Bio-electrocatalytic dechlorination of 2,4-dichlorophenol. Effect of pH and operational configuration

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Abbreviations

Bioelectrochemical system (BES)

Biochemical oxygen demand (BOD)

Chlorophenols (CPs)

Chemical oxygen demand (COD)

2-chlorophenol (2-CP)

4-chlorophenol (4-CP)

2,4-dichlorophenol (2,4-DCP)

Electrocatalytic hydrogenation (ECH)

Electrochemical reductive dechlorination (ERDC)

Extracellular electron transfer (EET)

Gas chromatography–mass spectrometry (GC-MS)

Hydrogen evolution reaction (HER)

High-performance liquid chromatography (HPLC)

Joint Committee on Powder Diffraction Standards (JCPDS)

Linear sweep voltammetries (LSV)

Microbial electrolysis cell (MEC)

Microbial fuel cell (MFC)

Reference electrode (RE)

Working electrode (WE)

X-Ray diffraction (XRD)

ABSTRACT

Bioelectrochemical systems (BESs) are regarded as effective green technologies for wastewater treatment, with low associated energy costs. This work studies the influence of the cathode pH and operational mode, as microbial fuel cell (MFC) or microbial electrolysis cell (MEC), on the electrocatalytic hydrodechlorination (ECH) of 2,4-dichlorophenol (2,4-DCP) in an abiotic cathode. When operating as MFC, the results showed that more acid cathode pH enhances the ECH reactions. Practically a total dechlorination was obtained after 72 hours at cathode pH=5, whereas only an 88% dechlorination was obtained at pH=7. Also, ECH was further enhanced by operating under MEC mode, where the cathode was poised towards more negative potentials and higher current densities were achieved. The MEC presented a faster kinetics, reaching an 81% of dechlorination after 24 hours of operation in batch mode and the full dechlorination after 48 hours. Additionally, when operating as MEC, the phenol obtained after the dechlorination reaction was further hydrogenated to cyclohexanone under these mild operating conditions, which would drastically reduce the toxicity of the effluent.

Keywords: *Bioelectrochemical System; Microbial Electrolysis Cell; Microbial Fuel Cell; Chlorophenols; Electrocatalytic hydrodechlorination*

1. INTRODUCTION

Chlorophenols (CPs) are a group of chemicals that, due to their antimicrobial properties, have been widely used in the formulation of herbicides, pesticides, preservatives and disinfectants, but also dyes, phenolic resins and paper (Wen et al., 2013; Ya et al., 2017). They are characterized by strong odour, high toxicity, carcinogenic effects and low biodegradability depending on the number and position of chlorines in the aromatic ring (Igbinosa et al., 2013). Their extended use and high persistence in the environment have led to the pollution of superficial and ground water resources as well as soils, for this reason their disposal has become a major environmental concern (Aristov and Habekost, 2010).

In the literature, biological aerobic and anaerobic treatments of CPs have been investigated. However, long acclimation and hydraulic retention times were required due to their low biodegradability and toxic effects of the CPs (Field and Sierra-Alvarez, 2008; Rodriguez et al., 2013). Advanced oxidation processes (AOPs), such as Fenton, ozonization, wet air oxidation and photochemical processes have also been studied for the degradation of organochlorinated compounds. However, effective and economical oxidation of chlorinated pollutants requires the choice of appropriate catalytic materials and may produce harmful byproducts (Garba et al., 2019; Sun et al., 2014; Sun et al., 2011).

During the last years, the electrochemical reductive dechlorination (ERDC) approach is considered as a promising method for the detoxification of chlorine-containing aromatic hydrocarbons due to its high reactivity, mild reaction condition and low maintenance requirements (Zhou et al., 2019). ERDC does not lead to complete degradation of the pollutant but generates more biodegradable intermediates that

could be subsequently removed by the most appropriate technology (Descorme, 2017).

