



Simulation tests of *in situ* groundwater denitrification with aquifer-buried biocathodes



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ABSTRACT

Bioelectrochemical systems (BES) application was proposed for a variety of specific uses, due to these systems' characteristics: electrodes can act as virtually inexhaustible electron acceptors/donors, offering a growth-support surface for microorganisms, and stimulating naturally-occurring microbial degradation activities. *In situ* groundwater denitrification therefore seems to be a potential candidate for their use. In this study, buried biocathodes were operated in laboratory settings for the simulation of *in situ* groundwater denitrification. Two alternative configurations were tested: biocathode buried in sand, and biocathode buried in gravel. A control test with a biocathode in absence of sand/gravel was also performed. In all the cases, biocathodes were driven by power supply or potentiostat to guarantee a steady electron flux to the cathode. The presence of sand and gravel strongly influenced the denitrification process: in both configurations, accumulation of intermediate N-forms was detected, suggesting that the denitrification process was only partially achieved. In addition, a significant decrease (in the 20–36% range) in nitrate removal rates was measured in sand and gravel setups compared to the control reactor; this issue could be attributed to lack of recirculation that limited contact between substrate and electrode-adherent biofilm. Biocathodes buried in gravel obtained better results than those buried in sand due to the lower packing of the medium. The results of this study suggest that, in order to achieve successful *in situ* treatment, special design of submerged-biocathodic BESs is necessary.

1. Introduction

Groundwater contamination is a widespread global issue, exacerbated by diffuse overexploitation of water resources, and sometimes by severe health issues arising from human intake of contaminated water. A wide variety of sources can generate groundwater pollution: agricultural and industrial activity, mining, and wastewater mismanagement all contribute to the contamination of this water resource [1, 2, 3].

Among other technologies, based on efficiency and sustainability considerations, bioelectrochemical systems (BES) have attracted in the last decade significant attention not only for civil [4, 5] and industrial wastewater treatment [6, 7] but also for groundwater remediation applications [8, 9].

BESs rely on the combination of different bacterial species to catalyze oxidation and reduction reactions and electrodes, acting as virtually unlimited electron acceptor or donor to fulfill a variety of tasks: contaminants removal [10], energy [11] and hydrogen production [12], synthesis of valuable chemicals and commodities [13], and biosensing

[14]. BESs have been applied for the removal of a wide range of different contaminants commonly found in polluted groundwater: arsenic [15], vanadium [16], cadmium [17], chromium [18], perchlorate [19], and petroleum hydrocarbons [20].

In particular, BESs' performance in terms of nitrate removal from groundwater has been recently investigated: biocathodic autotrophic denitrification has been achieved at the cathode of microbial fuel cells -MFC- [21, 22, 23, 24, 25] and potentiostatically-controlled or power supply-operated biocathodes [26, 27]. In the former cases, electrons necessary for nitrate reduction were supplied by organic matter oxidation at the bioanode, while in the latter ones the electron flux depended on the external application of a potentiostat or a power supply (PS). The main advantage in the use of the potentiostatic/power supply-assisted biocathodic technology is the overcoming of the limitations connected to the presence of a bioanode, that might not be able to supply a sufficient amount of electrons to achieve complete denitrification and thus limit the biocathodic process; on the other hand, such BESs are more energy-consuming than a MFC due to the necessary use of the external

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power source [28]. Under these approaches, BESs may substitute current technologies for nitrogen removal from groundwater, either biological [29] or physical-chemical [30].

Generally, when dealing with groundwater contamination, two different approaches for remediation are possible: *in situ* and *ex situ* treatment. In the latter, groundwater is extracted and then treated in the proximity of the well (*ex situ* on-site treatment) or transferred elsewhere for processing (*ex situ* off-site treatment). In case of *in situ* treatment, remediation occurs within the contaminated matrix, with no need for extracting the water from the aquifer.

