Autotrophic nitrous oxide removal in bioelectrochemical systems

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Introduction & Objectives

Bioelectrochemical systems (BESs) are devices where the oxidation of an electron donor at the anode is coupled with the reduction of an electron acceptor at the cathode, using bacteria to catalyze one or both reactions (Rabaey and Rozendal, 2010). Recently, it has been shown that biocathodes can perform autotrophic denitrification by using the electrons and protons supplied by a bioanode (Clauwaert et al., 2007; Puig et al., 2011; Virdis et al., 2008). The final step in the denitrification pathway is the reduction of nitrous oxide (N_2O) to dinitrogen gas (N_2) and was, until now, never thoroughly investigated in denitrifying biocathodes. N_2O is also an important greenhouse gas with an impact of about 298 times stronger than that of carbon dioxide (Solomon et al., 2007), and is also considered as a significant ozone-depleting substance (Ravishankara et al., 2009). Moreover, anthropogenic sources of N_2O represent at this moment almost 40% of the total N_2O emission (Reay et al., 2007).
This study investigates the N_2O removal in a BES with a denitrifying biocathode. This is the first proof of principle for BES technology as a possible technique for the biological removal of N_2O emissions from anthropogenic point sources.

Materials & Methods

A stack-type BES was used comprising an anodic and cathodic compartment (0.12 L compartment), separated by a cation exchange membrane. Both compartments were filled with granular graphite, resulting in a net anodic (NAC) and net cathodic (NCC) compartment of 0.06 L each. The anode was always fed continuously with acetate at a loading rate of 2.39 kg COD m^{-3} NAC d^{-1}. The cathode was operated in batch by adding a certain volume of 100% N_2O in the headspace of the recirculation vessel. N_2O was the sole electron acceptor present.

Results & Discussion

The cathode of the BES was switched to a batch-fed operation mode with N_2O after a 30-stable period of feeding the denitrifying biocathode continuously with nitrate (loading rate: 0.209±0.001 kg NO_3^--N m^{-3} NCC d^{-1}; removal efficiency: 100±0%). The removal of N_2O in the BES, current production and cathode potential in function of time are presented in Fig. 1. The total nitrogen removal rate clearly followed the same trend as the current production and the cathode potential. During the first 2.5h, a steady nitrogen removal rate of 4.57±0.15 mg N h^{-1} (R^2 = 0.9931) or 1.83±0.01 kg N_2O-N m^{-3} NCC d^{-1} and a maximum current production and cathode potential of 7.3 mA (122 A m^{-3} NCC) and -0.14 V vs SHE were observed, respectively. From that moment on, a gradual decrease of the nitrogen removal rate, current production and cathode potential could be seen, until all N_2O was depleted. The obtained removal rate and current production were in the same range as the values reported for denitrifying BESs with other electron acceptors (nitrate or nitrite), when normalized to the amount of electrons needed to complete the denitrification reaction to N_2 (Clauwaert et al., 2007; Puig et al., 2011; Virdis et al., 2008). The cathodic coulombic efficiency amounted

99%, indicating that all electrons generated and used for current production where recovered for the biological reduction of N_2O to N_2. Furthermore, no ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) were detected in the cathodic liquid.
Control experiments (data not shown) revealed that no N_2O was removed both during open circuit operation (no passing through of electrons from anode to cathode) and during operation with an abiotic autoclaved cathode. This demonstrated that electrons derived from the anodic oxidation reaction of acetate where the sole electron donors present in the cathode, and that denitrifying microorganisms catalyzed the reduction reaction of N_2O to N_2.

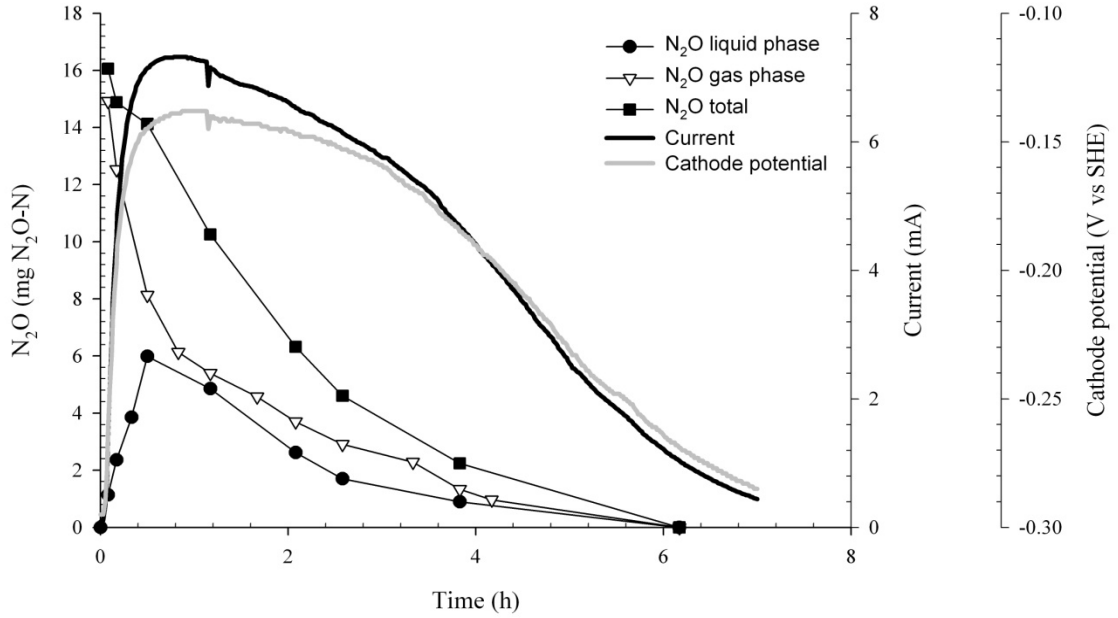

Figure 1. Amount of N_2O (total, gas and liquid), current production and cathode potential in function of time in the BES.

The results obtained in this study demonstrated that a denitrifying biocathode is capable to reduce N_2O as the sole electron acceptor present. Furthermore, the proof of principle is shown for BES technology as a possible biological treatment technique for N_2O emissions from anthropogenic point sources.

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