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ANION EXCHANGE RESIN-SUPPORTED nZVI PERMEABLE REACTIVE BARRIERS FOR REMOVAL OF NITRATES FROM GROUNDWATER

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Introduction

The use of zero-valent iron nanoparticles (nZVI) as a reactive medium in permeable reactive barriers (PRBs) has often been used to remediate contaminated groundwater especially with oxo-anions such as nitrates and chromates, as well as chlorinated organics. Nitrates have received special attention because they can easily reach groundwater, the main source being agricultural activities. However, ZVI nanoparticles have some limitations in practical applications. The main drawback is that they are extremely small and can easily agglomerate due to their colloidal and magnetic characteristics.

To solve the issue regarding the nZVI tendency to be agglomerated when used alone, a wide range of supporting materials were used to immobilize nZVI without decreasing its reactivity. In this respect, both organic materials (i.e. ion exchange resins, chelating resins, polymeric substrates, etc.), as well as inorganic materials (i.e. clay minerals, metal oxides, zeolites, etc.) were used. The physical-chemical characteristics of the materials used as support have a major influence on the size and distribution of nZVI particles immobilized on them. In addition, the support material has the role of concentrating the reactive phases by adsorption, which favors the redox reactions that take place in the system.

Therefore, this paper tests the performance of a new reactive barrier, based on nZVI deposited on a strongly basic anion exchange resin for removing nitrates from a simulated groundwater.

Materials and methods

Zero-valent iron nanoparticles (nZVI) were obtained by the reduction reaction of ferrous ions with sodium borohydride (NaBH₄) at the surface of a strong base anion exchange resin (Purolite A400). Thus, a solution of ferrous sulfate was prepared and contacted with the ion exchange resin at various solid-liquid mass ratios. Sodium borohydride was then added dropwise with continuous stirring under an oxygen-free atmosphere. The black solid particles formed were first separated by filtration, rinsed several times with ethanol, dried and kept in an oxygen-free atmosphere until use. The new permeable reactive barrier (nZVI-Purolite A400) was tested for the removal of nitrates from a simulated groundwater under various working conditions. The composition of the simulated groundwater was set as 30 mg/L SO₄²⁻, 140 mg/L Na⁺, 30 mg/L Cl⁻, 100 mg/L HCO₃⁻, 80 mg/L Ca²⁺, and 50 mg/L K⁺. Therefore, the simulated groundwater containing 10, 40, and 100 mg/L NO₃⁻, were mixed under

continuous stirring with the reactive barrier at a liquid-to-solid mass ratios of 5 for a contact time of 2 to 60 minutes. The experiments were carried out at a simulated groundwater pH of 3 and 8.

Results and conclusions

The results shown in Fig. 1 indicate a sharp decrease in nitrate content in the first 10 minutes of contact between simulated groundwater and the reactive barrier, after which the nitrate content remains approximately constant. The nitrate removal efficiency at this contact time is approximately 80% for the initial acidic conditions, and approximately 65% for the initial slightly alkaline conditions, regardless of the initial nitrate concentration in the simulated groundwater. The much better result of nitrate removal efficiency obtained in acidic conditions can be explained by the fact that the protons introduced into the system not only favor the reduction of nitrates, but also inhibit the formation of iron oxides. Also, a large part of ferrous ions are formed in the system by the reduction of these protons by zero-valent iron, which subsequently favor the reduction of nitrates. After the first 10 minutes of reaction in the initial acidic conditions, the pH of the aqueous solution increases from 3 to about 9. In the initial slightly basic conditions the pH increases from 8 to about 9.5 (with a slight difference between the initial nitrate concentration of 10 mg/L and 100 mg/L), after which it remains approximately constant. These results could indicate an inactivation of the reactive barrier by the formation of iron oxides at pH values higher than 7.

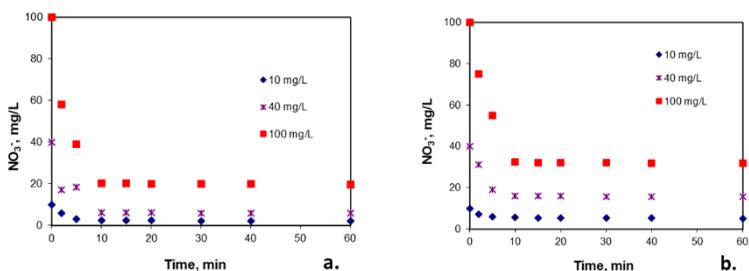


Figure 1. Nitrate removal rate from simulated groundwater: a) pH 3; b) pH 8.

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