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Effects of process operating conditions on the autotrophic denitrification of nitrate-contaminated groundwater using bioelectrochemical systems

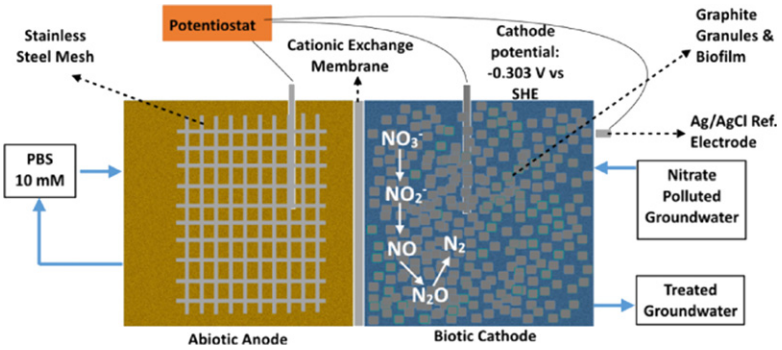
D. Cecconet [a], M. Devecseri [b], A. Callegari [a], A.G. Capodaglio [a,*]

[a] Department of Civil Engineering and Architecture (DICAr), University of Pavia, Via Ferrata 3, 27100 Pavia, Italy
[b] Department of Sanitary and Environmental Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, 1111 Budapest, Hungary

HIGHLIGHTS

- A dual chamber MFC was used for autotrophic denitrification of groundwater.
- Cathode was poised with a potentiostat at −0.303 V vs SHE.
- Different HRTs, nitrate loads, and configurations of the system were tested.
- Max NO_3^- removal rate 62 gNO_3^--N $m^{-3}d^{-1}$; highest TN removal rate 35 gTN $m^{-3}d^{-1}$
- Low energy process consumption was measured.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrates have been detected in groundwater worldwide, and their presence can lead to serious groundwater use limitations, especially because of potential health problems. Amongst different options for their removal, bioelectrochemical systems (BESs) have achieved promising results; in particular, attention has raised on BES-driven autotrophic denitrification processes. In this work, the performance of a microbial electrolysis cell (MEC) for groundwater autotrophic denitrification, is assessed in different conditions of nitrate load, hydraulic retention time (HRT) and process configuration. The system obtained almost complete nitrate removal under all conditions, while nitrite accumulation was recorded at nitrate loads higher than 100 $mgNO_3^-$ L^{-1}. The MEC system achieved, in different tests, a maximum nitrate removal rate of 62.15 ± 3.04 gNO_3^--N $m^{-3}d^{-1}$, while the highest TN removal rate observed was 35.37 ± 1.18 gTN $m^{-3}d^{-1}$. Characteristic of this process is a particularly low (in comparison with other reported works) energy consumption: $3.17 \cdot 10^{-3} \pm 2.26 \cdot 10^{-3}$ kWh/gNO_3^-N removed and $7.52 \cdot 10^{-2} \pm 3.58 \cdot 10^{-2}$ kWh m^{-3} treated. The anolyte configuration in closed loop allowed the process to use less clean water, while guaranteeing identical performances as in other conventional configurations.

1. Introduction

Due to an ever growing world population, exploitation of water resources for drinking water supply is constantly rising everywhere. Groundwater has become, in large parts of the world, the most important source of drinking water (USEPA, 2008); consequently, its quality

* Corresponding author.
E-mail address: capo@unipv.it (A.G. Capodaglio).

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has to be carefully monitored (Capodaglio, 2017a, b; Copetti et al., 2017; Viviano et al., 2017; Capodaglio et al., 2016a) and maintained. Amongst different contaminants, nitrate plays a major role in the assessment of groundwater final quality and fitness for use. Nitrate is widely diffused in groundwater, its presence being assessed in Europe (Angelopoulos et al., 2009; González Vázquez et al., 2005; Strebel et al., 1989), Australia (Thorburn et al., 2003), Asia (Jalali, 2005; Zhang et al., 1996), Africa (Bijay-Singh and Sekhon, 1995), South America (Martínez et al., 2014) and North America (Burow et al., 2010; Kohn et al., 2016; Nolan et al., 1997; Power and Schepers, 1989). The use of fertilizers in agriculture is the most important anthropogenic source of nitrates in groundwater (Bouchard et al., 1992); other sources being animal farming feedlots, landfills, on-site wastewater disposal systems, and leaky sewers (Wakida and Lerner, 2005). High concentrations of nitrates have been detected also in drinking water (Mohebali et al., 2013; Sadler et al., 2016; Thompson, 2001).

The presence of nitrates in drinking water must be avoided, as it is linked to severe health issues in sensitive targets (infants and elders), including infant methemoglobinemia or *blue baby syndrome* (Fan and Steinberg, 1996; Pawełczyk, 2012; Terblanche, 1991). US EPA and WHO guidelines have set a maximum concentration of nitrates (NO_3^--N) in drinking water of 10 mg L^{-1} (USEPA, 2010; WHO, 2011); the maximum value of NO_3^--N acceptable in China has also been recently lowered from 20 to 10 mg L^{-1} (Fan et al., 2009). EU regulations are less strict concerning concentration of NO_3^--N alone (limit is 50 mg L^{-1}) but foresee a combined value with nitrite as well (COU, 1998). Presence of nitrate above regulatory limits in wells may increase water supply costs due to additional treatments needed (Lewandowski et al., 2008).

