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Nanoparticles based Permeable Reactive Barriers as an Eco-efficient Technology for nitrate remediation in soil and groundwater

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The need to increase agricultural yield led, among others, to an increase in the consumption of nitrogen based fertilizers. As a consequence, there are excessive concentrations of nitrates, the most abundant of the reactive nitrogen (Nr) species, in several areas of the world. The demographic changes and projected population growth for the next decades, and the economic shifts which are already shaping the near future are powerful drivers for a further intensification in the use of fertilizers, with a predicted increase of the nitrogen loads in soils. Nitrate easily diffuses in the subsurface environments, portraying high mobility in soils. Moreover, the presence of high nitrate loads in water has the potential to cause an array of health dysfunctions, such as methemoglobinemia and several cancers. Permeable Reactive Barriers (PRB) placed strategically relatively to the nitrate source constitute an effective technology to tackle nitrate pollution. Ergo, PRB avoid various adverse impacts resulting from the displacement of reactive nitrogen downstream along water bodies. A four stages literature review was carried out in 34 databases. Initially, a set of pertinent key words were identified to perform the initial databases searches. Then, the synonyms of those initial key words were used to carry out a second set of databases searches. The third stage comprised the identification of other additional relevant terms from the research papers identified in the previous two stages. Again, databases searches were performed with this third set of key words. The final step consisted of the identification of relevant papers from the bibliography of the relevant papers identified in the previous three stages of the literature review process. The set of papers identified as relevant for in-depth analysis were assessed considering a set of relevant characterization variables. A PRB consists of a permanent or replaceable reactive media placed in the subsurface which is often installed by trenching, across the flow path of the contaminant plume, which must move through it as it flows, usually under its natural gradient, and therefore creating an in situ passive treatment system. Such system is primarily tailored for shallow groundwater, where contaminants are immobilized or transformed to nontoxic products by means of physical-chemical or biological processes. The installation of PRB containing organic carbon in its composition, e.g. from wood dust, wood chips, or other, has been proven successful for the dinitrification of groundwater. This technology relies on the biologic activity of denitrifying bacteria to reduce nitrate into inert nitrogen gas. Nevertheless, the use of nanoparticles in PRB is relatively novel and emergent for soil and groundwater remediation. Among the most widely studied nanoparticles for soil and groundwater remediation is zero-valent iron (ZVI). The extensive use of nanoparticulate ZVI in environmental engineering applications derives not only from its versatility and economic reasonableness, high reactivity, large specific area, effectiveness of delivery to contaminated areas, thus their effectiveness in rapidly reducing a diverse array of priority source zone contaminants, but also by its allegedly non-toxicity. However, to be effective, nanoscale ZVI has to adequately be stabilized, otherwise due to ferromagnetism the nanoparticles will rapidly aggregate in media, giving rise to micro or milimetric aggregates, which reduce the environmental remediation effectiveness of the nanoparticles. The use of nanoscale zero-valent iron (NZVI), nanoscale Fe3O4, nano zero-valent iron as bimetallic Fe/Cu, zero valent iron nanoparticles produced via the reduction of FeSO4 by NaBH4, Poly[$\beta - (1 \rightarrow 4)$-2-amino-2-deoxy-D-ghicopyranose] based zero valent nickel nanocomposite, NZVI supported by polystyrene resins in the chemical reduction of nitrate leads to varying amounts of nitrite, ammonia, ammonium and occasionally to nitrogen gas. Liu (2013) demonstrated the effectiveness of obtaining nitrogen gas from nitrate by a two stage PRB comprised of ZVI and activated carbon as an immobilizing media for a denitrifying microbial consortium. A major advantage of PRB resides in its cost-effectiveness to control significant contaminated plumes in shallow groundwater. The method might involve a substantive initial capital investment, which increases with the depth of the PRB. Once installed, the PRB often requires negligible maintenance or further operational costs, a distinctive feature when compared with alternative groundwater treatment methods such as, e.g. pump and treat. Long (2011) refers several examples of PRB for dinitrification that sustain high levels of nitrate removal for extended lengths of time. This work highlights that nitrate pollution is a relevant contemporary environmental and health issue with foreseeable exacerbation in the long term, and to which the application of remediation approaches is required. Therefore, PRB is a relevant possible approach to address both point and non-point sources of nitrate pollution in soil and groundwater. The use of PRB for dinitrification applications involves cheap organic carbon sources to consummate the reduction of nitrate to nitrogen gas. The use of ZVI nanoparticles can be very relevant in stimulating the biologic activity but also in inducing the media characteristics that make the biotic denitrification activity viable. Moreover, PRB present a set of advantages that makes this technology an eco-efficient one, since denitrification can be effectively accomplished by such a structure throughout extended periods of time, with minimal maintenance costs.

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Permeable reactive barriers, Nitrate, Eco-efficient

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