Groundwater denitrification using BESs has been explored mainly in the *ex situ* configuration, but some attempts to perform *in situ* treatments have been reported: Tong and He [31] developed a BES to be placed within the aquifer medium, able to attract nitrate in the anode chamber, and remove it by heterotrophic denitrification. In another attempt, the current flow generated by a tubular BES induced nitrate migration out of groundwater, accumulating it in a concentration chamber; nitrate removal in this case was due mainly to physical migration induced by the generated electric current than by biological denitrification [32]. Zhang and Angelidaki [33] proposed a modification of the microbial desalination cell (MDC) setup, to attract nitrate into the cathodic chamber due to an electric current generated by the bioanode, removing it then via autotrophic denitrification. Recently, denitrification processes using biocathodes buried in a simulated aquifer have been investigated, showing that nitrate removal rates depend on the burial percentage of the electrode [34]. Other than for groundwater denitrification purpose, BES were applied for the removal of organic compounds from contaminated soils using the sediment (or soil) MFC setup, in which the anode is exposed to the soil in anaerobic conditions: the oxidation of organic compounds provides electrons for the generation of electricity [35, 36, 37].

There is, however, no definite evidence on the influence of the porous medium type for *in situ* denitrifying biocathodes, or on whether the performance of a buried biocathode is actually influenced by the type of soil (sand or gravel) in which it is immersed. The aim of this study is thus to investigate the influence of medium type on the performance of denitrifying buried biocathodes; for this purpose, two H-type biocathodes were built and operated, with electrodes buried in sand and gravel fed by a potentiostat or power supply, and verify whether buried biocathodes could be considered a sustainable technology for groundwater denitrification.

2. Materials and methods

2.1. Reactor setup

Two identical H-type BESs were built using four 130 mL glass half-cells (two for each BES), connected one to a power supply (PS) and the other to a potentiostat; these will be henceforth identified as BES-PS and BES-Pot, respectively. All BESs were equipped with stainless steel wire

mesh anode (4×2.5 cm), and granular graphite cathode (model 00514, diameter 2.5–5 mm, EnViro-Cell, Germany). Graphite granules were inserted in a plastic cuvette, with holes (diam. = 2 mm) to allow full contact between graphite and contaminated (synthetic) groundwater, without allowing them to disperse. The volume of the graphite electrodes was 10 mL, each. A stainless steel thread connected to the stainless steel mesh, and a graphite rod (100×4 mm, Sofacel, Spain) allowed electrical connections between anode and cathode, as shown in Fig. 1. In both BESs, an Ag/AgCl reference electrode (+0.197 V vs SHE, Xi'an Yima Opto-Electrical Technology Co., China) was inserted in the cathodic chamber. A cation exchange membrane (CEM, Membranes International Inc., USA) separated the anodic and cathodic chambers. Addition of electrodes decreased the internal net cell volume to 128 and 110 mL, respectively net anodic chamber (NAC) and net cathodic chamber (NCC). In case of BES-PS, a voltage of 1.0 V was applied between anode and cathode using a laboratory power supply (LABPS3005D, Velleman, Netherlands); this voltage value had been shown suitable to achieve denitrification by previous studies [27, 38]. In case of BES-Pot, the cathode potential was poised at -0.303 V vs SHE (-0.5 V vs Ag/AgCl) using a potentiostat (NEV4, Nanoelectra, Spain), based on previous experience by the authors [39, 40, 41].

2.2. Inoculation and operation

Both BES-PS and BES-Pot cathodes were inoculated using the effluent of a parent BES [40] with the addition of $0.216 \text{ g L}^{-1} \text{ KNO}_3$, with experiments starting once the BESs reached stable denitrification performance (after circa 30 batch cycles). After the inoculation phase, the BESs were operated in batch using synthetic groundwater as influent. Synthetic nitrate-contaminated groundwater was prepared with the addition of KNO_3 and inorganic carbon (NaHCO_3) to a phosphate buffer solution (PBS, 10 mM, pH = 7), with the following composition: $0.216 \text{ g L}^{-1} \text{ KNO}_3$, $0.551 \text{ g L}^{-1} \text{ NaHCO}_3$, $0.507 \text{ g L}^{-1} \text{ NaH}_2\text{PO}_4$, $0.819 \text{ g L}^{-1} \text{ Na}_2\text{HPO}_4$, $2.6 \text{ mg L}^{-1} \text{ KCl}$ and 0.1 mL L^{-1} micronutrients solution. A different PBS (10 mM, pH = 7), with the following composition: $0.507 \text{ g L}^{-1} \text{ NaH}_2\text{PO}_4$, $0.819 \text{ g L}^{-1} \text{ Na}_2\text{HPO}_4$, was fed to the anodes; the anodes were maintained abiotic.

