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Cathodic groundwater denitrification with a bioelectrochemical system

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ABSTRACT

Nitrate-contaminated groundwater has become a common issue during the last decades, due to the increased levels of detected contamination, the related potential health hazards caused by this contaminant presence in drinking water, and the applicable regulations on water supply quality. In this work, the design, start-up and operation of a bioelectrochemically-based system (BES) for groundwater autotrophic denitrification is described, with the aim to investigate its removal capacity in terms of nitrogen forms. The dual-chamber BES reactor was operated for 27 days, reaching stabile nitrate reduction in its cathodic chamber. Initially, an acetate oxidizing biofilm was grown in the anode chamber in step-feeding operation mode, at a fixed potential of +0.397 V vs. Standard Hydrogen Electrode (SHE). After a 3-day-long inoculation time, and 7 days operation as a microbial fuel cell (MFC), the anode and cathode electrodes were functionally inverted, originating a newly configurated BES process. The biologically active electrode was then fed with nitrate-enriched solution (NO_3^- concentration = 100 mg L^{-1}), functioning as a biocathode with fixed negative potential of −0.303 V vs. SHE. Results show that the successfully-induced switch in bacterial metabolism lead to consistent nitrate removal by the BES system with efficiency exceeding 90%. Determination of energy consumption by the process show that these are significantly lower than electrodialysis and other similar reported systems.

1. Introduction

Large part of world population relies on drinking water supplies from groundwater sources, hence concern over the latter's deterioration due to − among the others − increasing nitrate concentrations has risen significantly in recent years [1,2]. Excessive nitrate concentrations in drinking water, mostly deriving from anthropogenic agricultural sources, can lead to health problems and resource use limitations, due to applicable regulations [3,4] and may require careful additional monitoring of the resource [5]. The provision of alternative supply sources could be difficult or, simply, expensive. These issues may present themselves in both developed and developing countries alike, and may be caused by the intensive use of nitrogen fertilizers, crop irrigation with untreated wastewater, or the spread of manure and sludge residuals on agricultural land. Among various existing options for nitrate removal from acqueous solutions, such as ion exchange, reverse osmosis, electrodialysis or chemical reduction of nitrate [6,7], autotrophic denitrification using bioelectrochemical systems (BES) has recently shown interesting results [8]. Other examples of autotrophic denitrification processes for groundwater treatment include using those based on elemental sulfur as an electron donor, that have been extensively studied in recent years [9]. Recently it was shown also that pyrite minerals could be utilized by *T. denitrificans* as single electron donor for groundwater denitrification [10]. Nevertheless, the most common biological denitrification techniques rely on processes based on heterotrophic bacteria [11], in which organic matter plays both the roles of carbon source and electron donor. McAdam and Judd [12] reviewed applications of biological heterotrophic denitrification technologies for nitrate removal from drinking water, identifying membrane bioreactors (MBRs) as the most promising technology applicable at the moment. MBRs were originally developed as wastewater treatment processes, and may solve some issues (such as poor biomass retention) related to the application of traditional heterotrophic processes to drinking water denitrification. The same results could be obtained with similar types of reactor, like Biomass Concentrator Reactors (BCRs) that use different membrane-like media to achieve identical purposes [13–16]. Major cost components of groundwater denitrification treatment with heterotrophic processes remain: the needed addition of organic matter, to avoid process kinetics limitations linked to its otherwise generally low presence in that medium, and the implementation of some type of post-processing (settling, physical retention, and/or other) to remove and subsequently dispose the excess biomass formed during the process.

One of the main advantages of autotrophic denitrification compared

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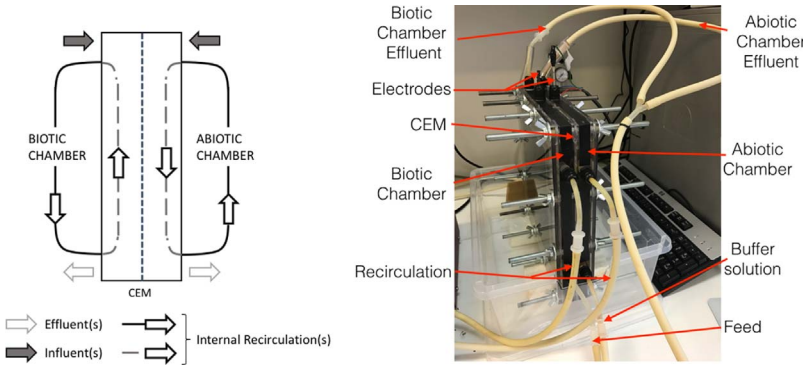

Fig. 1. Scheme (left) and view (right) of the BES-DEN system.

to heterotrophic processes, is the indifference of the presence of any organic matter in the treated solution. Autotrophic bacteria, in fact, source their carbon from inorganic compounds (e.g. bicarbonates), and their electron sources necessary for metabolism are of inorganic origin, as well (e.g. H_2, reduced sulfur, iron or manganese species). In a BES, electrons reach the cathodic chamber from an external source through the electrode: a continuous electron flow can therefore be maintained by a bioanode performing degradation of organic matter (such as in a Microbial Fuel Cell, MFC), or by an abiotic anode jointly with a potentiostat, to maintain cathodic potential at a desired reductive level (as in Microbial Electrolysis Cells, MEC), or by direct electric current (such as Biofilm-electrode reactors, BER).

