Permeable Reactive Barriers using nanoparticles to remediate nitrate pollution

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INTRODUCTION: Nitrate (NO_3^-) is pervasive in the biosphere [1, 2]. Contemporary agricultural practices are among the major anthropogenic sources of reactive nitrogen species, where nitrate is the most abundant of these [2]. Excessive amounts of reactive nitrogen in soils and groundwater are creating significant threats to human health and safety [3] as well as a host of undesirable environmental impacts [2]; it is currently considered the second most relevant environmental issue, after carbon dioxide emissions. Nowadays, among the most relevant and promising approaches to reduce nitrate concentration in water, namely groundwater, are denitrification-based processes [4]. Permeable reactive barriers (PRB) have been proven effective in reducing various contaminants in copious amounts, particularly in shallow groundwater [5]. However the possible added effectiveness of using nanoparticles in these structures to obtain nitrogen gas from nitrates requires further investigation.

OBJECTIVES: This work explores the possibility of employing permeable reactive barriers comprising nanoparticles as an effective end-of-pipe technology to tackle nitrate pollution in groundwater. By nitrate pollution it is considered a nitrate concentration in groundwater above 50 mg dm^3 NO_3^- (11, 3 mg dm^3 NO_3^--N) as limited by Nitrates Directive - Directive 91/676/EEC from 12th December 1991.

MATERIALS AND METHODS: A literature review was conducted in 34 databases, following a four steps methodological approach. First, a set of pertinent terms was used in the initial searches. Second, synonyms from the first set of terms were used to perform further searches. Third, from the selected papers, other relevant terms were identified to perform a third set of searches. In the forth step, the bibliography of the selected papers was researched for further relevant papers. The set of studies selected for in-depth analysis were exclusively laboratorial ones. Each study was assessed by set of relevant characterization variables.

RESULTS AND DISCUSSION: The degradation of nitrate from soil and groundwater can occur by physical adsorption, chemical reduction or biological denitrification. Physical adsorption is a surface mediated process where nitrate bonds to the surface of an adsorbent, e.g. biocharcoal, ion exchange resins, bamboo powder charcoal.

With chemical reduction, nitrate is chemically reduced by, e.g. nanoscale zerovalent iron (NZVI), bimetallic Fe/Cu nanoparticles, copper-coated zerovalent iron nanoparticles, bimetallic Fe/N nanoparticles, nanosized zero valent iron-polymeric anion exchanger composites, nanosized zero-valent iron supported by polystyrene resins, iron oxide/magnetite (Fe_3O_4), palladium-copper catalysts supported on cationic resin, Poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose] based zero valent nickel nanocomposite. Nitrate chemical reduction processes yield mostly ammonium, a soil and groundwater contaminant. Moreover, NZVI and zerovalent iron (ZVI) particles have been proven effective remediation agents for several pesticides, e.g. atrazine and achalor for the former, and flutriafol for the latter.

Whereas with physical and chemical processes the reactive nitrogen species are kept in the terrestrial or aquatic system, in biological denitrification, nitrate is transformed in a hypoxic media by bacteria into N_2, thus closing the natural nitrogen cycle. While autotrophic denitrification uses hydrogen gas from the oxidation of, e.g. iron as an electro donor, heterotrophic denitrification is reliant on source of organic carbon and electron donor for the denitrifying microorganisms. The organic carbon sources used for the promotion of heterotrophic denitrification encompass wood byproducts, mulch, compost and leaves. Autotrophic sulfur-oxidizers were also used to remove nitrate. Moreover, it has also been employed a two-layer permeable reactive biobarrier for the biotic reduction of nitrogen, where the first layer of the barrier addressed dissolved oxygen by ZVI, in order to create a down-gradient anaerobic environment for the heterotrophic denitrification to take place in the second layer of the barrier. NZVI also has affinity to react with dissolved oxygen, a characteristic which has to be accounted for when using such materials. Tests with different media by combining cotton burr compost, a sediment low in organic carbon and NVZI have proven that media made of

cotton burr compost removed nitrate at a faster rate than did the combination of cotton burr mixed with NZVI and/or sediment. Nitrate reduction processes can depart from ammonia; in such cases a prior microbial aerobic nitrification stage must be ensured so that the resulting nitrate can be then reduced into nitrogen gas.

The primary controls for the denitrification process are the amount of available NO_3^-, available carbon, the energy source, and the absence of gaseous oxygen. Other relevant factors in the denitrification process encompass pH, ion composition in the media and the redox potential.

CONCLUSION: Nitrate is considered to be the most ubiquitous groundwater contaminant in the world, being the agricultural runoff the major source of groundwater contamination by nitrate. The denitrification processes are complex and subject to an intricate interplay of several variables in the soil. Nevertheless, PRB have been proven effective to ensure denitrification, mostly by heterotrophic pathways. However how the denitrification effectiveness varies with changing particle size of the electron donor, for different electron donor substances, is not yet clear. Thus though there is a substantive body of knowledge on PRB, the use of nanoparticles in these structures is relatively novel and emergent for soil and groundwater remediation, so further research and advancements are required for a clear understanding of the principles that govern their effectiveness.

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