2.3. Tests

Three different test setups were run on each BES, in triplicate:

- one each with aquarium sand, or gravel (Aquadria, Italy) washed with deionized water prior to use and then dried at ambient temperature, added to both cathode and anode chamber. Based on ISO 14688-1:2002, sand and gravel (average size 0.6 mm and 3 mm, respectively) used in the experiments are classified respectively as medium sand and coarse gravel.
- Control, in the absence of any internal filler, in which a magnetic stirrer was operated to achieve complete mixing.

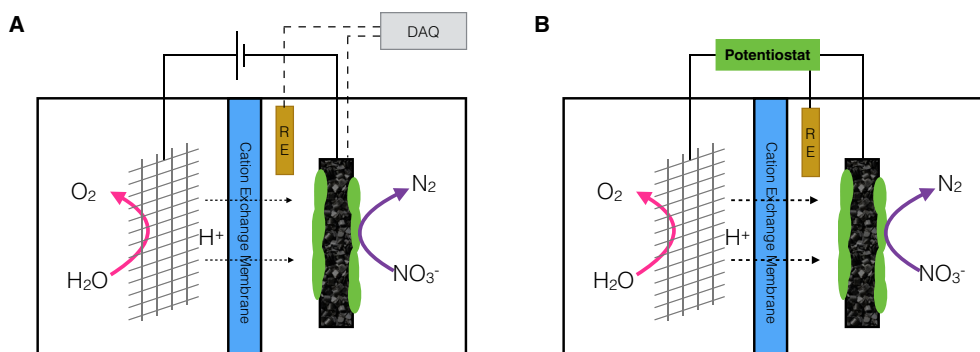


Fig. 1. A) Scheme of BES-PS; B) scheme of BES-Pot. RE: reference electrode; DAQ: data acquisition system. No sand or gravel are represented in the figure.

Tests were carried out in batch mode for 5 days each. The temporal limit of 5 days was considered fully representative of the processes occurring within the biocathodes, given their small volume (and hence their nitrogen content). In each of the tests with the BES containing sand/gravel medium, electrodes were completely submerged by it (Fig. 2), obtaining a buried electrode setup, similarly to the configuration described by Nguyen and co-workers [34]. In presence of filler medium, free volume in the cathodic chamber was reduced to 70 mL or 80 mL by addition of gravel or sand, respectively; in the control setup, the free volume was 110 mL. The presence of sand/gravel prevented the use of magnetic stirring for recirculation.

2.4. Monitoring and analytics

In case of BES-PS, cathode potential and electric current were monitored with a data acquisition system (NI-USB 6008, National Instruments Co., USA) connected to a computer. In case of BES-Pot, current and power were recorded every 60 s by the potentiostat itself.

A 3 mL sample was taken every day from each cathode chamber of the BESs. NO_3^- -N concentrations in the original feed and in daily samples from the BES-PS and BES-Pot were measured. NO_2^- -N, and total nitrogen (TN) concentrations were measured at the end of each test period (i.e. day 5). A spectrophotometer (HI 83224 Wastewater Treatment Photometer, Hanna Instruments) was used to carry out NO_3^- -N and TN measurements, while NO_2^- -N measurements were performed using nitrite test kits (HI3873, Hanna Instruments). All samples were stored at 4 °C prior to analysis for no more than 24 h. Conductivity and pH of influents and effluents were monitored at the beginning (day 0) and end of each test (day 5) using a multi-parametric probe (IntelliCAL™ equipped with HQd™ Digital Meter, Hach Lange, Italy). Amounts of nitrate and TN removed were calculated as difference between the concentrations in influent and effluent. Nitrate removal rate ($\text{gNO}_3^- \text{N m}^{-2} \text{d}^{-1}$) and TN removal rate ($\text{gN m}^{-2} \text{d}^{-1}$) were calculated by dividing respectively the mass of nitrate and TN removed in each experiment by the surface area of the cathode electrode.

