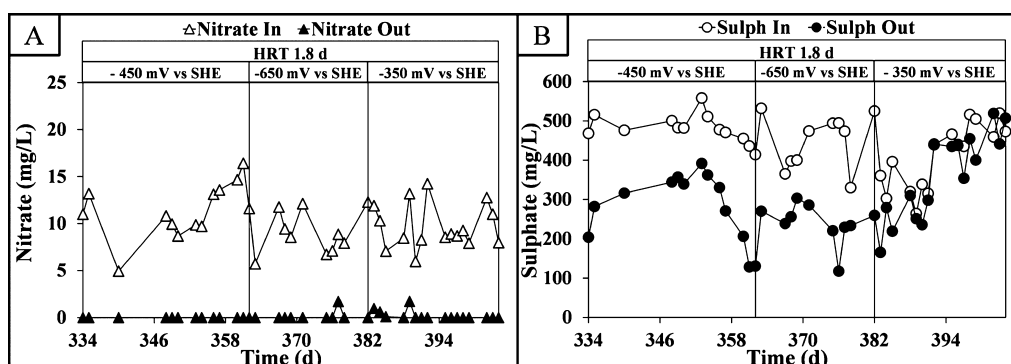


Figure 6. Nitrate (A) and sulfate (B) removal in the reductive reactor during the three operating periods at different applied cathodic potentials.

With respect to sulfate and nitrate reduction, methane generation gave a lower contribution in terms of reducing-power consumption, with Coulombic efficiencies in the range of 0.5–9% as reported in Table 5. During the exploration of

**Table 5. Methane Coulombic Efficiency Obtained under the Different Conditions Explored**

HRT (d)	4.1	1.8	1.2
CH <sub>4</sub> production rate (μmol/Ld)	94 ± 7	57 ± 4	27 ± 8
CE <sub>CH<sub>4</sub></sub> (%)	9 ± 3	2 ± 1	2 ± 1
E <sub>cath</sub> (mV vs SHE)	−450	−650	−350
CH <sub>4</sub> production rate (μmol/Ld)	6 ± 3	6 ± 2	1 ± 1
CE <sub>CH<sub>4</sub></sub> (%)	0.5 ± 0.1	0.44 ± 0.04	0.47 ± 0.12

the HRT effects on the investigated process, methanogenesis was considerably higher in terms of the highest production rate at an HRT of 4.1 d; moreover, the HRT decrease promoted the decrease in the methane production rate from 94 ± 7 to 27 ± 8 μmol/Ld. On the contrary, during the exploration of the cathodic potential, the methane production rate was much lower with respect to the HRT conditions with a methane production rate of 6 μmol/Ld at −450 and −650 mV versus SHE, while under a less reductive condition of −350 mV versus SHE, further methanogenesis inhibition has been detected due to the lower availability of reducing power. Methanogenesis was inhibited by a lower HRT, below 2 days, which led to a progressive inhibition during the study of the cathodic potentials, which was conducted at an intermediate HRT of 1.8 d. The analysis of the bioelectrochemical methane production clearly indicates the combined effect of HRT and cathodic potential in the mitigation of the methanogenesis side reaction.

**2.4. Overall Evaluation of the HRT and E<sub>cathode</sub> on the Reductive Reactor.** The overall analysis of the reductive reactor performance under the investigated operating condition allowed the evaluation of the RD reaction in the presence of side reactions such as nitrate and sulfate reduction. With the reductive reactor being operated under a potentiostatic condition, RD and nitrate/sulfate reduction are not competitive because higher species are able to be reduced and higher current flowed in the circuit. The current generation in

the reductive reactor was related to the sulfate load rate available in the cathodic chamber of the reductive reactor (controlled by HRT) and to the cathodic potential applied to the electrode. Indeed, Figure 7A shows the RD rates and current generation as a function of both HRT and cathodic potential. It is possible to underline that current generation has been driven mainly by the sulfate reduction reaction; for this reason, the regulation of the applied cathodic potential and the HRT allowed for the minimization of competing reactions with a limited influence on the RD rate. The increase in the flowing current is directly linked to an increase in the applied cell voltage and, for instance, to the energy consumption of the overall process; Table 6 and Figure 7B summarize the different energy consumptions obtained during the treatment of synthetic groundwater under all the explored conditions.

