**Scale up of a sequential reductive/oxidative bioelectrochemical process for chlorinated aliphatic hydrocarbons (CAHs) removal from contaminated groundwater**

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**1.Introduction**

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 which allowed for the complete mineralization of CAHs [1]. More in detail, dehalorespiring microorganisms can reduce PCE and TCE via the reductive dechlorination reaction (RD), while aerobic dechlorinating microorganisms oxidize low chlorinated compounds such as cis-dichloroethylene (cDCE) and vinyl chloride (VC) into CO2. The combination of reductive and oxidative dechlorination can be easily tuned by the adoption of bioelectrochemical systems, in which an electrodic material interact with so-called electroactive microorganisms acting like electron acceptor or donor of the microbial metabolism. Microbial electrolysis cells (MECs) are a particular bioelectrochemical systems application that require the utilization of an electric potential to overcome the thermodynamic and kinetic limitations of non-spontaneous reactions. MECs have been successfully adopted in the last years for the stimulation of the reductive and the oxidative dechlorination of CAHs through the polarization of a biocathode or a bioanode [2]. A sequential reductive and oxidative environment has been obtained by the utilization of different MEC configurations including the utilization of an ion exchange membrane as ionic separator or, the adoption of two membrane-less unit. Recently, as reported in previous paper, our research group adopted a new membrane-less MEC configuration consisting in a tubular reactor provided with an internal graphite counterelectrode [3]. The new MEC concept has been tested opening a new perspective for bio-electro remediation allowing a simple and cheap design of the reactors, particularly advantageous for the scale up of the technology. 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 scale application. The scale-up increased the reactor volume 42 times (from 10 L to 420 L) dividing the reductive and the oxidative sections into 4 different columns with a geometric volume of 105 L.

**2. Methods**

The lab scale sequential bioelectrochemical process consisted of two tubular reactors as reported in figure 1.1, the reductive and the oxidative reactor with an empty volume of 8.24 and 3.14 L (Table 1), respectively. Both reactors were equipped with an internal counter electrode made by a tube filled with graphite granules enveloped by a double layer of a grid in plastic material and a permeable textile membrane that avoided the shortcut of the circuit while allowing for electrolyte migration. The reductive reactor external chamber was filled with graphite granules as electrodic material to sustain the reductive dechlorinating biofilm while the oxidative reactor external chamber was filled with silica bed and present three pieces of a mixed metal oxide (MMO) electrode connected by a titanium wire. Both upscaled reductive and oxidative reactors have been realized keeping a constant dimensions and geometry with respect the lab scale reductive reactor. In order to allow a simpler handling of the pilot, the projected volume of 420 L has been split into 4 identical tubular units with a geometric volume of 105 L (Table 1). The reductive units consisted of a working and counter electrode made of graphite granules, while the two oxidative units were assembled with an external mixed metal oxides (MMO) electrodes inserted in a gravel bed, in which a graphite granules counter electrode was inserted.

**Table 1**. Volume of the working and counter electrodes in the lab scale and upscaled reactors.

|  |  |  |
| --- | --- | --- |
|  | Working electrode volume (L) | Counter Electrode volume (L) |
| Lab scale reductive reactor | 8.24 | 1.70 |
| Lab scale oxidative reactor | 3.14 | 0.18 |
| Upscaled reductive reactor | 105 | 23 |
| Upscaled oxidative reactor | 105 | 23 |

**3. Results and discussion**

The preliminary results performed on the upscaled reductive and oxidative reactors allowed for the determination of the hydraulic parameters by tracer tests while information about their electrochemical behaviour have been performed by some polarization tests. Figure 1 shows the polarization curves obtained for the upscaled reductive and oxidative reactor by controlling the reactor with a three-electrode configuration. More in detail, the polarization test for the reductive reactor was performed by controlling the external graphite cathodic chamber in the range of 0 to -750 mV vs SHE, while the oxidative reactor working electrode (i.e., the MMO anode) was polarized in the range of +0.8 to +2.0 V vs SHE.



**Figure 1.** Polarization curves of the upscaled reductive (A) and oxidative (B) reactors.

**4. Conclusions**

The presented study presents the characterization and the design of an upscaled bioelectrochemical process for chlorinated aliphatic hydrocarbons (CAHs) removal. After the laboratory validation of the technology under several operating conditions, the design, and the realization of an upscaled process allowed for a 42 times volume increase of the technology for its filed scale validation. Preliminary polarization curves and tracer tests allowed for the characterization of the electrochemical and hydraulic behavior of the upscaled units.

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**References**

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