The ERDC of chlorinated organics by electrocatalytic reductive process involves the direct degradation pathway based on the direct electron transfer and the indirect degradation pathway by the atomic H*, mechanism known as electrocatalytic hydrogenolysis (ECH), (Zhou et al., 2019). This process can be described by eq. 1-4 (Chen et al., 2006; He et al., 2016).

In the ECH process, protons (H⁺) in aqueous solution are reduced to atomic hydrogen (H*, a strong reducing agent) on the cathode surface, which subsequently attacks and cleaves C–Cl bonds to achieve hydrodechlorination. H* may also evolve into molecular hydrogen (H₂) as side reaction at a more reductive potential, competing with the ECH pathway (Jiang et al., 2017). Some factors such as the applied potential, electrode material and operating pH are crucial to achieve an efficient ERDC process (Jiang et al., 2018; Peters et al., 2014). Various catalyst, composites and alloys for ERDC have been tested. Among them, Pd has shown much more effectiveness in promoting the dechlorination reaction due to its excellent ability to absorb hydrogen into its lattice (Sun et al., 2011).

Regarding the energy consumption, during the last years bioelectrochemical systems (BESs) have emerged as an efficient tool to achieve the ERDC at reduced anode

potentials due to the energy contributed by the microbial metabolisms (to -300 mV vs SHE at OCP) (Wen et al., 2013).

BESs can present different configurations, but in most of the cases they are based on a biotic anode and an abiotic cathode. At the biotic anode, the electrochemically active microorganisms bio-catalyze the oxidation of an organic substrate, releasing electrons to the anode. At the abiotic cathode, the electrons are consumed in a reduction reaction such as the reduction of oxygen to water, protons to hydrogen, or different types of organic pollutants to obtain more reduced and less refractory forms.

Depending on the thermodynamic energy balance, two different configurations can be observed in BESs. On the one hand, when the anodic and cathodic reactions are spontaneous the chemical energy is converted into electrical energy behaving the system as a Microbial Fuel Cell (MFC). However, when the reactions are not spontaneous, it is necessary to supply energy by means of a power supply to transform the chemicals behaving the BES as a Microbial Electrolysis Cell (MEC) (Wang and Ren, 2013). In the literature it has been reported that, for a defined chemical transformation, the energy consumed by a MECs is lower than that of a pure electrochemical system due to the energetic contribution of the microorganisms (Wen et al., 2013).

There are some works dealing with the transformation of different types of organochlorines in wastewater by means of BES, both in bioanodes, oxidizing the organochlorines (Hassan et al., 2016; Hassan et al., 2018; Lai et al., 2017; Wang et al., 2019), or biocathodes, where the target is the dechlorination of the molecule (Chen et al., 2019a; Chen et al., 2019b; Huang et al., 2014).

The coupling of bioanodes with the electrocatalytic dechlorination of CPs is a recent focus of study, arising as a feasible and promising technology with lower power consumption compared to the established pure electrochemical technologies (Leon-Fernandez et al., 2019; Wen et al., 2013).

This work studies the effect of the cathodic pH and operating mode of BESs (as MFC or MEC) on the electro-dechlorination of 2,4-dichlorophenol (2,4-DCP). The 2,4-DCP is a relevant chemical compound because it is commonly used in chemical industry (Cao et al., 2016) and especially as raw product for the fabrication of widely used pesticides such as 2,4-dichlorophenoxyacetic acid (Carboneras et al., 2017). Research coupling bioanodes and ERDC processes at the cathode is still scarce, and no studies for 2,4-DCP dechlorination by means of BESs have been reported to date. **Because of the lack of studies, it was considered interesting to study the pH and operating mode with the aim to enhance the dehalogenation process.**

