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Selection of organic substrates as potential reactive materials for use in a denitrification permeable reactive barrier (PRB)

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Abstract

The aim of the present study was to select a suitable natural organic substrate as a potential carbon source for use in a denitrification permeable reactive barrier (PRB). A number of seven organic substrates were first tested in batch tests. The materials attained varying degrees of success at promoting denitrification. Some of the organic substrates performed very well, achieving complete nitrate removal (>98%), while others were considered unsuitable for a variety of reasons, including: insufficient nitrate or nitrogen removal, excessive release of leachable nitrogen from the substrate or excessive reduction of nitrate to ammonium rather than removing it as gaseous N_2. The top performing substrate in terms of denitrification extent (>98%) and rate (0.067 mg NO_3^-–N dm^{-3} d^{-1} g_{sub}^{-1}) was then selected for two bench-scale column experiments in an attempt to simulate the PRB. The inlet concentration was 50 mg dm^{-3} NO_3^-–N and the columns operated at two different flow rates: 0.3 cm^3 min^{-1} (Column 1) and 1.1 cm^3 min^{-1} (Column 2). The two columns showed different general patterns, making it clear that the flow rate was a key factor at the nitrate removal. Nitrate was completely removed (>96%) by the passage through Column 1, while only partially removed in Column 2 (66%). The results indicated that the selected organic substrate (Softwood) was applicable for further use as a filling material for a PRB.

Keywords: Denitrification; Groundwater nitrate; Organic substrate; Passive remediation; Permeable reactive barrier

1. Introduction

Groundwater contamination by inorganic nitrogen (in the form of NO_3^-, NO_2^- and/or NH_4^+) constitutes a major environmental concern worldwide. It usually originates from anthropogenic sources, mainly as a result of the intensive application of fertilizers and animal manure to agricultural land and wastewater discharges (Bedessem et al., 2005; Della Rocca et al., 2005; Su and Puls, 2006).

The European "Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources" (Nitrate Directive 91/676/EEC) emphasizes the importance of preventing pollution and decreasing existing nitrate concentration in groundwater to values under the EU limit of 50 mg dm^{-3} NO_3^- (11.3 mg dm^{-3} NO_3^-–N). Denitrification-based processes are nowadays regarded as one of the most promising approaches. Denitrification is the dissimilatory microbial process whereby nitrate is reduced to nitrogen gas according to the following reaction (Robertson et al., 2000; Su and Puls, 2006):

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 5HCO_3^- + 2H_2O + H^+$$

where CH_2O represents a generic organic compound. NO_3^- is first converted to NO_2^-, which may itself be further reduced to innocuous N_2 (Ovez, 2006; Foglar et al., 2005).

Denitrifying bacteria have specific environmental requirements that must be met to enable their activity, such as the presence of a carbon source (which acts as a nutrient and as the electron donor), reducing conditions (denitrifi-

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cation has been reported to start at +300 mV) (Brettar et al., 2002; Chung et al., 2004), a suitable pH and temperature (between 5.5 and 8.0 and 25 and 35 °C, respectively, though denitrification may occur beyond these limits) (Dinçer and Kargı, 2000; Ovez, 2006), low levels of oxygen (though recent research works have reported that denitrifying bacteria can tolerate DO concentrations of up to 4.5 mg dm^{-3}) (Gómez et al., 2002; Foglar et al., 2005), a physical support for a suitable bacterial attachment (Ovez, 2006). In subsurface environments, the lack of readily available organic carbon has often been reported as the most common limitation to denitrification (Bedessem et al., 2005; Hunter, 2003).

Until recently, the use of denitrifying bacteria for groundwater treatment has generally been limited to ex situ treatment in bioreactors. However, latterly attention has focused on their application in in situ passive systems, such as permeable reactive barriers (PRB) (Su and Puls, 2006; Hunter, 2003; Schipper and Vojvodić-Vuković, 2001). A permeable reactive barrier (PRB) consists of placing in the path of a groundwater plume a porous reactive material able to remove the contaminants from the plume as it flows through it. Despite the fact that this technology has been widely used for chlorinated solvents, data on denitrification PRBs are scarce (Robertson et al., 2000; Schipper and Vojvodić-Vuković, 2001).

