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Enhanced removal of 1,2-dichloroethane by anodophilic microbial consortia

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ABSTRACT

1,2-Dichloroethane (1,2-DCA) is a well-known recalcitrant groundwater contaminant. New environment-friendly approaches for the removal of 1,2-DCA that does not bring about volatilization of the compound are required. In this study, different anodophilic consortia enriched in microbial fuel cells (MFCs) operated under airtight conditions were shown to effectively degrade 1,2-DCA (up to 102 mg per liter reactor volume per day), while concomitantly generating a current. An anodophilic consortium previously enriched with acetate as the electron donor changed its composition at the rate of 48% per week and increased its richness (Rr) 3-fold, upon adapting to 1,2-DCA as the new electron donor. After being stable, during 1 month of operation, it removed up to 95% of the 1,2-DCA amount in the medium in the first 2 weeks, while converting 43 ± 4% of electrons available from the removal to electricity. A natural consortium from a 1,2-DCA contaminated site changed its composition at the rate of 9% per week and increased its Rr 2-fold, upon adapting to the MFC anode conditions with 1,2-DCA as the electron donor. After being stable, during 1 month of operation, it removed up to 85% of the 1,2-DCA amount in the medium in the first 2 weeks and the coulombic efficiency was 25 ± 4%. The operation of the MFCs under closed circuit conditions resulted in higher 1,2-DCA removal rates than the operation under open circuit conditions, indicating that bioelectrochemical activities enhanced the removal of 1,2-DCA in the MFC anode. The production of ethylene glycol, acetate and carbon dioxide indicated that the anodophilic bacteria oxidatively metabolized 1,2-DCA, probably by means of a hydrolysis-based pathway. The results show that MFCs can be potentially used as a practically convenient technology for the biological removal of 1,2-DCA.

1. Introduction

1,2-Dichloroethane (1,2-DCA), or ethylene dichloride, is the most abundant chlorinated industrial product (Bhatt et al., 2007; De Wildeman et al., 2003). It is also an intermediate in some other industrial processes (such as the synthesis of fluorocarbon and 1,1,1-trichloroethane) (Bhatt et al., 2007; Dinglasan-Panlilio et al., 2006). Poor disposals practices resulted in a wide spreading of this compound in groundwater (Janssen et al., 1984, 1994). This is of major concern since the compound may cause damages to kidney, liver and nerve systems in humans and is a suspected carcinogen (Hughes et al., 1994). Moreover, the possibility of human exposure to it through groundwater is considerable (Hughes et al., 1994).

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Approaches to degrade 1,2-DCA have been investigated intensively. Together with physical and chemical methods, biodegradation of 1,2-DCA using microorganisms deserves attention as it offers environment-friendly and low cost remediation (De Wildeman and Verstraete, 2003; Marzorati et al., 2006). 1,2-DCA can be microbially degraded both under aerobic and anaerobic conditions (Dinglasan-Panlilio et al., 2006). A number of pure cultures capable of aerobically degrading 1,2-DCA have been isolated; most of them belonging to the bacterial genera of *Pseudomonas*, *Xanthobacter* and *Ancylobacter* (Hage and Hartmans, 1999; Janssen et al., 1985; Stucki et al., 1983; Vandenwijngaard et al., 1992). These bacteria use 1,2-DCA as the electron donor and the degradation occurs either through a hydrolysis dehalogenation pathway or through an oxidation pathway both leading to the formation of intermediates such as 2-chloroethanol and monochloroacetate and finally to the formation of CO_2 (Dinglasan-Panlilio et al., 2006; Nobre and Nobre, 2004). Anaerobic degradation of 1,2-DCA is mainly based on reductive dechlorination, in which the compound plays the role of an electron acceptor (Bhatt et al., 2007). Bacteria capable of doing this are *Dehalococoides ethenogenes* (He et al., 2003; Maymo-Gatell et al., 1999) and some methanogens such as *Methanobacterium thermoautotrophicum*, *Methanosarcina barkeri* and *Methylosinus trichosporium* that can cometabolically dechlorinate 1,2-DCA to ethene (Egli et al., 1987; Oldenhuis et al., 1989). Notably, a pure culture, *Desulfitobacterium dichloroeliminans* DCA 1, was reported to be capable of complete reductive dehalogenation of 1,2-DCA to ethene (De Wildeman et al., 2003; Maes et al., 2006; Marzorati et al., 2007). Only recently, anaerobic oxidation of 1,2-DCA with nitrate as the electron acceptor has been reported for the first time (Dinglasan-Panlilio et al., 2006).