2. MATERIALS AND METHODS

2.1. Experimental set-up

The set-up used in this work consisted in 3 replicates of a BES. Additionally, a reference test cell with abiotic anode was used to isolate the contribution of the anodic electroactive bacteria. The BESs were operated at 25°C; with an external resistor of 120 Ω (when working as MFC) or with an external voltage input of 0.6 V (when working as MEC). Each BES consisted of two chambers, with 0.1 L volume each, separated by a proton exchange membrane (PEM, Nafion® 117, DuPont). Carbon felt (KFA10, SGL Carbon Group®) was used as anode material due to its capacity for supporting the biofilm (Leon-Fernandez et al., 2019). The dimensions of the carbon felt electrode were 2.5 × 2.5 × 0.8 cm, specific area of 3.53 × 10⁵ cm² g⁻¹ and a porosity of 0.95. Carbon cloth was used as cathode, with Pd load of 0.5 mg cm⁻². Its dimensions were 2.5 × 2.5 cm. A scheme of the set-ups used in this work is presented in Figure 1a.

Figure 1. (a) Conceptual description of the BES reactor. (b) Expected reductive dechlorination mechanisms at the cathode.

The catalyst ink for Pd deposition on the cathode consisted of commercial 40% Pd/C Vulcan XC-72R Carbon Black (Fuel Cell Store), Nafion™ ionomener (alcohol-based dispersion at 5 wt. %), and isopropanol as a dispersing solvent. The ratio 40% Pd/C – Nafion solution was 1:8 and the catalyst loading on the cathode was 0.5 mg Pd/cm². The crystal structure of the electrodeposit was analyzed with a Philips PW-1700 X-ray diffractometer with rotating anode, using Cu K α radiation with $\lambda = 1.5413 \text{ \AA}$. Figure SM1 reports on X-ray diffraction analysis of the carbon cloth electrode with 0.5 mg cm⁻² Pd load, corresponding the peaks to Pd (He et al., 2016).

2.2. Anolyte and catholyte composition

The synthetic wastewater with 300 ppm of 2,4-DCP was used as catholyte. 100 mmol L⁻¹ phosphate buffer was used to keep the cathodic pH at 7 or 5. The phosphate buffer to keep pH=7 was made of 8.660 g L⁻¹ of Na₂HPO₄ and 5.308 g L⁻¹ of KH₂PO₄; and 0.207 g L⁻¹ of Na₂HPO₄ and 13.410 g L⁻¹ of KH₂PO₄ for pH=5.

Anode microbial growth medium consisted of: CH₃COONa 1 g L⁻¹, Na₂HPO₄ 3 g L⁻¹, KH₂PO₄ 0.7 g L⁻¹, (NH₄)₂SO₄ 0.8 g L⁻¹, MgSO₄·7H₂O 0.2 g L⁻¹, and (NH₄)₂Fe(SO₄)₂·6H₂O 0.04 g L⁻¹. The fresh anolyte medium had a pH of about 7.44 and a conductivity of 5.71 mS cm⁻¹.

2.3. Start-up and stationary operation

The anodic compartment of the BES was inoculated with a microbial consortium from another acetate-fed MFC. During the start-up and maintenance stages, 80% of the anolyte was replaced by fresh anodic medium every 2 days. In order to facilitate the

anodic biofilm development, oxygen reduction to water was used as cathodic reaction **by pumping air to the catholyte**. In the literature, it has been described that coupling the bio-catalyzed acetate oxidation with the oxygen reduction reactions is a simple way to induce the electrical response of electroactive bacteria, with low maintenance (Gonzalez del Campo et al., 2014).

Once the electrogenic biofilm was developed and the MFCs performed reproducible batch cycles of exerted voltage (maximum cell voltage of around 0.23 V every cycle), the cathodic reduction reaction of oxygen was substituted by the electroreductive dechlorination of 2,4-DCP. To do that, the cathode aeration was stopped and the synthetic wastewater containing 300 mg L⁻¹ of 2,4-DCP and phosphate buffer was added to the cathodic compartment. Moreover, in order to ensure anaerobic conditions, anolyte and catholyte were purged with nitrogen gas at the beginning of each batch experiment.

