



Research article

Tracing the role of endogenous carbon in denitrification using wine industry by-product as an external electron donor: Coupling isotopic tools with mathematical modeling



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ABSTRACT

Nitrate removal through enhanced biological denitrification (EBD), consisting of the inoculation of an external electron donor, is a feasible solution for the recovery of groundwater quality. In this context, liquid waste from wine industries (wine industry by-products, WIB) may be feasible for use as a reactant to enhance heterotrophic denitrification. To address the feasibility of WIB as electron donor to promote denitrification, as well as to evaluate the role of biomass as a secondary organic C source, a flow-through experiment was carried out. Chemical and isotopic characterization was performed and coupled with mathematical modeling. Complete nitrate attenuation with no nitrite accumulation was successfully achieved after 10 days. Four different C/N molar ratios (7.0, 2.0, 1.0 and 0) were tested. Progressive decrease of the C/N ratio reduced the remaining C in the outflow and favored biomass migration, producing significant changes in dispersivity in the reactor, which favored efficient nitrate degradation. The applied mathematical model described the general trends for nitrate, ethanol, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations. This model shows how the biomass present in the system is degraded to dissolved organic C (DOC_{en}) and becomes the main source of DOC for a C/N ratio between 1.0 and 0. The isotopic model developed for organic and inorganic carbon also describes the general trends of $\delta^{13}\text{C}$ of ethanol, DOC and DIC in the outflow water. The study of the evolution of the isotopic fractionation of organic C using a Rayleigh distillation model shows the shift in the organic carbon source from the WIB to the biomass and is in agreement with the isotopic fractionation values used to calibrate the model. Isotopic fractionations (ϵ) of C-ethanol and C-DOC_{en} were -1‰ and -5‰ (model) and -3.3‰ and -4.8‰ (Rayleigh), respectively. In addition, an inverse isotopic fractionation of $+10\text{‰}$ was observed for biomass degradation to DOC_{en}. Overall, WIB can efficiently promote nitrate reduction in EBD treatments. The conceptual model of the organic C cycle and the developed mathematical model accurately described the chemical and isotopic transformations that occur during this induced denitrification.

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1. Introduction

Nitrate (NO_3^-) is one of the most common groundwater pollutants (Nolan, 2001; Puckett et al., 2011). NO_3^- contamination is originated either from diffuse (non-point) sources, linked to intensive use of synthetic and organic fertilizers and livestock, or

from point sources such as septic system effluents. High NO_3^- ingestion affects human health, promoting cancer and producing methemoglobinemia in infants, also known as blue baby syndrome (Magee and Barnes, 1956; Ward et al., 2005). Furthermore, an increase of NO_3^- can produce eutrophication of surface water bodies (Rivett et al., 2008; Vitousek et al., 1997). Consequently, the European Union has established a NO_3^- concentration threshold of 0.80 mM (50 mg/L) for human water supplies (Directives 98/83/CE, 91/676/CEE). This limit is exceeded in many aquifers worldwide because NO_3^- is highly mobile in groundwater and often persists in

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aquifers (He et al., 2011). Therefore, groundwater remediation has become a necessary strategy to prevent the public health and environmental impacts of NO_3^- . One of the most efficient treatments for removing NO_3^- involves enhanced biological denitrification (EBD) within the aquifer (Khan and Spalding, 2004; Tartakovsky et al., 2002; Vidal-Gavilan et al., 2013). Denitrification is the process where NO_3^- is reduced to dinitrogen gas (N_2) by anaerobic facultative bacteria (Knowles, 1982). In natural systems, denitrification is predominantly restricted by the availability of electron donors (Korom, 1992). To overcome this natural limitation, biostimulation of heterotrophic denitrification by adding an organic carbon source is a feasible technique to reduce NO_3^- pollution in groundwater and wastewater (Vidal-Gavilan et al., 2013; Borden et al., 2011; Leverenz et al., 2010).

A number of studies have tested different soluble organic compounds, including pure compounds such as alcohols (ethanol, methanol), sugars (glucose, sucrose) and other organic compounds such as lactose, volatile fatty acids, acetic acid, propionate, and molasses (Fernández-Nava et al., 2008; Gómez et al., 2000; Peng et al., 2007). Recently, there has been increasing interest in alternative sources of organic carbon solid compounds such as palm tree leaves, compost or saw dust to promote water remediation for different pollutants (Grau-Martínez et al., 2017; Schipper and Vojvodic, 2000; Trois et al., 2010). The use of by-products from the food industry as organic carbon sources may provide an economical alternative solution while providing waste recycling. Furthermore, these industrial by-products may provide both an easily accessible carbon source and micronutrients. In this context, liquid waste from wine industries may be a feasible reactant to enhance heterotrophic denitrification. The proposed wine industry by-product (WIB) where organic carbon is mainly composed of ethanol (95%), and is generated during brandy distillation, after which residual liquid in the container is discarded. The liquid waste is usually treated in a wastewater treatment plant at an elevated cost for the wine companies (Petta et al., 2017).

