

# POLY ( $\epsilon$ -CAPROLACTONE) AS BIOFILM SUPPORT AND CARBON SOURCE FOR GROUNDWATER DENITRIFICATION

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## Abstract

The application of biodegradable polymers (solid carbon sources) has been gaining importance in groundwater denitrification process. Solid carbon sources serve not only as sources of reducing power for denitrification but also as solid matrices for biofilms development. Moreover, in contrast to conventional processes, the use of this kind of carbon sources has no potential risks of release of excess dissolved organic carbon with the resultant deterioration of water quality.

The aim of the present work was to investigate the feasibility and efficiency of nitrate removal from groundwater by biological denitrification in column laboratory reactors packed with supports of poly ( $\epsilon$ -caprolactone) (PCL).

The maximum denitrification rate attained with PCL was 4.38 mg/L.h N-NO<sub>3</sub> at velocity of 0.08 m/h, at 20 °C and pH 7.0.

**Keywords:** Groundwater; denitrification; biodegradable polymer; biofilm

## Introduction

Groundwater is widely used as a drinking water source in most countries of the world. However, groundwater nitrate contamination has steadily been increasing over the years as a consequence of anthropogenic activities. Elevated nitrate concentrations in drinking water sources can cause diseases such as methahemoglobinemia and stomach cancer (Wolfe & Patz, 2002).

Nitrate is characterized by elevated stability and solubility, therefore, has a low potential for adsorption or coprecipitation. In this regard nitrate removal by conventional water treatment technologies such as lime softening and filtration is not efficient (Heredia *et al*, 2006). Physical and chemical processes such as reverse osmosis, ion exchange, electrodialysis and chemical denitrification have been used for nitrate removal from water but despite their effectiveness, they are very expensive. Other alternative solutions are needed.

The use of biological denitrification to convert nitrate to harmless N<sub>2</sub> gas and nitrous oxide represent a good alternative treatment process for the remediation of groundwater contaminated with nitrate due to the elevated specificity of denitrifying bacteria, low cost and high denitrification efficiency (Rivett *et al*, 2008).

Typically, contaminated groundwater with nitrate is severely limited in organic carbon and the addition of an external soluble carbon source (e.g. acetic acid, sucrose, ethanol and methanol) is the usual procedure to achieve nitrogen removal (Rivett *et al*, 2008). Nevertheless, the costs associated and the risk of additional contamination of the environment involved in this procedure demand the development of innovative treatment strategies. In this context, a promising strategy for nitrogen removal consists on the utilization of biodegradable polymers that support the growth of a denitrifying biofilm and serve as a source of organic carbon.

The aim of this work was to evaluate the feasibility and efficiency of nitrate removal by denitrification from groundwater using poly ( $\epsilon$ -caprolactone) as a carbon source.

## Methods

The laboratory setup is schematically depicted in Fig 1. A poliacrylic column (1.04 m long with an inner diameter of 0.042 m) was filled with supports (each support: 0.0018 m<sup>2</sup> of surface area) of PCL.

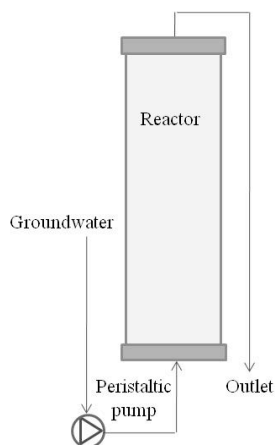


Figure 1. Schematic of experimental setup.

The column was fed with simulated groundwater (Dang *et al*, 2009, Ovez *et al*, 2006) with increasing concentrations of nitrate (0, 10, 20, 30, 40 and 50 mg/L N-NO<sub>3</sub>) during 70 days. The pH was adjusted to 7.0 and a mixed culture was used as inoculum. The column was operated in an upflow mode at a velocity ( $v$ ) of 0.08 m/h which corresponded to a feed rate of 1.83 ml/min. The flow was regulated by a peristaltic pump (Watson Marlow, 101R).

In order to establish anoxic conditions in the reactors, the medium was sparged with N<sub>2</sub>. All experiments were conducted at room temperature of 20 °C.

Samples were collected at the inlet and outlet ports for nitrate, nitrite and  $\epsilon$ -caprolactone analysis. Biofilm samples from PCL supports were sampled according to Rodrigues *et al* (2008) at the beginning and end of the experiments for suspended solid (SSV) analysis. Nitrate and nitrite were measured according to the colorimetric methods and SSV were determined according to the gravimetric methods which are described in Standard Methods (APHA, AWWA, WPCF, 1998). Soluble  $\epsilon$ -caprolactone was measured by high performance liquid chromatography (HPLC, Knauer) using a UV-Vis detector. Gas samples were taken at the end of the experiments for gas chromatography analysis (CO<sub>2</sub>, N<sub>2</sub>O e N<sub>2</sub>) using a chromatograph (GC Chrompack CP 9001). Measurements were made in duplicate.