2.4. Analytical measurements

Chlorophenols were determined by using high-performance liquid chromatography (HPLC) (Jasco, Japan) using a column Kinetex 5 μ m Biphenyl 100 Å, 150mm×4.5 mm (Phenomenex, Torrance, CA, USA). The mobile phase consisted of 30:70 v/v acetonitrile/0.1% phosphoric acid (flow rate of 1 mL min⁻¹). The injection volume was 20 μ L and the UV detection wavelength was 220 nm.

Chloride concentration was determined using a Metrohm 930 Compact Ion Chromatograph coupled to a conductivity detector. The column employed to determine the anions was a Metrosep A Supp 7 column, using a mobile phase consisting of 85:15 v/v 3.6 mM Na₂CO₃/acetone at a flow rate of 0.8 cm³ min⁻¹.

Sodium acetate concentration was determined through HPLC analysis using an Agilent 1260 Infinity equipment containing a column Hi-plex H (300 × 7.7 mm, 8 μm). The mobile phase was 5 mmol L⁻¹ H₂SO₄, the wavelength was 210 nm and the flow rate 0.4 mL min⁻¹.

Chemical oxygen demand (COD) was determined using Spectroquant® COD cell tests and a Pharo 100 Merck spectrophotometer. Conductivity and pH were determined with a Crison Cm 35 and a GLP22 Crison devices, respectively

To determine the biodegradability, BOD tests were performed in an Oxitop IS 6-Var. BOD is determined measuring the oxygen consumed by the microorganisms, which oxidize the organic matter contained in the sample. The samples were inoculated with 2.0 mL of activated sludge taken from a conventional WWTP described elsewhere (Rodríguez Mayor et al., 2004) and trace minerals solution was added (Eaton et al., 2005). In addition, 2 droplets of *N-Allylthiourea* reagent were added to the samples for nitrification inhibition throughout the tests.

2.5. Electrochemical characterization

Linear sweep voltammetries (LSVs) were performed at 25°C by using an Autolab potentiostat/galvanostat (PGSTAT-302N) at a scan rate of 0.5 mV s⁻¹ and with magnetic stirring. The carbon cloth electrode with Pd load was used as working electrode (WE), and an Ag/AgCl electrode and a Pt wire were used as reference (RE) and counter electrodes, respectively.

Polarization and power curves were carried out by changing the external resistance.

During the bio-electro-dechlorination experiments, electrical current produced by the BESs was recorded every 5 minutes by means of a Keithley 2000 multimeter. Current density was calculated considering the projected cathodic area.

The cathode and anode potential of the BESs were measured against an Ag/AgCl RE.

Nitrogen gas was sparged into the solutions before the experiments to remove the dissolved oxygen.

2.6. Faradaic Efficiencies

Cathodic (eq. 5, reductive dechlorination reactions) and anodic faradaic efficiencies (eq. 6, oxidation of sodium acetate) were calculated as follows (Modin et al., 2017):

$$\eta_c = \left(\frac{\int_0^t I dt}{F \sum (n_i \Delta m_i)} \right)^{-1} \quad (5)$$

$$\eta_a = \left(\frac{\int_0^t I dt}{F \sum (n_i \Delta m_i)} \right) \quad (6)$$

where I is the current intensity in A, t is the time in seconds, F is the Faraday's constant (96485.3 C mol⁻¹), n_i is the number of electrons involved in the electrochemical reaction per mol of reactant and Δm_i is the molar variation of reactant i in mol.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization.

Fig. 2a presents the linear scan voltammetries with the 0.5 mg cm⁻² Pd load carbon cloth electrode as WE to study the electrocatalytic dechlorination of 2,4-DCP. The electrolyte used was the solution employed as synthetic wastewater, with 300 ppm of 2,4-DCP and 100 mM of phosphate buffer. The reductive dehalogenation reactions proposed were based on the ECH mechanisms, defined in eq. 1-4. To accomplish this, H⁺ reduction reaction is required. These LSVs were carried out from OCP to more negative potentials at two different pH values, 7 and 5, in order to identify the pH effect. The expected dechlorination reactions taking place on the WE are those presented in equations 7 and 8. In these equations x-CP represents both 2-CP and 4-CP.

