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Biological groundwater denitrification systems: Lab-scale trials aimed at nitrous oxide production and emission assessment

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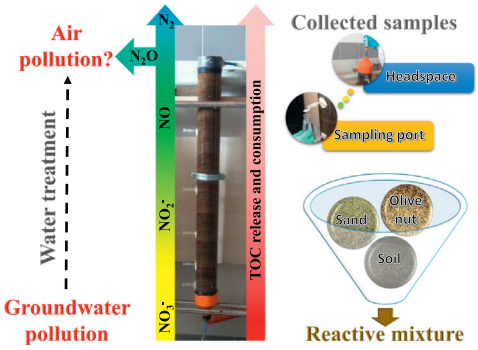
HIGHLIGHTS

- Nitrous oxide produced in biological groundwater denitrification has been assessed.
- Influence of inlet nitrate concentration has been investigated.
- The increase of inlet nitrate concentration resulted in a carbon limitation.
- Higher nitrate concentration caused an increase in nitrous oxide production.
- Off gas emission increased with the decrease of denitrification efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Bio-trenches are a sustainable option for treating nitrate contamination in groundwater. However, a possible side effect of this technology is the production of nitrous oxide, a greenhouse gas that can be found both dissolved in the liquid effluent as well as emitted as off gas. The aim of this study was to analyze NO_3^- removal and N_2O production in lab-scale column trials. The column contained olive nut as organic carbon media. The experimental study was divided into three phases (I, II and III) each characterized by different inlet NO_3^- concentrations (30, 50, 75 mg NO_3-N L^{-1} respectively). Sampling ports deployed along the length of the column allowed to observe the denitrification process as well as the formation and consumption of intermediate products, such as nitrite (NO_2^-) and nitrous oxide (N_2O).
In particular, it was observed that N_2O production represent only a small fraction of removed NO_3^- during Phase I and II, both for dissolved (0.007%) and emitted (0.003%) phase, and it was recorded a high denitrification efficiency, over 99%. Nevertheless, significantly higher values were recorded for Phase 3 concerning emitted phase (0.018%). This fact is due to increased inlet concentration which resulted in a carbon limitation and in a consequent decrease in denitrification efficiency (76%).

1. Introduction

In recent years, anthropogenic activities significantly modified the natural cycle of nitrogen leading to more nitrogen spreading through the water and air (Galloway et al., 2003). Groundwater nitrate–nitrogen contamination has become an environmental concern and public health

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problem. Indeed, nitrate being a very mobile form of nitrogen in soil, represents a dangerous pollutant of waters, and may cause many diseases, including metahemoglobinemia in infants (WHO, 2004). Furthermore, nitrogen excess in environment is potentially connected with eutrophication of freshwater, resulting in the intensive development of toxic algal blooms and, often, the exclusion of affected freshwater from drinking water resources (Rabalais, 2002).

A way to mitigate nitrate water pollution is to stimulate the natural denitrification process.

Denitrification is a multistep biological process carried out by facultative heterotrophic bacteria under anoxic conditions where NO_3, NO_2, NO and N_2O are used as alternative electron acceptor (Zumft, 1997). Depending mainly on the environmental conditions, the final product of heterotrophic denitrification is not always N_2, but could be in the form of undesirable intermediates such as nitrous oxide (Rivett et al., 2008) or ammonium (Gibert et al., 2008).

Carbon remains as the electron donor for all of the possible reduction steps and its presence influences process performances. Groundwater can be enriched in organic carbon via passive systems such as carbon-rich denitrification trenches (Capodici et al., 2014; Obiri-Nyarko et al., 2014; Robertson, 2010; Schipper et al., 2010). Briefly, an organic matter is placed into soil through which groundwater passes; the organic matter provides dissolved organic carbon available for the biochemical reaction promoted by microorganisms.

One of the crucial steps of this technology is the proper selection of the organic carbon source. Indeed, it is preferable that this reactive substrate is easily available and low-cost for the economic sustainability of remediation technique (Schipper et al., 2010). Moreover, in order to avoid groundwater pollution by an excessive release of carbon, it is important that the organic media ensures a slow release (Capodici et al., 2014; Warneke et al., 2011a). Furthermore, an excess of dissolved carbon could enhance the antagonistic dissimilatory nitrate reduction to ammonium (DNRA); the latter represents an antagonistic reduction reaction that starting from nitrate evolves up to the formation of ammonia (Gibert et al., 2008; Healy et al., 2012; Rivett et al., 2008).

Generally, a new reactive media is usually tested in column setup before a bio-trench is carried out in a field scale plant (Gavaskar, 1999).

In this context, previous research has identified wooden media as capable to promote high denitrification rate over longer time with no adverse effects (N_2O emissions, carbon pollution, DNRA) if compared with other carbon source (Cameron and Schipper, 2010; Warneke et al., 2011b).