## Results and Discussion

The effect of nitrate load was studied by changing the inlet nitrate concentration in five subsequent steps from 10 to 50 mg/L N-NO<sub>3</sub>, (Fig 2). Complete nitrate removal was achieved in the column for nitrate concentrations in the range of 10–40 mg/L N-NO<sub>3</sub>. However, when a concentration of 50 mg/L N-NO<sub>3</sub> was tested, nitrate concentrations in the outlet increased to 10 mg/L N-NO<sub>3</sub> and remained constant over time.

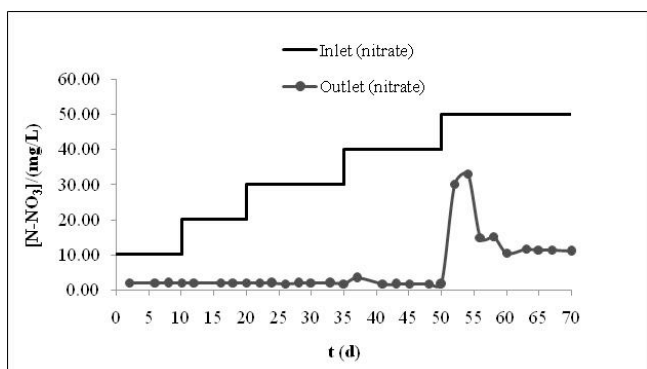


Figure 2. Inlet and outlet concentrations of nitrate.

The maximum nitrate removal achieved in the present study was 4.38 mg/L.h N-NO<sub>3</sub>. The concentration of nitrite was very low with a maximum of 0.02 mg/L N-NO<sub>2</sub>. It increases slightly to 0.06 mg/L N-NO<sub>2</sub> for a concentration of inlet nitrate of 50 mg/L N-NO<sub>3</sub> (Fig 3).

The gas composition analyses showed that the values of N<sub>2</sub>O were below 1.9 % for concentrations of nitrate between 10 and 40 mg/L N-NO<sub>3</sub> in the inlet, and 5.8 % for 50 mg/L N-NO<sub>3</sub>. Regarding the SSV values of biofilm, they increased from the beginning (0.08 g/L) to the end (0.15 g/L) of the experimental work.

The concentration of soluble  $\epsilon$ -caprolactone was in all cases below 0.54 mg/L achieving zero for inlet nitrate concentrations of 40 and 50 mg/L N-NO<sub>3</sub>. These results indicate a limitation of nitrate for concentrations lower than 40 mg/L N-NO<sub>3</sub> and a limitation of carbon for upper nitrate concentrations in a denitrification process (Fig 4).

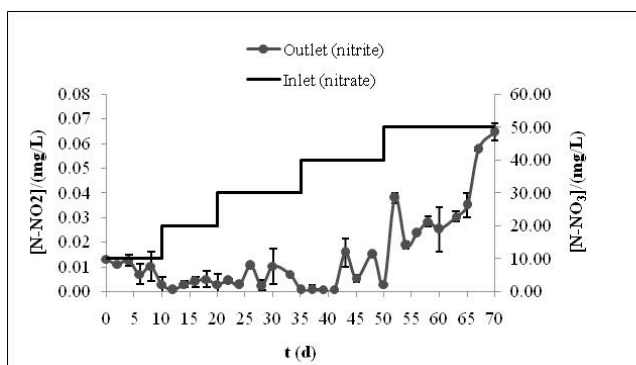


Figure 3. Inlet concentrations of nitrate and outlet concentrations of nitrite.

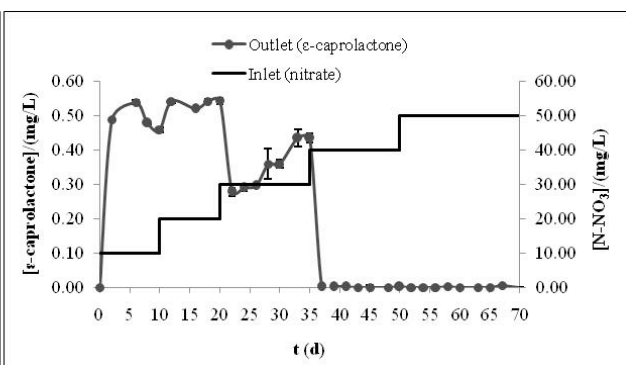


Figure 4. Inlet concentrations of nitrate and outlet concentrations of  $\epsilon$ -caprolactone.

## Conclusions

A maximum denitrification rate of 4.38 mg/L.h N-NO<sub>3</sub> was achieved at 20 °C and pH 7.0.

Denitrification was limited by nitrate for inlet concentrations lower than 40 mg/L N-NO<sub>3</sub> and limited by carbon for higher nitrate concentrations.

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