The starting potential of the LSV was 0.24 V vs Ag/AgCl at pH=7 and 0.33 at pH=5, being shifted towards a more positive value. The same effect occurs with H₂ evolution reaction (HER) along with electrocatalytic hydrogenolysis (ECH) mechanisms, both pH dependent, which implies water electrolysis and atomic hydrogen adsorption (as described in ECH mechanisms, eq. 1 - 4). The starting potential for H⁺ reduction occurred at around -0.16 V and -0.06 V vs Ag/AgCl at pH 7 and 5, respectively, being shifted towards more positive values at pH=5 as detailed above.

After the LSV tests, samples of the electrolyte were taken and read through liquid chromatography, allowing to identify the peaks corresponding to 4-CP, 2-CP and

phenol, verifying the initial hypothesis of the electrocatalytic hydrodechlorination.

Negligible current was generated by using the bare-carbon cloth electrode as blank, without Pd deposition. In this case, the concentration of 2,4-DCP remained constant and its 2-CP, 4-CP and phenol were not found through liquid chromatography.

In order to discard that the region of limiting current was due to the direct electron transfer dechlorination, owing to mass transfer limitations of the organochlorines from the bulk to the electrode surface, a chronoamperometry test was run. This test was carried out during 24 hours, fixing the potential at 0 V at pH=7 and at 0.15 V vs Ag/AgCl at pH=5, and no intermediates of 2,4-DCP dechlorination were identified through HPLC analyses, disregarding this hypothesis. In addition, to complement this test and to evaluate the minimum potential to achieve dechlorinating response, successive 6 hours chronoamperometry test were run, increasing the fixed potential in each step (see Fig. SM2). This test was run at pH=7 and pH=5, obtaining slight dechlorinating activity at potentials of -0.05 and 0.1 V vs Ag/AgCl, respectively (small peaks corresponding to the intermediates were found through HPLC analyses). The dechlorinating response increased gradually with the potential applied, as expected.

The LSV test was also run in absence of 2,4-DCP, where the electrolyte was only containing 100 mM phosphate buffer. The profile of the LSV, for both pHs, did not show significant differences to the ones shown in Fig. 2a. This demonstrates again that the pathways for 2,4-DCP dechlorination is through ECH mechanisms, where H^+ reduction and adsorption onto the Pd active sites is required.

Fig. 2b shows the LSV of the carbon felt electrode once the electroactive culture was developed. The OCP value was -0.493 V vs Ag/AgCl, negative value in agreement with the literature for a properly developed biofilm (Kato, 2017). The current generated

corresponds to the biological assisted electrochemical oxidation of sodium acetate to HCO_3^- through extracellular electron transfer (EET), as also corroborated by HPLC analysis, where the concentration of sodium acetate was lower than at the beginning of the test. The concentration of sodium acetate remained constant when the LSV was performed to the blank carbon felt electrode without electroactive biofilm developed on its surface. The value of the limiting current was around 0.73 mA cm^{-2} , value reached at potentials over $-0.2 \text{ V vs Ag/AgCl}$. In addition, the test was also run on the biofilm developed electrode in absence of sodium acetate. In this case, the current exerted by sweeping the potential towards more oxidative potentials is far lower compared to the previous one containing substrate, justifying that the current exerted comes from the bio-catalyzed sodium acetate oxidation.

