DEHALOGENATION OF TRICHLOROETHYLENE IN MICROBIAL ELECTROLYSIS CELLS WITH BIOGENIC PALLADIUM NANOPARTICLES

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INTRODUCTION

Nanopalladium catalysts can be synthesized by the precipitation of palladium (Pd) on the surface of bacteria leading to the production of biogenic Pd nanoparticles (bio-Pd). For example, *Shewanella oneidensis* can reduce Pd(II) and subsequently precipitate it as Pd(0) nanocrystals on their cell wall and in their periplasmic space when a hydrogen donor is provided (De Windt *et al.*, 2005). No expensive and harmful chemicals are required as the bacteria serve as reductant for the Pd salt and as stabilizer of the Pd nanoparticles. Bio-Pd has been reported to catalyze efficiently the dehalogenation of the groundwater contaminant trichloroethylene (TCE) (Hennebel *et al.*, 2009). In this conversion, bio-Pd was used as catalyst. Thus an external electron donor such as hydrogen gas or formate was required. In large-scale applications, the use of hydrogen gas can give rise to large costs and technical difficulties.

Microbial electrolysis cells (MECs) can be used for the production of hydrogen gas, however this innovative technology was never considered to deliver hydrogen for bio-Pd catalyzed dehalogenation reactions. In MECs, organic material is oxidized by electrochemically active microorganisms at the anode. Subsequently, the microorganisms transfer the electrons resulting from this oxidation to the anode. Through an electrical circuit, the electrons are transported to the cathode, where they are consumed for hydrogen formation (Mu *et al.*, 2009). In contrast with microbial fuel cells (MFCs), in which electrical energy can be extracted from the electrical circuit, one needs to supply electrical energy to the electrical circuit of an MEC by means of a power source.

In this study, the application of bio-Pd in the cathode of an MEC as a catalyst for pollutant reduction was compared with an MEC without bio-Pd and tested in the dehalogenation reaction of the groundwater pollutant TCE. Additionally, it was tested if different amounts of bio-Pd at the cathode influenced the dehalogenation reaction at the cathode.

MATERIAL AND METHODS

**Microbial electrolysis cell construction and operation**

The MEC was made of two Plexiglas frames (12.5 \times 8 \times 1.5 \text{ cm}^3 \text{ per frame}; 0.15 \text{ L total cathodic compartment (TCC) of which 0.07 L net cathodic compartment (NCC)}). The anodic and cathodic frames were filled with 160 g graphite granules (type 00514, Le Carbone, Belgium) and were connected to the external electrical circuitry with a graphite rod current collector (Morgan,
Belgium). A cation exchange membrane (CEM) (Ultrax CMI7000, Membranes International Inc.) was used between the anodic and cathodic frame. As electrolyte for anode and cathode a minimal medium, consisting of 6 g L⁻¹ Na₂HPO₄·2H₂O, 3 g L⁻¹ KH₂PO₄, 0.1 g L⁻¹ (NH₄)₂PO₄, 0.1 g L⁻¹ Ca₃(PO₄)₂ and 0.5 mL L⁻¹ of a tracemetal solution (Clauwaert et al., 2009) was used. The electrolyte (400 mL) was sparged with N₂ and pumped through cathode and anode in a separate recirculation mode at a flow rate of 24 mL min⁻¹. The anode medium was inoculated with a mixture of anaerobic sludge and anode medium of an active MFC and 1 g L⁻¹ sodium acetate was added as feed. After the successful start-up of the MEC, the cathode medium was spiked with 100 mg L⁻¹ TCE for the dehalogenation experiments. The headspace and the electrolyte of the cathode were sampled via a sample port without opening the system at time t = 0, 1, 2, 3, 4, 5, 6, 7 and 24 hours. For operation in MEC-mode, an external power source (PL-3003D, Protek, USA) was used to apply a potential difference of -0.8 V between anode and cathode. The voltage difference between the anode and the cathode was measured to verify the applied cell voltage. The voltage between the cathode and an Ag/AgCl reference electrode was monitored to measure the cathode potential. The voltage drop over a 1 Ω resistor in circuitry was used to measure the current flowing from anode to cathode. These voltage differences were measured with a 34970A Data Acquisition Switch unit (Agilent, Belgium).

Production of bio-Pd coated graphite
Bio-Pd was produced as described by De Windt et al. (2005). Different amounts of a 500 mg L⁻¹ bio-Pd suspension were mixed with the graphite granules and dried for 48 h at 100°C to result in 1 mg Pd g⁻¹ graphite and 5 Pd mg g⁻¹ graphite, respectively. The cathode compartment was supplied with 160 g of bio-Pd coated graphite granules. For the anode compartment, only non-coated granules were used.

Analytical methods
Analysis of TCE and lower chlorinated reaction products such as vinyl chloride and dichloroethylenes, was performed by gas chromatography (GC) (CP-3800, Varian, USA) with a flame ionization detector (FID). GC conditions are described by Hennebel et al. (2009). Chloride (Cl⁻) concentration was determined using a Methrom 761 Compact Ion Chromatograph (Methrom, Switzerland) equipped with a conductivity detector.