For this reason, wooden materials represent nowadays the largest part of full-scale applications. This is due mainly to the lignocellulosic structure of the wooden media (Gibert et al., 2008; Moorman et al., 2010; Schipper et al., 2010; Schipper and Vojvodic, 2001).

In details, the hemicellulose content indicates the amount of cross-links between lignin and cellulose and, consequently, it affects the slow release of organic carbon and the reactive substrate endurance over time (Ahmad et al., 2007).

Nevertheless, the availability of large amount of organic carbon becomes critical where NO_3^- is present in high concentration (Schipper et al., 2010) and this is because the influent nitrate concentration affects denitrification reaction kinetic (Cameron and Schipper, 2010; Christianson et al., 2012; Robertson, 2010).

However, the environmental impact of nitrate contamination extends beyond the surface waters. As a matter of facts, the biological denitrification processes that can naturally occur in groundwater contaminated by nitrates, has been identified in many recent studies as sources of N_2O emissions to the atmosphere (Groh et al., 2015; Kampschreur et al., 2009).

Consequently, denitrification is on the one hand the key process for the removal of reactive N from the terrestrial biosphere, but on the other hand it is also one of the dominating sources for the atmospheric greenhouse gas N_2O (Davidson and Seitzinger, 2006).

N_2O, a primary ozone-depleting substance, is a powerful greenhouse gas with a global warming potential 310 times higher than carbon dioxide (IPCC, 2007; Ravishankara et al., 2009).

Concerns about negative denitrification process by-products like nitrous oxide are ongoing (Groh et al., 2015), and this aspect lead researcher interest in refining more advanced design and management strategies aimed at reducing the N_2O formation and emission (Christianson and Schipper, 2016).

Recent works reported about the way to mitigate N_2O production from different system in which denitrification processes is developed like biofilter (Bollon et al., 2016; Zhang et al., 2016), agricultural crops (Lognoul et al., 2017), wetlands (Ye and Horwath, 2016), soil with excess nitrogen fertilizer (Feng and Zhu, 2017; Liu et al., 2017; Wu et al., 2017). Nevertheless, few studies have yet examined the production of N_2O in denitrifying bio-trenches for the treatment of groundwater.

In particular, dissolved N_2O-N production in woodchip bioreactors was found to range from 0.6% to 0.85% of removed NO_3–N (Elgood et al., 2010; Moorman et al., 2010). In a column experiment with woodchips, dissolved N_2O production was low ranging from 0.003% to 0.033% of removed NO_3-N (Greenan et al., 2009).

Christianson et al. (2013) found more N_2O loss dissolved in the water leaving their bioreactors than the amount emitted from the woodchip or soil surfaces (about 0.4%). Warneke et al. (2011a) found dissolved N_2O from a denitrification bed that increased the fraction of nitrate lost as N_2O from 1% (emitted from bed surface) to 4.3% overall.

David et al. (2016) found that less than 1% of the nitrate removed was released as N_2O from the surface of a bioreactor, although dissolved N_2O losses were not measured (David et al., 2016).

In addition to that, nitrous oxide presence is also affected by the type of reactive media because released carbon represents a key factor in order to control both the production and reduction of N_2O in the sequential reaction.

In a study carried out with different carbon media in bioreactors, the production of N_2O relative to nitrate removal was consistently greater using woodchip (9.7%) than corn cobs (1.1%) or a combination of corn-cobs-woodchip (0.9) (Feyereisen et al., 2016). On the contrary, in bioreactor beds filled by corn and soybean, authors found little N_2O emission approximately consisting in 0.004% of nitrate removed (Woli et al., 2010).

Furthermore, studies on denitrification process showed that hydraulic residence time (HRT) affects positively the denitrification rate and, consequently, the N_2O reduction (Addy et al., 2016; Benyoucef et al., 2013; Greenan et al., 2009; Healy et al., 2012; Hoover et al., 2016; Pluer et al., 2016). In particular, it was found that NO_3^- effluent concentration and N_2O emission decrease by the HRT increasing (Healy et al., 2012).

In the light of this, Christianson and Schipper (2016) have suggested that future research must think more broadly to address bioreactor impacts on greenhouse gas balances to allow investigation of mechanisms within the bioreactor “black box”. Likewise, mechanisms to reduce the production of N_2O will need to be investigated when bio-trenches are operated to groundwater denitrification.

In the light of what discussed above, the paper was aimed at evaluating NO_3^- removal performance in a lab-scale bioreactor filled by olive nut as reactive carbon media and to assess how influent NO_3^- concentration could affect the N_2O production.

2. Materials and methods

2.1. Experimental apparatus and operational conditions

The experimental layout consisted of a cylindrical Plexiglas plug-flow column reactor, with 10 cm of inner diameter and 100 cm of height, filled with a reactive solid mixture, completely submerged and operating in up flow mode. In Fig. 1 a draft of the pilot plant lay out is depicted.