Since the starting potential of the HER (and ECH) is over the starting potential of the sodium acetate oxidation to HCO_3^- , this redox couple is thermodynamically feasible. Therefore, these systems are able to work under MFC mode, with no external energy input required. Fig. 2c reports on the polarization and power curves performed to the MFCs, for cathode at pH=7 and pH=5. As the cathodic reactions are promoted under more acid pH, greater power and current intensity were achieved when working with cathode pH=5. The arrows indicate the initial operating conditions of the experiments, for an external resistor of 120Ω .

Figure 2. (a) LSV for 2.5 x 2.5 cm carbon cloth electrode with 0.5 mg cm⁻² Pd load, 350 rpm magnetic stirring (blank: no Pd load on WE). (b) LSV for 2.5 x 2.5 x 0.8 cm carbon felt with electroactive biofilm, 60 pm magnetic stirring (blank: abiotic anode). (c) Polarization and Power curves performed to the MFCs at cathode pH=7 and pH=5.

3.2. Evaluation of the cathodic dechlorination in the BESs.

Bioelectrochemical systems operated as MFC were run in different catholyte pH conditions in order to study the effect of this variable on the dechlorination rate.

Additionally, the effect of applying electrical energy to promote the electrochemical reactions was studied, working the systems as MEC at cathode pH=7.

To do that, three batch experiments were run. The first batch test was performed operating under MFC mode at pH=7 in the catholyte and external resistance of 120 Ω . The second test was performed with the same MFC configuration but setting the pH of the catholyte at 5. The third test was carried out operating as MEC at pH 7, with an external voltage input of 0.6 V. Additionally, abiotic reference tests were carried out in all the cases to isolate the performance of the microorganisms. In all the cases, 3 replicates were performed to ensure the reproducibility.

Figure 3 shows the evolution in the BESSs of 2,4-DCP, the dechlorination percentage and the acetate profiles throughout the batch processes. The % of dechlorination were calculated according to [equation 9](#) (concentration in mol L⁻¹).

$$\% \text{ dechlor. (t)} = \frac{[\text{Cl}^-]_t}{2 \cdot \{[2,4\text{-DCP}]_t + [4\text{-CP}]_t + [2\text{-CP}]_t + [\text{phenol}]_t\}} \cdot 100 \quad (9)$$

Figure 3. Evolution of the species in the BESSs. (a) 2,4-DCP evolution over time, (b) % of dechlorination over time, (c) sodium acetate evolution over time.

All the BES configurations studied showed a good performance on the electro-dechlorination of 2,4-DCP. The MEC and MFC with cathode at pH=5 achieved practically a total dechlorination. In the case of the MFC with cathode pH=7, it was achieved an 88% of dechlorination after 3 d of treatment. By decreasing the cathode pH, the 2,4-DCP removal rate was slightly enhanced, and the generation of phenol was slightly promoted, as shown in Fig. 4 where the generation of phenolic species throughout the batch experiments is presented. Before reaching the final dechlorinated product (phenol), mono-chlorophenols are formed. Analyzing the results presented in Fig. 4, it seems that the chlorine in para position is more likely to abandon the aromatic ring than the chlorine in ortho position, since the selectivity to 2-CP was higher than for 4-CP. Similar results were previously reported in the literature (Sun et al., 2014; Tsyganok and Otsuka, 1999).

Figure 4. Evolution of phenolic species and chlorides generated throughout the dechlorination batch experiments. (a) MFC mode ($r_{ext} = 120 \Omega$), catholyte with $pH = 7$; (b) MFC mode ($r_{ext} = 120 \Omega$), catholyte with $pH = 5$; (c) MEC mode ($V_{cell} = 0.6 V$), catholyte with $pH = 7$.

At lower pHs, ECH reactions are promoted and occur at more positive potentials (Fig. 2a). Hence, the dechlorination process was enhanced and the cell potential exerted by the MFC increased operating at cathode pH=5, as can be seen in Fig. 2c.