The specific energy consumptions in terms of mass of NO_3^- -N removed (SEC_N , $\text{kWh kgNO}_3^- \text{N}^{-1}$) were calculated for BES-PS and BES-Pot as proposed by Molognoni et al. [42] (eq. 1):

$$\text{SEC}_N = \frac{\int_0^t P(t) dt}{m_{\text{NO}_3^- \text{N removed}}} \quad (1)$$

where $P(t)$ is the recorded power demand recorded by the potentiostat, t is time, and $m_{\text{NO}_3^- \text{N removed}}$ represents the mass of removed NO_3^- -N by the considered BES.



Fig. 2. Experimental BES-Pot, gravel test setup.

To better characterize the energy consumption of BESs taking in consideration also the presence of intermediate N-forms, the SEC in terms of TN removed (SEC_{TN} , kWh kgN^{-1}) was calculated as proposed in Cecconet and co-workers [39], as reported in Eq. (2):

$$\text{SEC}_{\text{TN}} = \frac{\int_0^t P(t) dt}{m_{\text{TN removed}}} \quad (2)$$

where $m_{\text{TN removed}}$ represents the mass of TN removed by the considered BES.

The specific surface area (SSA, $\text{m}^2 \text{m}^{-3}$) of the cathode electrode was calculated, based on the assumption that the graphite granules were spherical, using Eq. (3) [43]:

$$\text{SSA} = \frac{6 \times (1 - \theta)}{d} \quad (3)$$

where θ is the packed bed porosity and d is the average particle size; porosity was assumed to be 0.55 [44].

3. Results and discussion

3.1. Nitrate removal

Monitoring of denitrification performance led to the definition of nitrate trend curves during the experiments, shown in Fig. 3 (points

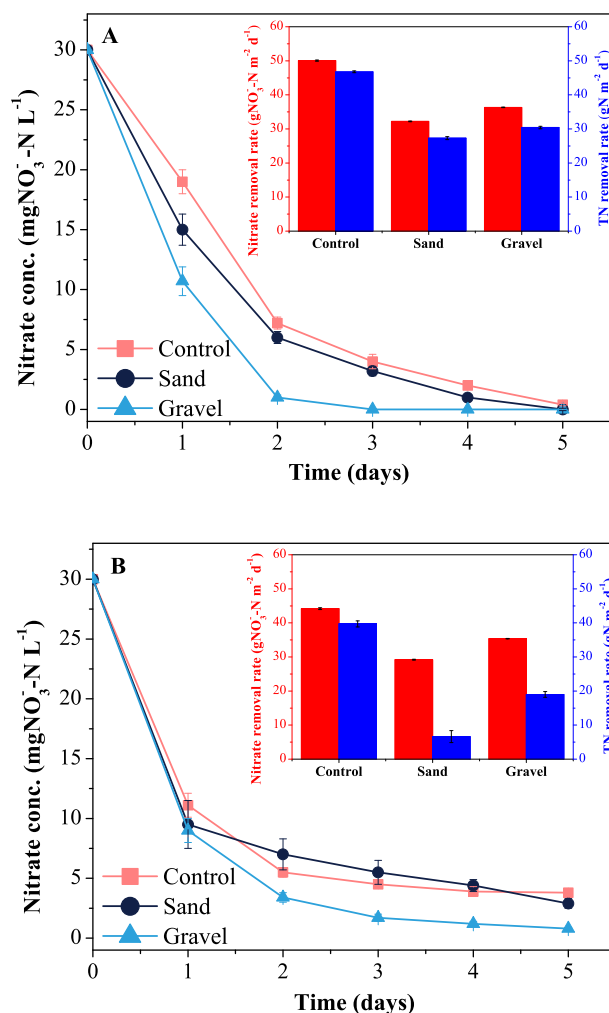


Fig. 3. (A). Main: denitrification performance, BES-PS; Inlet: nitrate removal rates and TN removal rates for BES-PS (B). Main: denitrification performance, BES-Pot; Inlet: nitrate removal rates and TN removal rates for BES-Pot.

shown are the average of each experiment triplicate set).

