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The impact of woodchip-gravel mixture on the efficiency and toxicity of denitrification bioreactors

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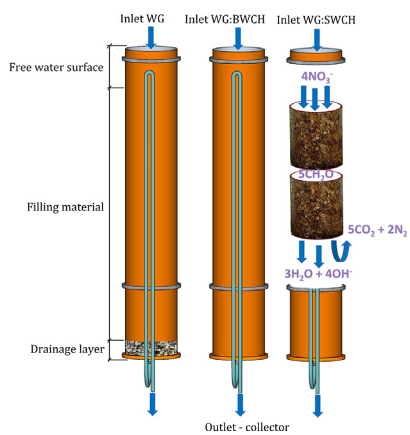
HIGHLIGHTS

- Pure OM rises high organic carbon concentration risk in bioreactor runoff.
- High TOC and FNI concentrations correlated with various aquatic organism inhibitions.
- Mixed-material filter performed during the study period similar denitrification level as pure woodchip material.
- Hydraulic retention time of 4.1 days, enough to reach 96% denitrification

GRAPHICAL ABSTRACT



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ABSTRACT

Woodchip-based denitrification bioreactors are widely used for treatment of high loads of nitrate pollution in agricultural run-off water. A concern raised recently, as a consequence of various organic fillings being experimented with, is whether the positive effect given by nitrate reduction could override the negative effects of such bioreactors, mainly caused by degradation of wood and the production of potentially harmful conditions for aquatic ecosystems. This paper presents the results of the experimental testing of two different filling materials: birch (BWCH) and spruce (SWCH) woodchip, and their mixture with washed gravel (WG) in volumetric ratio 10:1. We have focused on the leaching of organic carbon and phenols, and its impact on selected aquatic organisms, as well as on their denitrification efficiency and NO_3^- load removal rate (LRT). The results show that TOC, DOC and FNI (phenolic index) leaching is higher for the pure woodchip materials and is closely correlated with the growth inhibition of tested organisms (*Vibrio fischeri*, *Daphnia magna*, *Desmodesmus subspicatus*, *Lemna minor*). The highest denitrification efficiency and the highest load removal rates were recorded in mixed filling material (96% and 1.4 mg $NO_3^- \cdot dm^3 \cdot d^{-1}$ for WG:BWCH; 85% and 1.2 mg $NO_3^- \cdot dm^3 \cdot d^{-1}$ for WG:SWCH). Denitrification bioreactors with mixed woodchip filling material present a promising, cheap, and extensive technology for the treatment of agricultural field run-offs.

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1. Introduction

Surface and groundwater nitrogen pollution is a worldwide problem that calls for novel approaches for its reduction (Winiwarter et al., 2011). This is especially the case in Europe where special attention is paid to the problem of nitrate pollution due to the implementation of Council Directive 91/676/EEC concerning the protection of fresh waters against pollution caused by nitrates from agricultural sources (EU, 1991). Denitrification bioreactors are an effective groundwater and agricultural tile drainage nitrate removal method which were tested, for the first time, >20 years ago in the United States (Blowes et al., 1994). In addition to nitrate removal, the technology is reported to be also applicable to Salmonella and *E. coli* removal from tile drainage (Soupir et al., 2018). This method is based on anaerobic reduction of nitrates by heterotrophic bacteria and uses a solid organic carbon source for the growth of denitrifying bacteria. The first field scale series of tests was run almost at the same time (Robertson and Cherry, 1995). That was followed by various studies focused on improving the method, mainly by applying different types of organic carbon sources, namely woodchips (Greenan et al., 2009; Moorman et al., 2010) and other materials such as sawdust (Healy et al., 2006), corncobs (Schipper et al., 2010a), and cardboard fibers or soybean oil (Greenan et al., 2006). Recently new material such as biochar is also being used (Bock et al., 2018). Different combinations of organic and inorganic material have been suggested to address the unsatisfactory hydraulic properties of pure organic-based filters being caused by the degradation of organic material (Burbery et al., 2014). Schmidt and Clark (2012) reported a successful application of a 1:1 mixture of pine sawdust and washed sand. Woodchip degradation could cause more problems than just decreasing the filter's hydraulic conductivity. For instance, compounds such as phenols, resin acids, tannins, lignins and volatile fatty acids, as a result of wood degradation, could appear in the leachate which could be toxic to aquatic plants and animals (Hedmark and Scholz, 2008). Colour, smell, and higher released TOC levels in the bioreactor effluent, especially in the startup period, could be also problematic (Schipper et al., 2010b). Although such a potentially negative effect of woodchip based denitrification barriers should not be underestimated, only a few studies, so far, have been concerned with ecotoxicological impacts of wood leachates. The toxicity of trembling aspen woodchipwater leachate has been reported for trout, daphnids, and algae (Taylor et al., 1996), and aspen chips have been shown to have a negative impact on marine bacteria *Vibrio fischeri* (Rex et al., 2016). Despite such observations, studies that have been specifically focused on the toxic impact of denitrification bioreactors on the aquatic ecosystems, via experimenting the filter's medium and its influence on the treated water's characteristics, are lacking. In this study we used two different woodchips, namely BWCH and SWCH, as pure organic filters or in combination with gravel (in a V/V ratio of 10:1), to investigate their impacts and toxicity on the aquatic organisms as well as their denitrification efficiency. Pure woodchip based material and mixed materials were chosen to compare their denitrification rates. Moreover, we expected that and planned to check if, the latter could eliminate the abovementioned risks which are related to the pure woodchip material application. To the best of our knowledge, this is the first report to tackle the efficiency and toxicity of denitrification bioreactors with a woodchip-gravel medium. The tests have been done in lab-scale bioreactors, the results of which will enable us to determine better filling material, judged by its ecological impact and nitrate removal efficiency. The outcomes, hence, could be used at larger dimensions for further investigations, and also for application in the field.