If autotrophic bacteria are performing denitrification, the obvious electron acceptor is not oxygen, but nitrate and, in addition, nitrite, nitric oxide and nitrous oxide, which represent possible intermediate nitrogen forms prior to the ultimate reduction step to N_2 gas [17]. The aims of this study are the investigation of the removal capacity of nitrates in a BES denitrification reactor (BES-DEN) while monitoring its biochemical activity during the process. A well-functioning BES-DEN could be a valid substitute for other, more costly and less sustainable technologies, for groundwater denitrification.

2. Materials and methods

2.1. System design

The system object of this study is based on a few, simple principles of bioelectrochemical processes that are here briefly summarized: studies had in fact shown, that electroactive biofilm grown in BESs oxidizing organic substrate (e.g. acetate) in anodic conditions, could then be switched to perform nitrate reduction in cathodic conditions [18]. Such “switchable” bioelectrochemical system can thus degrade organic matter, transferring electrons to the anode, but is also capable of transferring electrons from the cathode to nitrates in an anoxic environment, in the absence of organic matter, by activating the same donating and accepting extracellular electron transfer (EET) mechanisms [19]. Application of fixed potentials in the biotic chamber has shown to ensure optimal and reproducible microbial culture conditions since the beginning of system inoculation [19–21].

In this study, a BES-DEN reactor was designed and built, in which the above described phenomena could occur in a controlled fashion, in order to achieve groundwater autotrophic denitrification. Initially the system was inoculated and operated as a MFC [22], under a controlled start-up protocol [20,22]. When the system reached steady conditions, it was switched to operation as a MEC according to the procedure followed by Pous et al. [18]. The BES-DEN system was run for almost one month.

2.2. Experimental set-up

A dual chamber BES-DEN was constructed based on a previously described MFC design [23], consisting of a biotic and an abiotic chambers, located on opposite sides of a single methacrylate 300 × 300 mm cell, separated by a Cation Exchange Membrane (CMI-7000, Membranes International Inc., USA). Purpose of the CEM in a MFC is to allow internal ionic fluxes while preventing mixing of anodic reducing solution and cathodic oxidant. The biotic chamber was filled with granular graphite (mod. 00514, diam. 1.5–5 mm, EnViro-cell, Germany), resulting in a free (net) biotic compartment (NBC) volume of 675 mL. The abiotic chamber contains a folded, thin stainless steel mesh (40 × 20 cm), used as electrode, decreasing the chamber volume to 760 mL net abiotic compartment (NAC). A graphite rod electrode (250 x ϕ4 mm) and a stainless steel rod electrode (250 x ϕ5 mm) are positioned, respectively, in the biotic and abiotic chamber, to allow external electrical connections. Finally, an Ag/AgCl reference electrode (+0.197 V vs. SHE), positioned in the biotic compartment, provides electrical measurement references (Fig. 1). The internal resistance of the cell was estimated, from previous experiences with similarly designed systems, at 33 Ω, and the same external resistance was imposed during the start-up phase as a MFC.

Separated, internal recirculation loops in both chambers were activated (except for the inoculation phase) in order to improve internal mixing of the treated water, and avoid partialisation of reactor volumes. Marprene® tubing connections were used throughout the system, to avoid unwanted oxygen permeation from silicone tubing, with possible loss of anoxicity. Fig. 1 shows the scheme and a view of the system.

2.3. Inoculation and operation

System start-up consisted of three phases: inoculation, MFC-mode operation, MEC-mode operation.

The BES-DEN biotic chamber was initially inoculated with 0.25 L return activated sludge from a local wastewater treatment plant, plus 1.75 L acetate solution as organic substrate. The inoculation procedure followed a protocol perfected during previous successful MFC start-ups [24]. The biotic compartment graphite electrode and filling granular medium provided not only good electrical connection throughout the chamber volume, but also a significantly high specific internal surface area for colonization by the growing biofilm. A phosphate buffer solution (PBS) was introduced in the abiotic chamber, instead. Both solutions were recirculated continuously at a flow rate of 35 ± 5 L d^{-1} for 3 days to allow intensive mixing and uniform inoculation of the entire volumes of both compartments.

During the inoculation/MFC-mode phases, the PBS anodic solution contained 1393.5 mg L^{-1} $CH_3COONa{\cdot}3H_2O$, 20 mg L^{-1} NH_4Cl, 1238 mg L^{-1} Na_2HPO_4, 153 mg L^{-1} NaH_2PO_4 (10 mM, pH = 7.7), 2.6 mg L^{-1} KCl and 0.1 mL L^{-1} trace nutrients solution. The cathodic feed solution was exposed to air insufflation (oxic conditions), while the anodic chamber was air-sealed (anoxic). During this entire period, the potential of the biotic chamber was fixed at +0.397 V vs. SHE using an external potentiostat (NEV3, Nanoelectra, Spain) [18]. These data are summarized