Different options are available for the removal of nitrates from groundwater, including: physical techniques such as adsorption (Bhatnagar and Sillanpää, 2011; Capodaglio et al., 2015a); chemical techniques as chemical reduction by zero valent iron (Fu et al., 2014), photocatalytic degradation using Au/TiO_2 photocatalysts (Anderson, 2011), electrochemical denitrification (Li et al., 2010), electrocatalytic nitrate reduction (Duca and Koper, 2012), electrodeionization (Zhang and Chen, 2016), reverse-osmosis coupled with nanofiltration (Epsztein et al., 2015) or electrodyalisis (El Midaoui et al., 2002).

Biological process technologies also play a leading role. Biological denitrification can be heterotrophic, widely used in wastewater treatment (Capodaglio et al., 2016b), or autotrophic (Molognoni et al., 2017). In the former case, heterotrophic bacteria use organic matter as source of carbon and electron donor; nitrate is used instead of dissolved oxygen as electron acceptor, and it is reduced step by step to N_2 gas. In autotrophic denitrification, no organic matter is required: bacteria utilize carbon from inorganic compounds (e.g. carbonates) and, since the electron donor is inorganic as well (sulfides, H_2, iron species), this process has the natural advantage, when applied to groundwater treatment (that normally contains little, or no organic matter, but plenty of carbonates), of not requiring organic matter addition that would otherwise be required with heterotrophic denitrification. Hence, heterotrophic groundwater denitrification has higher chemical and treatment costs.

Both types of denitrification processes have been tested using bioelectrochemical systems (BES), showing interesting results. In the case of denitrification using BES, electrons reach the acceptor (nitrate and its reduced products) from an external source. When electrons are produced in the anodic chamber from organic matter degradation, and transferred to the biocathode, the BES is actually a Microbial Fuel Cell (MFC) (Capodaglio et al., 2013). When potential is applied at the biocathode using a potentiostat at a desired reductive level, in combination with an abiotic anode, the configuration is called Microbial Electrolysis Cell (MEC) (Capodaglio et al., 2016c). If electrons are provided using a direct current between anode and cathode, the BES is called Biofilm-Electrode Reactor (BER) (Cast and Flora, 1998).

Heterotrophic denitrification has been performed using BERs (Cast and Flora, 1998) or Microbial Fuel cells (Pous et al., 2013); heterotrophic and autotrophic bacteria in fact can cooperate and coexist simultaneously (Tong et al., 2013; Zhao et al., 2012; Zhou et al., 2007), obtaining an almost complete removal of nitrate from groundwater. Autotrophic denitrification has been applied using BER (Feleke and Sakakibara, 2002; Islam and Suidan, 1998), multi-cathode BER (Prosnansky et al., 2002; Sakakibara and Nakayama, 2001), upflow BER (Ghafari et al., 2009), MEC (Molognoni et al., 2017; Nguyen et al., 2015; Pous et al., 2015a), microbial desalination-denitrification cell (Zhang and Angelidaki, 2013) and bioelectrochemically-assisted constructed wetland (Xu et al., 2017). BESs have shown to be able to induce migration of nitrate out of groundwater in an accumulation chamber, performing also partial biological removal (Tong and He, 2014). The majority of BES treatments for groundwater have been applied in a single stage after groundwater extraction (*pump & treat systems*), but there are a few examples of in situ treatments: electric potential was applied to withdraw nitrate from groundwater and then heterotrophic denitrification was applied at the anode of a groundwater-immersed BES (Tong and He, 2013); buried biocathodes were used to remove nitrate from a simulated aquifer (Nguyen et al., 2016), obtaining a decrease in nitrate reduction rates with increases of the sinking of the electrode in the sand

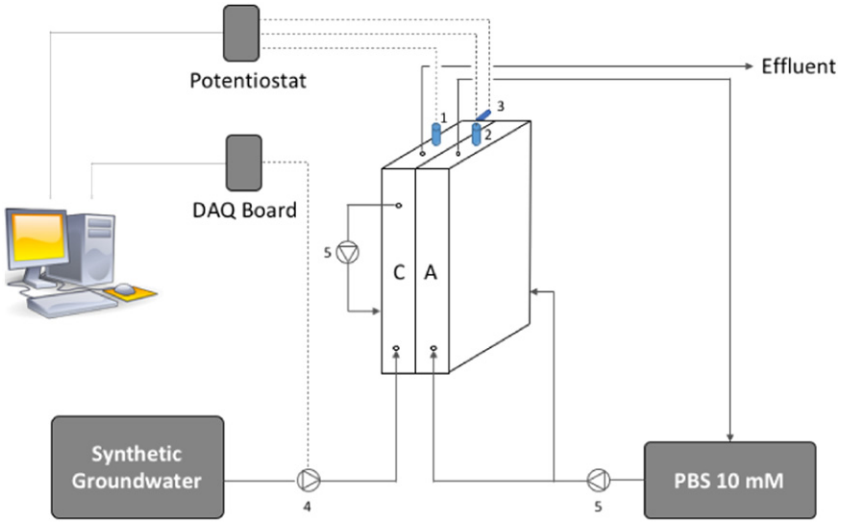

Fig. 1. Liquid, electric and controlling schemes: anodic and cathodic circuits – continuous lines; electric and controlling circuits – dashed lines. Legend: (A) anode chamber; (C) cathode chamber; (1) cathode (working) electrode; (2) anode (counter) electrode; (3) Ag/AgCl reference electrode; (4) feeding pump; (5) recirculation pumps.