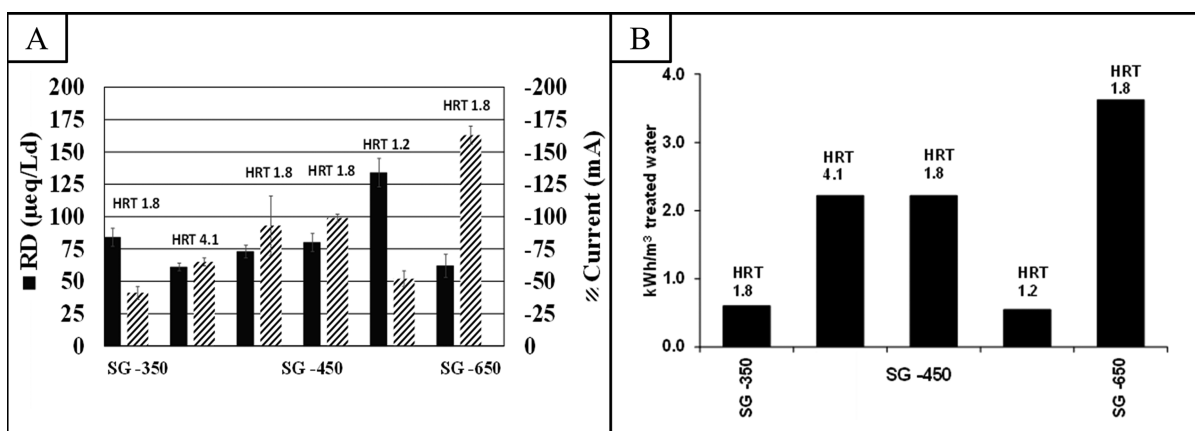
**Table 6. Energy Consumption (kW h/m<sup>3</sup>) in the Treated Synthetic Groundwater for the Different Operating Conditions Explored**

E <sub>cath</sub> (mV vs SHE)	−350	−450	−650
HRT 4.1 (d)		2.2 ± 0.1	
HRT 1.8 (d)	0.6 ± 0.1	2.2 ± 0.3	3.6 ± 0.2
HRT 1.2 (d)		0.6 ± 0.1	

Finally, by regulating the HRT and the applied cathodic potential, the current, generated mostly by sulfate reduction, can be adjusted to the desired optimum which, in this case, indicates the necessity to minimize the current and the consequent Coulombic efficiency of the RD reaction and the energy consumption of the bioelectrochemical reactor.

### 3. CONCLUSIONS

In this paper, bioelectrochemical sulfate and nitrate reduction reactions as side reactions of PCE RD have been investigated at three different HRTs and cathodic potentials. The HRT decrease from 4.1 to 1.8 promoted a considerable increase in sulfate reduction which contributed to the current increase, while a further decrease in HRT to 1.2 d led to a partial inhibition of sulfate reduction, promoting the consequent current decrease. Applying the intermediate HRT of 1.8 days with three different cathodic potentials (−350, −450, and −650 mV vs SHE) showed their predominant effect on sulfate and nitrate reduction and consequently on current generation



**Figure 7.** Current generation and RD reaction rate in the reductive reactor as a function of HRT and cathodic potential (A) and energy consumption (pumping not included) for the synthetic groundwater treatment as a function of applied cathodic potential and HRT (B).

and energy consumption. By using the less reductive potential of  $-350$  mV versus SHE, the sulfate reduction strongly reduced, promoting a considerable current decrease and energy consumption minimization. RD Coulombic efficiency maximized under the  $-350$  mV versus SHE condition with an HRT of 1.8 d; that is, the RD rate remained almost constant despite the obtained current decrease. The present research study suggests that in the bioelectrochemical process under investigation, side reaction control, mainly represented by sulfate and nitrate reduction, is fundamental to limit current generation and energy consumption in favor of a higher Coulombic efficiency for the RD reaction.

## 4. EXPERIMENTAL SECTION

**4.1. Reactor Setup and the Operating Conditions Explored.** The reductive reactor consisted of a borosilicate glass column with an empty volume of 8.24 L. Three sampling ports allowed for the insertion of the Ag/AgCl reference electrode (3 M KCl +0.199 V vs SHE) and the electric connections for the working and counter electrode. The working electrode of the reactor was an external chamber filled with granular graphite which constituted the cathode, while the internal counter electrode chamber was made by a tubular envelopment of a plastic material containing granular graphite. The two concentric chambers were electrically separated using a double-layer HDPE web pointed with a nonwoven fabric membrane, which allowed electrolyte diffusion.