Regarding with the current density experienced by the BES systems under the different operating conditions, they are presented in Fig. 5. As expected, slightly higher current was attained under MFC mode with cathode at pH 5 compared to pH 7 during the first 2 days of operation. The current dropped progressively with the depletion of the chlorophenols (electron acceptors), as sodium acetate was still available in the anolyte (Fig. 3c), not being the limiting factor.

Figure 5. Current density produced by the BESs in the batch experiments under different operating mode.

When the BESs were run under MEC mode, by applying 0.6 V to promote the electrochemical reactions, the dechlorination rate was enhanced compared to the systems in MFC mode, achieving the total dehalogenation after 2 days (Fig. 3). Moreover, the accumulation of 4-CP and 2-CP was practically negligible, what means that by supplying external energy input the dechlorination rate of the mono-chlorophenols was also enhanced (Fig. 4c). Phenol and chlorides generation occurred faster and the amount of Cl^- agrees with the mass balance. However, and in contrast with the experiments under MFC mode, the concentration of phenol started to decrease after the first 24 hours of operation. This apparent imbalance was due to a further electrocatalytic hydrogenation of phenol to cyclohexanone, which was identified by GC-MS analysis. Other possible products from phenol hydrogenation such as cyclohexanol or cyclohexane were not found. This further reduction of phenol to cyclohexanone as the main product has been previously reported for pure electrochemical dechlorination of 2,4-DCP in electrolysis cells using Pd catalyst load on the WE (Sun et al., 2012a; Sun et al., 2012b). Complementarily, Table SM1 shows the biodegradability (in terms of BOD at $t = \infty$ and BOD/COD) of the different chlorinated products and cyclohexanone. The less chlorines bonded to the molecule, the higher the biodegradability, being cyclohexanone the most biodegradable one after phenol. This highlights the relevance of the electrocatalytic hydrogenation process studied in this work.

A far higher current density was achieved in the MEC systems compared to MFC mode as the electrodes are polarized, promoting the electrochemical reactions. However, most of the current is not intended for the dechlorination reactions, but for H_2 evolution; the fluctuations on the current density experienced during the first 30 hours

are due to the manual control of the cathodic pH to 5, since it increases faster under MEC operational mode due to the promotion of the HER, which consumes protons. Figure 6 reports on cathode and anode potentials of the BESs under the different operating modes. The cathode potential when working as MEC mode was shifted towards more negative values as the electrodes were polarized because of the external voltage input. It was reached a steady value of about -0.68 V vs Ag/AgCl during the first 1.5 days and dropping to -0.6 V vs Ag/AgCl after the depletion of the 2,4-DCP. At this potential, the promotion of H_2 is more important (see Fig. 2a), what leads to higher current densities (Fig. 5) but lower faradaic efficiencies, as discussed later. In addition, at higher current densities and more negative potentials, ECH mechanism is promoted (competing with the HER), since this pathway for the electrocatalytic dechlorination implies water electrolysis and H^* chemisorption on Pd active sites. Hence, working under MEC mode allowed to achieve faster dechlorination rates. In addition, working under MEC mode promoted the bio-assisted anodic oxidation of sodium acetate through EET pathways, leading to the complete removal after 2 days of operation.

Figure 6. (a) Cathode potential; (b) Anode potential.

Under MFC mode, the cathode potential at pH=5 was slightly higher than that for pH=7 at the initial conditions since the formal potential of the cathode reactions was shifted to more positive values. In the MEC, the cathode potential was poised at more negative values, potential at which HER and ECH are further promoted. The cathode potential was always positive in the reference tests with abiotic anode; around 0.167 V vs Ag/AgCl in the MEC reference test and close to the equilibrium potential (starting potential of the LSVs, Fig. 2a) for pH=5 and pH=7, 0.33 and 0.26 V vs Ag/AgCl respectively in MFC reference tests. Hence, no dechlorination reaction took place in the reference tests.