The design of any PRB should contemplate the execution of laboratory feasibility tests, whose main objectives are the selection of a viable reagent for the PRB and the evaluation of its capacity for removing the contaminant of interest. Typically, this knowledge is achieved in a first step through batch and column experiments (Gavaskar, 1999).

The present study reports the results of batch and column experiments conducted within the LIFE Environment Project entitled "Remediation of agricultural diffuse nitrate polluted waters through the implementation of a permeable reactive barrier (NITRABAR)", which aims to implement a PRB to treat nitrate-contaminated groundwater (http://nitrabar.eu). A number of seven organic substrates were evaluated in batch experiments to assess their capacity for promoting denitrification. The optimal organic substrate was then selected for bench-scale dynamic column experiments to better simulate the PRB.

2. Methods

2.1. Substrates used as reactive materials

2.1.1. Substrate description

Seven natural raw substrates were selected as potential carbon sources to promote and stimulate denitrification. They were namely: Softwood (branches and bark with small amounts of leaves from a variety of trees), Hardwood (mixture of coarse wood chips, small branches, stems and leaves), Coniferous (coniferous small twigs and leaves), Mulch (mixture of wood chips, shredded bark and topsoil), Willow (willow wood chips), Compost (obtained from the biological decomposition of organic wastes – wood trimmings, leaves, rotten vegetables and food scraps) and Leaves (freshly fallen beech leaves). They all were coarse textured with irregular pieces of organic material generally seized between 5 mm and 5 cm. The selection of the organic substrates was made on the basis of their widespread availability, easy handling and no/low-cost.

Additionally, native soil from the site was used as blank of the experiments. The soil sample was collected from the upper layer of the site and consisted of fine sand with pockets of silt with a relatively high content of organic carbon (average of 2.68% on a dry weight basis).

2.1.2. Elemental analysis of substrate

Solid samples were dried and ground to a homogeneous fine powder using a cryogenic impact grinder (Spex Certiprep Freezer Mill 6850, Glen Creston Ltd.) and analysed for elemental composition. The content of C, H and N was determined by dry combustion of an accurately weighted amount of sample (usually 1.5–2.5 mg) using a Perkin–Elmer 2400 Series 2 CHNS Elemental Analyser. The sample was combusted completely, and the gas mixture carried in a He flow through a reducing agent. The level of C, H and N was determined using a thermal conductivity detection system. The elemental composition is given in Table 1.

2.1.3. Leaching tests

Leaching tests were carried out to determine the leachable nitrogen of each reactive material. An amount of sub-

Table 1
Elemental composition and contents of leachable nitrate, nitrite, ammonium and TOC of the evaluated organic substrates (all contents computed on dried sample)

Organic substrate	Elemental composition			Leachable amounts (mg g_{sub}^{-1})			
	C (%)	H (%)	N (%)	NO_3^-–N	NO_2^-–N	NH_4^+–N	TOC
Softwood	28.11	5.61	1.09	<0.01	0.02	0.01	0.62
Hardwood	36.13	4.64	0.51	0.05	<0.01	0.05	1.41
Coniferous	44.09	5.66	0.64	0.02	<0.01	0.04	1.30
Mulch	26.08	3.87	1.11	0.07	0.06	0.11	0.88
Willow	47.23	5.62	0.35	0.09	0.04	0.18	4.87
Compost	14.53	2.32	1.10	0.28	0.03	0.03	0.94
Leaves	41.70	5.41	0.55	0.04	0.04	0.13	1.37
Native soil	7.65	2.77	0.30	<0.01	<0.01	0.02	0.38