The influent solution, named synthetic groundwater, was prepared from tap water in which 450 mg/L  $\text{Na}_2\text{SO}_4$  and 30 mg/L  $\text{NaNO}_3$  were added according to the composition of real groundwater. The synthetic groundwater was contaminated by PCE at a theoretical concentration of 100  $\mu\text{L}$ . Both influent and effluent solutions were collected in self-collapsing bags that allow the containment of the feeding solution without the creation of a gas phase. More details about the reactor setup can be also found in previous work.<sup>41</sup> The reactor was polarized by using a three-electrode configuration, controlling the reductive potential of the external cathodic chamber by using a VSP300 Biologic potentiostat (BioLogic).

During this study, three different HRTs and three different cathodic potentials have been used for process performance characterization. Table 7 summarizes the operating conditions adopted.

**Table 7. Resume of the Explored Conditions**

HRT (d)	4.1	1.8	1.2
$E_{\text{we}}$ potential	-450	-350 -450 -650	-450

**4.2. Analytical Methods.** The analysis of the CAHs in the inlet and in the outlet of the reactor is made by the manual injection of a 50  $\mu\text{L}$  head space gas phase in a Dani Master gas chromatograph with a flame ionization detector. The injection was made by using a gastight syringe (gas-tight syringe, Hamilton Company USA, Nevada) with a sample lock to maintain the same pressure of the sampling cells for the injected volume. The analysis of nitrate and sulfate anions was made using a ionic liquid chromatograph (Dionex) equipped with a suppressor and by using a mobile phase that consists of a solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ ; the liquid phase for the anion analysis was sampled directly from the bags.

**4.3. Calculation.** The Coulombic efficiency represents the fraction of flowing current generated by proton reduction, which comes from water autoproteolysis, that is used for reductive reactions. The RD Coulombic efficiency can be expressed with the equation

$$\text{CE}_{\text{RD}} (\%) = \frac{\text{RD (mA)}}{i \text{ (mA)}} \times 100$$

in which RD is the quantification of the RD product in milliamps, calculated with the subsequent equation

$$\begin{aligned} \text{RD (mA)} = & \{ ([\text{TCE}] \times 2) + ([\text{cDCE}] \times 4) \\ & + ([\text{VC}] \times 6) + ([\text{Eth}] \times 8) \} / 1000 \\ & \times Q_{\text{out}} \times (F/86400) \end{aligned}$$

where  $Q_{\text{out}}$  = liquid flow rate;  $F$  = Faraday's constant = 96,485 C/mol; and 86,400 are the seconds in one day.

The nitrate and sulfate Coulombic efficiencies are calculated by using the same expressions by replacing the numerator term with the quantification of the nitrate and sulfate removal and total reduction in milliamps

$$\text{CE}_{\text{NR}} (\%) = \frac{\text{NR (mA)}}{i \text{ (mA)}} \times 100$$

$$\text{CE}_{\text{SR}} (\%) = \frac{\text{SR (mA)}}{i \text{ (mA)}} \times 100$$

in which

$$\begin{aligned} \text{SR (mA)} = & \frac{\{ [\text{SO}_4^{2-}]_{\text{in}} - [\text{SO}_4^{2-}]_{\text{out}} \}}{\text{MW}_{\text{SO}_4^{2-}}} \times 8 \times Q_{\text{out}} \\ & \times \frac{F}{86400} \quad \text{MW}_{\text{SO}_4^{2-}} = 96.06 \text{ g/mol} \end{aligned}$$

and

$$\begin{aligned} \text{NR (mA)} = & \frac{\{ [\text{NO}_3^-]_{\text{in}} - [\text{NO}_3^-]_{\text{out}} \}}{\text{MW}_{\text{NO}_3^-}} \times 5 \times Q_{\text{out}} \\ & \times \frac{F}{86400} \quad \text{MW}_{\text{NO}_3^-} = 62 \text{ g/mol} \end{aligned}$$

The energy consumption in terms of kW h per  $\text{m}^{-3}$  of treated water was calculated using the following equations

$$\frac{\text{kW h}}{\text{d}} = i \text{ (mA)} \times \Delta V \text{ (mV)} \times 10^{-6} \times 24$$

$$\frac{\text{kW h}}{m_{\text{treatedwater}}^3} = \frac{i \text{ (mA)} \times \Delta V \text{ (mV)} \times 10^{-6} \times 24}{Q_{\text{in}} \times 10^{-3}}$$

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## ABBREVIATIONS

CAHs, chlorinated aliphatic hydrocarbons; PCE, perchloroethylene; TCE, trichloroethylene; cisDCE, cis dichloroethylene; VC, vinyl chloride; Eth, ethylene; BES, bioelectrochemical systems; MEC, microbial electrolysis cell; RD, reductive dechlorination; CE, Coulombic efficiency; HRT, hydraulic retention time

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