It is possible to observe how, in both BES-PS (Fig. 3A) and BES-Pot (Fig. 3B), the best performance in terms of nitrate removal was scored when the biocathode was buried in gravel; in particular in the BES-PS, the system was able to almost completely remove nitrate within 2 days. When comparing removal rates (for nitrate and TN, shown in Fig. 3A (inlet) for BES-PS and 3B (inlet) for BES-Pot) in presence of sand and gravel, a significant difference (evaluated using pairwise t-test, p value < 0.05) in favor of gravel was found in both the tested configurations (BES-Pot and BES-PS), and it is particularly evident in the case of the TN removal rate. This may suggest that a biocathode buried in a gravel medium could achieve better results than one buried in a sand medium; nevertheless, in both cases the limited TN removal rate showed that the denitrification process was incomplete, and that intermediate N-forms (nitrous oxide and nitrite) were present at the end of the batch. An hypothesis could postulate that this phenomenon could derive from the smaller size of the sand particles, causing a more tightly packed bed, resulting in a lower (though already limited) possibility of contact between substrate and electrodes' biofilm; ion movement in the BES in absence of recirculation was due to the electric field generated in proximity of the electrodes, causing an electro-kinetic effect that enhanced mass transport and mixing [45]. The movement of microorganisms and contaminants temporarily immobilized can be caused also by electro-osmosis, that may increase the contact between substrate and bacteria [46, 47]; it has been reported though its independence from hydraulic conductivity [48, 49], and thus electro-osmosis cannot be claimed as responsible for the differences in the performances of biocathodes buried in sand or gravel.

When performances of the buried biocathodes are compared against the control biocathode, it immediately appears that the control test achieved the highest nitrate and TN removal rates, as shown in Fig. 4, even though at the end of the tests some nitrate was detected in the effluent (as shown in Fig. 3). It should be highlighted, however, that due to the different free cell volume between the three setups, a different amount of nitrate ($3.8 \text{ mgNO}_3\text{-N}$ in the control test, $2.7 \text{ mgNO}_3\text{-N}$ in the gravel test, and $2.4 \text{ mgNO}_3\text{-N}$ in the sand test) had to be removed in each case. It seemed as the greater mass present in the control setup may have led to a non-complete reduction of nitrate, probably due to the higher amount of terminal electron acceptors (TEAs, composed by the different N-forms) present. This hypothesis is confirmed by the fact that, in the case of the control, an higher percentage of TN ($92 \pm 1\%$ and $78 \pm 2\%$ respectively with power supply and potentiostat) was removed by the biocathodes compared to the BES-PS ($84 \pm 1\%$ TN removal in both tests, sand and gravel) and BES-Pot ($52 \pm 2\%$ TN removal in the gravel test and $20 \pm 5\%$ in the sand test). Therefore, in the control test the denitrification