RESULTS AND DISCUSSION
Bio-Pd was coated on the graphite of the cathode to enhance TCE dechlorination. Two different Pd concentrations were applied, i.e. 1 and 5 mg Pd g⁻¹ graphite, and the Cl⁻ and ethane formation were monitored over 24 hours (Figure 1). When applying a cell voltage of -0.8 V, a clear difference between the varying concentrations could be observed. One mg Pd g⁻¹ graphite in the cathode did not result in an improved formation of Cl⁻ or ethane in comparison to non-bio-Pd containing graphite. Moreover, the Cl⁻ concentration after 24 hours amounted to 32 ± 6 mg L⁻¹ Cl⁻, which was lower than the formation of 50 ± 3 mg L⁻¹ Cl⁻ in the case no bio-Pd was used. The
same trend was observed for ethane production. After 24 hours, 12 ± 6 % of the added TCE could be recovered as ethane with 1 mg Pd g⁻¹ graphite versus 17 ± 7 % in the case of catalyst-free granules. In contrary, coating the granules with 5 mg Pd g⁻¹ graphite resulted in faster and higher formation of both Cl⁻ and ethane. After 2 hours, already 80 ± 30 mg L⁻¹ Cl⁻ was formed versus 11 ± 5 mg L⁻¹ Cl⁻ in the case of not-coated granules. At the end of the experiment 100 ± 30 mg L⁻¹ Cl⁻ was detected in the cathode (Figure 1 a). The ethane formation was produced more rapidly and to a larger extent as well. After 4 and 24 hours respectively, 18 ± 3 % and 26 ± 4 % of the initially added TCE amount could be recovered as ethane (Figure 1 b). Because the decreased activity in the case of the 1 mg bio-Pd g⁻¹ graphite was observed, batch experiments were conducted to investigate whether the granules coated with bio-Pd as such had a catalytic activity for TCE dechlorination. When external hydrogen gas was supplied, a TCE decrease of 63 % was observed after 24 hours. The Cl⁻ formation of 86 mg L⁻¹ corresponding to app. 30 % TCE (estimated on the base of 3 mol Cl⁻ correspond to 1 mol TCE) confirmed the catalytic transformation of TCE. To investigate the influence of bio-Pd on TCE dehalogenation, cathode granules were coated with bio-Pd at two different concentrations. In case of the 1 mg Pd g⁻¹ graphite, the TCE removal deteriorated while using 5 mg Pd g⁻¹ graphite enhanced the dehalogenation process. However, batch tests pointed out that the 1 mg Pd g⁻¹ graphite coated granules were catalytically active for hydrodechlorination reaction of TCE. It is hypothesized that 2 mechanisms can occur at the same time: (1) electrochemical reduction of TCE and (2) catalytical dehalogenation with bio-Pd as catalyst and electrochemically formed H₂ as the hydrogen donor. Coating the granules with bio-Pd might negatively affect the first mechanism due to the bacterial matrix, which is electrically less conductive, but can enhance the second mechanism. However, also the Pd concentration plays a crucial role as only 5 mg Pd g⁻¹ graphite resulted in higher removal rates. Hence, opting for the second mechanism requires a certain threshold of bio-Pd catalyst and a cathode potential that allows for H₂ production. In this study, -0.8 V was applied to obtain hydrogen at a cathodic potential of about -1 V vs. SHE. However, in theory, an applied voltage of only -0.14 V and a cathodic potential of -0.42 V (vs. SHE) is required for hydrogen production through biocatalyzed electrolysis of acetate (12). In practice, it can be expected that more than -0.14 V will be required for this reaction to proceed due to overpotentials of the system. Further research needs to aim at avoiding these overpotentials. An option can be a variation in reactor design in order to make this an energy efficient process. For example, Rozendal et al. (2006) obtained H₂ production at an applied voltage of -0.5 V and expected to lower this amount to -(0.3 - 0.4) V. In any case, biocatalyzed electrolysis achieves very low energy requirements for hydrogen production while water electrolysis in practice operates at applied voltages well above 1.6 V (Rasten et al., 2003). This means that biocatalyzed electrolysis requires four (Rozendal et al., 2006) to two (this study) times less external energy. The price of hydrogen produced through water electrolysis is strongly dependent on the electricity price. The lower consumption of electrical energy per unit of hydrogen is a strong advantage of biocatalyzed electrolysis. This opens perspectives for the economical and durable production of hydrogen for bio-Pd catalyzed reaction. For example, the hydrogen costs in a pilot-scale
fluidized bed reactor with bio-Pd as catalyst amounted to 2000 € kg\(^{-1}\) hexachlorocyclohexane removed (Hennebel et al., 2010). The use of bioelectrochemically produced hydrogen gas would decrease the costs of this process with a factor of at least 2-4.

**Figure 1**: Influence of the presence of bio-Pd (0, 1 and 5 mg bio-Pd g\(^{-1}\) graphite) coated onto cathode graphite granules on (a) chloride (in mg L\(^{-1}\)) and (b) ethane (in mol % of added TCE) formation versus time; MEC setups were all applied with -0.8 V external potential. Every experiment was performed in triplicate and mean ± standard deviation are shown.

**REFERENCES**