An essential concern in EBD is to design an efficient feeding strategy that can avoid the production of undesirable compounds such as nitrite (NO_2^-) and nitrogen oxides (Vidal-Gavilan et al., 2014) as well as minimize the risk of bioclogging due to denitrifier biomass growth (Rodríguez-Escales et al., 2016b). One of the key factors controlling these risks is the amount of dissolved organic carbon (DOC) inoculated. It should be enough to guarantee a sufficient NO_3^- reduction, but it should not exceed the stoichiometric requirements of the reaction to avoid undesirable reactions such as sulfate reduction. The DOC inoculated is commonly calculated by considering only the organic carbon injected into the system. However, as the denitrifier biomass grows and dies, a new carbon pool, formed by dead and lysed cells, appears in the system and has the potential to become a new source for denitrification (Carrey et al., 2014a; Rodríguez-Escales et al., 2016b; Rodríguez-Escales et al., 2014; Torrentó et al., 2011). The total denitrification rate is the combined reduction of NO_3^- due to the different organic carbon sources, including external, or exogenous, and internal, or endogenous, sources. Normally, endogenous respiration is slower than exogenous; it does not depend on the organic substrate availability (Orozco et al., 2010) and thus becomes more important when the external carbon source has been exhausted. The incorporation of endogenous carbon into the calculation of the C/N (carbon/nitrogen) ratio will reduce the amount of external DOC, decreasing the cost of EBD as well as minimizing the risk of bioclogging in the system.

The role of endogenous carbon in the denitrification rate cannot be addressed only by traditional hydrochemistry. In addition to microbiological molecular tools, mathematical modeling with

stable carbon isotopic data is a powerful tool to understand the carbon cycle during denitrification. Furthermore, incorporating isotopes into the biogeochemical model allows the determination of the isotopic fractionation (ϵ) of complex processes that cannot be analyzed using traditional equations (Abe and Hunkeler, 2006; van Breukelen, 2007; van Breukelen and Prommer, 2008). Typically, ϵ is calculated as a Rayleigh distillation process (Mariotti et al., 1981) (Eq. (1)) and it is expressed in per mil units (‰):

$$\ln\left(\frac{R_t}{R_0}\right) = (\epsilon) * \ln\left(\frac{C_t}{C_0}\right) \quad (1)$$

where C_0 and C_t are the initial and residual concentration at time t (ML^{-3}), respectively, and R_0 and R_t are the isotopic ratios (ratio of heavy to light isotopes) at the initial time and at time t , respectively, that are calculated according to Eq. (2):

$$R = \left[\left(\frac{\delta}{1000} \right) + 1 \right] \quad (2)$$

where δ is the isotopic composition in per mil units (‰). The term ϵ is calculated from the slope of the linear regression analysis in the double-logarithmic plot of $\ln(R_t/R_0)$ versus $\ln(C_t/C_0)$ according to Eq. (1). Following the recommendations of Coplen (2000), ϵ will be expressed as $\epsilon^i \text{E}_{P/Q}$, where $\epsilon^i \text{E}$ is the isotopic fractionation for the element E (where i is the heavier isotope) between substances P (product) and Q (reactant) for a specific transformation. To facilitate comparison with literature values, ϵ is expressed in per mil units (‰).

The main goal of this work is to evaluate, by coupling carbon isotopes and modeling, the role of endogenous carbon in denitrification using WIB as a carbon source. The side objectives are i) to evaluate the viability of using WIB to remediate NO_3^- contaminated water using different C/N ratios, focusing on the generation of undesirable compounds such as NO_2^- , and ii) to study the feasibility of using the Rayleigh equation to determine the isotopic fractionation of the different carbon pools. To achieve these goals, a flow-through experiment was set up, and chemical, isotopic and biological characterization was performed. In addition, a complete model integrating the hydrochemistry and the carbon isotope signatures was developed.

2. Methodology

2.1. Experimental set-up

A flow-through glass column was built to simulate a 1D lab-scale model and installed in a temperature-regulated chamber (Fig. 1 in Supporting Information). The experimental system included a 2 L inflow water reservoir, a 70 cm long and 8 cm diameter glass column, and a 500 mL outflow reservoir, all of them connected by Tygon® R-3603 tubes. Synthetic water flowed through the column from the bottom to the top. Inflow and outflow rates were set constant at an average rate of 360 mL/d using a peristaltic pump (Reglo Digital peristaltic micropump, ISMATEC) connected to both ends of the column. The resulting hydraulic residence time is about 5 days. Eight sampling points were established: one at the inflow water reservoir (I), six across the glass column at 10 cm intervals (sampling points 1 to 6), and one at the outflow (O).

The column was filled with sterilized silica balls (5 mm in diameter) to obtain an unreacted and homogeneous matrix. Synthetic water was prepared 3 times during the experiment (at days 0, 30 and 60). Table 1 presents a summary of the average theoretical

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