The anode potential under MEC mode got more positive values than those for MFC mode, at around 0.21 V vs Ag/AgCl during the first 1.5 days and at 0.03 V vs Ag/AgCl afterwards due to the sodium acetate abatement in the anolyte. The anode potential under MFC mode for pH=7 and pH=5 stabilized at -0.43 V vs Ag/AgCl.

3.3. Electrical performance of the BES

Figure 7 reports on the faradaic efficiencies of the BESs for the different operational configurations. Anodic faradaic efficiencies give an idea of how much sodium acetate is been oxidized through bioelectrochemical pathways to give electrons. On the other hand, cathodic faradaic efficiencies give an idea of how many electrons are intended for the dechlorination of the CPs and how many to other side reactions (in this case, essentially hydrogen evolution). The BESs showed similar cathodic efficiencies when they were run under fuel cell mode for both cathode pH=7 and pH=5, decreasing with

time due to the depletion of chlorophenols at the cathode, that function as final electron acceptors. Therefore, the dechlorination reactions became less important than the H_2 evolution leading to lower faradaic efficiencies. However, the cathode potential when working the systems under MEC mode was polarized towards more negative potentials, what resulted in higher dechlorination rates but also favoring the H_2 evolution as side reaction, what resulted in lower cathodic faradaic efficiencies compared to MFC mode.

Regarding the anode performance, again when working under MFC mode for both cathodic pH=7 and pH=5, the systems reported similar behavior. The efficiencies showed a decreasing trend due to the growth of non-electroactive species of microorganisms over time, which lead to the biodegradation of the sodium acetate through non-(bio)electrochemical pathways. The values for the anodic faradic efficiencies under MFC mode are in agreement with the literature for bioanodes inoculated with a mixed culture (Beegle and Borole, 2018). Nevertheless, as the electrochemical reactions are promoted under MEC mode, the anode performance showed higher efficiencies compared to the MFCs. It can be notice that after the second day, the anodic efficiencies increased dramatically, reaching values over 100%. As the sodium acetate concentration was almost depleted during the last 24 hours, results from Ec. (6) are very sensitive to small variations on the current exerted by the MECs, which also was very low during the last day of experiment. As the sodium acetate concentration was almost nil, the electrons generated at the anode are mainly due to endogenous respiration of electroactive bacteria, leading to positive efficiencies over 100%.

Figure 7. Evolution of the faradic efficiencies in the BESs. (a) Cathodic efficiencies, (b)

Anodic efficiencies

Regarding the energy efficiency, conventional electrochemical technologies applied for the electrochemical dechlorination of 2,4-DCP need to operate under electrolysis mode, with significant energy input required (Sun et al., 2012; Sun et al., 2014b). In this sense, BESs for this application may have lower kinetics (which can be slightly enhanced by working under electrolysis mode or catholyte acidification), but they are able to accomplish this process with coupled power generation and cheap anode materials. In addition, for the sake of clearness in this study, sodium acetate was used as fuel at the anode and perfectly monitored to better assess the electrical behavior of the systems; however, other organics from wastewaters could be used as fuel, accomplishing the simultaneous treatment of both wastewaters: removal of organic matter at the anode through bio-catalyzed oxidation and the dechlorination at the cathode.

4. CONCLUSIONS

The main conclusions that can be extracted from this work are the following:

It is feasible to achieve the bio-assisted electrocatalytic hydrodechlorination of 2,4-DCP in the abiotic cathode of an MFC under mild operating conditions. Results show that a more acid cathode pH enhances the electrochemical dechlorination because of the promotion of the electrocatalytic hydrogenolysis (ECH) mechanism. Power generation was also enhanced at more acid cathode pHs.

When operating as MEC by poisoning the cathode towards more negative potentials, the ECH kinetics was further enhanced and higher current densities were observed. 81% of dechlorination was reached after 24 hours of operation in batch mode and practically a total dechlorination after 48 hours. Moreover, phenol, the final dechlorinated product, was further hydrogenated to cyclohexanone under these mild operating conditions in MEC mode.

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