One challenge to the current 1,2-DCA degradation technologies is that the compound is volatile (Gordon et al., 2002) and thus can escape into the air from groundwater, causing a secondary pollution. Therefore, a technology that can cope with this challenge is needed. As both aerobic and anaerobic oxidation of 1,2-DCA is feasible, the bioanode of a microbial fuel cell could be used to degrade 1,2-DCA under gastight conditions. In bioanodes, microorganisms catalyze the oxidation of substrates, converting part of the chemical energy available in substrates into electrical energy (Allen and Bennetto, 1993; Clauwaert et al., 2008). Reductive dehalogenation of chlorinated compounds using MFCs has been reported (Aulenta et al., 2007, 2008; Strycharz et al., 2008). However, in those studies, the process was mainly based on the activity of microorganisms at the cathode. In addition, no MFC studies have addressed 1,2-DCA removal. In this article, we reported for the first time the use of a microbial fuel cell for an accelerated removal of 1,2-DCA, based on the anode oxidation of this compound.

2. Experimental section

2.1. MFC reactors

Each microbial fuel cell reactor used in this study was constructed with Perspex frames and contained an anode compartment and a cathode compartment (Fig. 1A). A cation-specific membrane (Ultrex CMI7000, Membranes International Inc., US) separated the two compartments. Each compartment included an endplate ($10 \times 10 \times 1.5\ cm^3$) and a square-holed subframe ($8 \times 8 \times 0.9\ cm^3$), with 0.9 cm being the distance from the endplate to the membrane (Fig. 1A). There were two side holes on each frame for the influent and effluent. The working space of each compartment had a $7 \times 7 \times 0.9\ cm^3$ dimension. The anodic electrode was a graphite plate ($5 \times 4 \times 0.3\ cm^3$) (Le Carbone, Belgium) in contact with a graphite rod (0.5 cm diameter) (Le Carbone, Belgium) that penetrated the anode endplate through a hole (0.5 cm diameter). Hence, the net anodic capacity (NAC) was 38 mL (cm^3) or $38 \times 10^{-6}\ m^3$ (=the anode working space − the inserting electrode volume $= 7 \times 7 \times 0.9\ cm^3 - 5 \times 4 \times 0.3\ cm^3$). The cathode working space was filled with graphite granules (diameters between 1.5 and 5 mm, Le Carbone, Belgium) in contact with a graphite rod (0.5 cm diameter) (Le Carbone, Belgium) that penetrated the cathode endplate through a hole (0.5 cm diameter). The catholyte was an aqueous solution of 50 mM $K_3Fe(CN)_6$ and 100 mM KH_2PO_4 buffer (Merck, Belgium) adjusted to pH 7 with 1 M NaOH. It was recirculated through the cathode matrix and replenished before its decoloration (Aelterman et al., 2006). The anode and cathode graphite rods

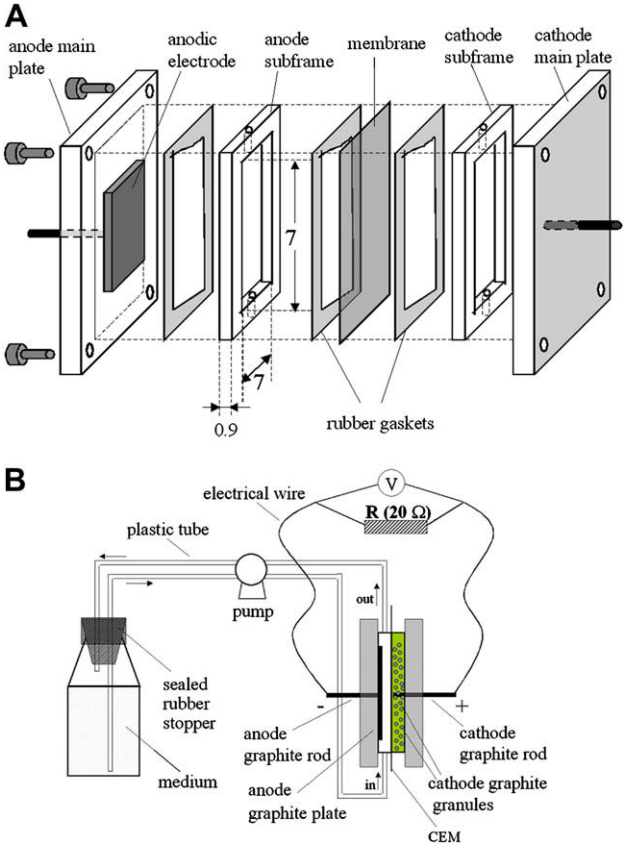

Fig. 1 – Descriptive plot of the MFC reactor (A) and simplified scheme (B) of the setup to treat 1,2-DCA used in this study. R: external resistor; CEM: cation exchange membrane. Not shown in the figure is the cathode loop recirculating the catholyte (hexacyanoferrate). The unit of the dimensions of the anode working space indicated in (A) is cm.