reached a step further compared to the cases in which sand or gravel were added in the BES. This fact may suggest that the limited nitrate and TN removal was due to the competition for electrons by the different TEAs, namely the various N-forms; such a competition was reported by Puig et al. [21] and Srinivasan et al. [44]. The critical process step can be identified in the reduction of N_2O to N_2 , since N_2O constitutes the large majority of non-nitrate TN in the effluent (more than 92% at day 5 in all the tests), while NO_2^- , which is commonly identified in denitrifying BESs' effluents [42, 44], was almost absent in all the configurations. The accumulation of N_2O in BESs was highlighted in previous studies by Van Doan et al. [50] and Cecconet et al. [39]. Even though it is not toxic, N_2O is a known greenhouse gas (GHG), and is commonly produced during denitrification processes in wastewater treatment [51, 52]; consequently its emissions should be preferably limited. Accumulation of intermediate N-forms may be attributed to the lack of recirculation (impeded by the presence of sand/gravel that did not allow magnetic stirring) within the BES and thus of the necessary contact between the denitrifying biofilm on the electrode and the substrate contained in the synthetic groundwater [53]; recirculation has been reported as crucial for bioelectrochemical processes [54, 55]. Nguyen et al. [34] reported a 30% decrease of nitrate removal rates when recirculation (using a magnetic stirrer) was impeded by addition of sand at the bottom of the cathode chamber. A similar decrease was noticed in the BESs in this study's experiments: the highest values of nitrate removal rates were scored in the control test in both BES-PS and BES-Pot ($50.06 \pm 0.17 \text{ gNO}_3\text{-N m}^{-2} \text{ d}^{-1}$ and $44.18 \pm 0.26 \text{ gNO}_3\text{-N m}^{-2} \text{ d}^{-1}$ respectively). The BES-PS showed a 36% and 28% decrease in nitrate removal rate, observed in the presence of sand and gravel, respectively; in the BES-Pot, a lower performance difference was detected (a decrease of 34% and 20%, respectively in sand and gravel setups) (Fig. 3B, inlet). In addition, the highest TN removal rates were scored in the control setup ($46.78 \pm 0.26 \text{ gN m}^{-2} \text{ d}^{-1}$ and $39.70 \pm 0.90 \text{ gN m}^{-2} \text{ d}^{-1}$ for BES-PS and BES-Pot). Therefore, results confirm that recirculation is not only essential for the good outcome of a bioelectrochemical denitrification in terms of speed (indicated by removal rates), but also to achieve complete reduction of all the intermediate N-forms (testified by the presence of N_2O and NO_2^- at the end of each batch test). In addition, the higher packing resulting from sand presence led to lower denitrification efficiency compared to the presence of gravel. Based on that, the simple displacement of electrodes in the aquifer may not be optimal for *in situ* groundwater denitrification, and the design of more appropriate (and complex) BES setups may be necessary to overcome the connected limitations.

Rather surprisingly, BES-PS achieved better denitrification results than BES-Pot, obtaining both higher removal percentages and rates in all considered cases. In particular, a wide difference was observed in the TN removal rates, sensibly lower in BES-Pot compared to BES-PS in presence of sand (-76%) and gravel (-38%) (Fig. 4B), while nitrate removal rates were similar (Fig. 3). This apparent contradiction may be attributed to the fact that in a BES-PS, the cathode potential was actually able to adapt to the different conditions, as shown in Fig. 4, while in the BES-Pot, where the potential was set by the potentiostat, at a value not necessarily optimal for the different denitrification steps, this was not possible.

3.2. Energy consumption

The energy consumption of BES-PS and BES-Pot was carefully monitored during the various tests, and the indexes SEC_N and SEC_TN were calculated to allow comparisons *intra* and *inter* the experimental tests. In the case of BES-PS, it is possible to observe how the energy consumption in terms of SEC_N (Fig. 5A), and SEC_TN (Fig. 5B) is lower in the control reactor (thus in absence of sand/gravel), suggesting that the operation of the denitrifying system with the presence of some recirculation may reduce the specific energy consumption of the power supply-operated biocathode.

Observed energy consumption was higher when accumulation of intermediate N-forms (and thus in the presence of sand or gravel cell fillers)

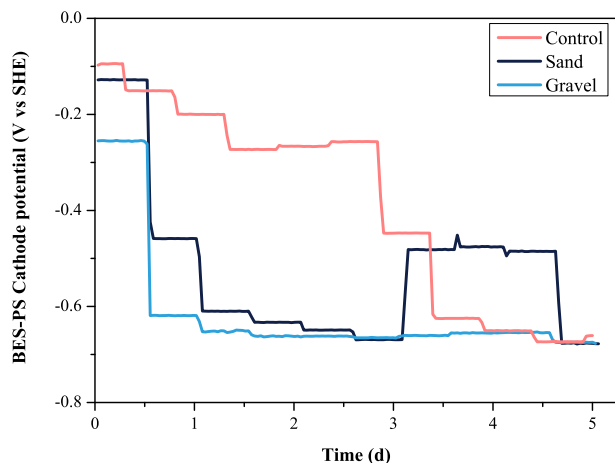


Fig. 4. Cathode potential trend measured in the different setups during first test of BES-PS operation.