2. Materials and methods

2.1. Filling materials

Two organic and one inorganic filling material were chosen to be tested: BWCH, SWCH and washed gravel (WG), respectively. Woodchip-based materials were chosen based on Blowes et al. (1994). WG was chosen on the grounds of its application in operational constructed wetlands (Vymazal, 2005). The characteristics of the filling materials are summarized in Table 1. Pure woodchips and woodchip mixture (volume ratio 10:1 V/V) were tested in the first set of experiments, i.e. leaching tests. Mixed materials and pure washed gravel were chosen to be tested in another set of experiments – column tests.

2.2. Leaching tests

Pure organic and mixed filling materials were used in one-stage batch leaching tests with a liquid to solid ratio of 10 $l \cdot kg^{-1}$ without size reduction, consistent with European standards (EN 12457-4 and EN 14735). Using the calculated dry matter content of each material determined at the beginning, the equivalent mass of raw material (without any pre-treatment) was put into the 2 l reagent bottles and filled with 1.6 l of tap water. In total, five samples were prepared for each material. Reagent bottles were placed on the overhead shaker and mixed for 1–5 days at laboratory temperature with 5 RPM. One sample of each material was decanted, centrifuged, and filtered using membrane paper (size of pores 4 μm) on a daily basis. From each sample 1 l of filtrate was transported to the laboratory for ecotoxicological assays. The rest of the filtrate was analysed for total organic carbon (TOC), dissolved organic carbon (DOC) and phenol index (FNI). Analysis of TOC and DOC was done based on the European standard (EN 1484) using combustion catalytic oxidation method with final detection with infrared spectrophotometer. FNI analysis was done using standard direct 4-aminoantipyrine spectrophotometric method after distillation (ISO 6439). The results obtained in $mg \cdot l^{-1}$ were then recalculated to describe the total amount of leached component related to total mass of the sample in $g \cdot kg^{-1}$ of dry matter using the following equation:

$$A = C \cdot [(L/M_D) + (MC/100)], \text{ where}$$

A	is the mass of the leached component from DM at L/S = 10 (in $g \cdot kg^{-1}$ of DM)
C	concentration of the component in leachate (in $mg \cdot l^{-1}$)
L	total volume of leaching liquid (in l)
MC	humidity described in % of DM
M_D	mass of dried analytical sample (in kg)

The phenol index was chosen, among others, for the evaluation of water quality as it is correlated with the negative effects of the contaminated water on aquatic organisms. Phenolic compounds in wood are reported to be responsible for micro-biocide and insecticidal effects (Samis et al., 1999).

2.3. Ecotoxicological assays

To describe the potential risk of the organic material leachate to aquatic ecosystems, four different ecotoxicological assays were covered. Aquatic microorganisms (*Vibrio fischeri*), invertebrates (*Daphnia*

Table 1
Characteristics of filling material.

Material	Abbreviation	Bulk density ($kg \cdot m^{-3}$)	Dry matter (%)	Porosity (%)
Washed gravel	WG	1533	100	32.1
Birch woodchips	BWCH	94	75.8	61.4
Washed gravel + Birch woodchips	WG:BWCH	1500	98.5	33.1
Spruce woodchips	SWCH	137	87.6	74.4
Washed gravel + Spruce woodchips	WG:SWCH	1311	98.9	39.8