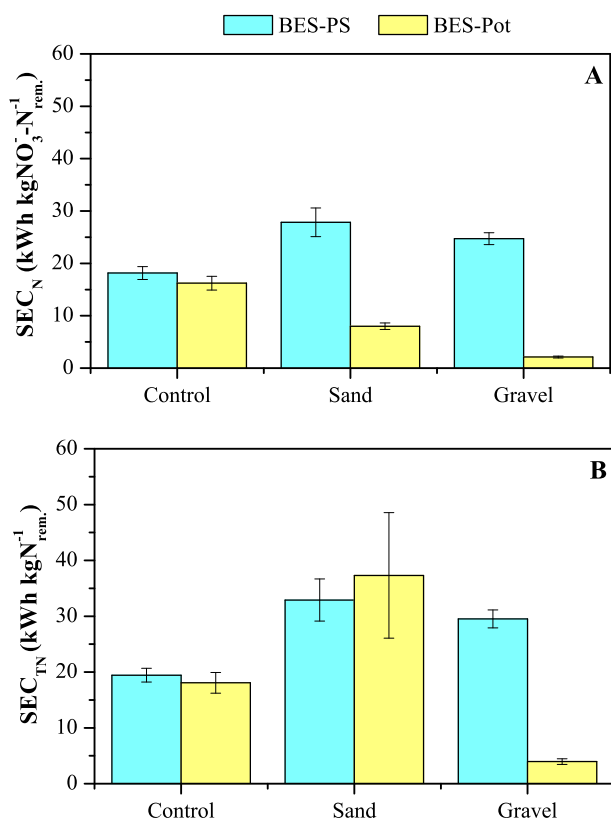


Fig. 5. SEC calculated for the different cases.; A) SEC_N; B) SEC_{TN}.

occurred, as previously observed in other BES applications by the authors [39]. An increase of the BES energy consumption reflects obviously on the calculated specific energy indexes SEC_N and SEC_{TN}, due to lower TN removal compared to the control (medium-less setup). Considering the BES-Pot energy consumption, measured in terms of SEC_N, this is lower than that of the BES-PS, but at the same time the former scored lower results in terms of TN removal compared to the latter. This latter observation is reflected in highest SEC_{TN} scored with the sand setup, in which TN removal was 20%, leading to increase of the related index (SEC_{TN} is defined as the ratio between the energy consumption and the TN removed by the system). Lower energy consumption, compared to BES-PS, may be attributed to the different structure of the system (use of a potentiostat, instead of power supply).

Surprisingly, in case of BES-Pot, the values of and SEC_N are lower in the presence of sand and gravel fillers than in the absence of a medium, with a trend exactly contrary to that of the BES-PS system. This pattern is in contrast with previous experiences from the authors [39, 40, 42].

4. Conclusions

Experimental results concerning the application of buried biocathodes in different filler media (sand or gravel) for *in situ* groundwater denitrification showed that, even if such an application is possible, with overall positive results observed, process performances are lower than those observed in the control setup (absence of porous media) in terms of both TN and nitrate removal efficiency. This result could be ascribed to a lack of recirculation inside the built reactors, due to the presence of a filler medium, with resulting slow movement and low micro-turbulence in the medium itself, reducing contact possibilities between active bio-film and the necessary electron acceptor (N-forms). Better performances were scored by the biocathodes in the case of gravel medium, in both BES-Pot and BES-PS setups, due to lower packing. BES-PS generally performed better than BES-Pot, due to the ability of the cathode to adapt its potential to the N-forms produced during the denitrification.

The findings herein reported suggest that a BES setup based on a straightforward buried biocathode application may not be the optimal solution for *in situ* groundwater denitrification, and that the development of specially-designed, more efficient BES configurations could be necessary if effective *in situ* denitrification is to be achieved.

Declarations

Author contribution statement

Daniele Cecconet: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Silvia Bolognesi: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Arianna Callegari, Andrea G. Capodaglio: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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