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Electrochemical removal of nitrate using ZVI packed bed bipolar electrolytic cell

Joo-Young Jeong, Han-Ki Kim, Jung-Hwan Kim, Joo-Yang Park *

Department of Civil and Environmental Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea

HIGHLIGHTS

- ▶ The packing ratio of 1:1 and 2:1 (sand:ZVI) showed better current efficiency.
- ▶ The feed flow rate of 30 mL min^{-1} showed optimum current efficiency.
- ▶ Effluent pH was proportional to nitrate influx concentration.
- ▶ The nitrate was converted to ammonia as final product of nitrate reduction.
- ▶ The magnetite was found on the surfaces as corrosion products of ZVI.

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ABSTRACT

The present study investigates the performance of the zero valent iron (ZVI, Fe^0) packed bed bipolar electrolytic cell for nitrate removal. The packing mixture consists of ZVI as electronically conducting material and silica sand as non-conducting material between main cathode and anode electrodes. In the continuous column experiments for the simulated groundwater (initial nitrate and electrical conductivity of about 30 mg L^{-1} as N and 300 μS cm^{-1}, respectively), above 99% of nitrate was removed at the applied potential of 600 V with the main anode placed on the bottom of reactor. The influx nitrate was converted to ammonia (20% to maximum 60%) and nitrite (always less than 0.5 mg L^{-1} as N in the effluent). The optimum packing ratio (v/v) of silica sand to ZVI was found to be 1:1–2:1. Magnetite was observed on the surface of the used ZVI as corrosion product. The reduction at the lower part of the reactor in acidic condition and adsorption at the upper part of the reactor in alkaline condition are the major mechanism of nitrate removal.

1. Introduction

Nitrate contamination in groundwater has become an ever-increasing and serious environmental problem since 1970s. The excessive application of fertilizers in agriculture causes the infiltration of large quantities of nitrate into underground and surface water (Zhou et al., 2007). The international drinking water quality standards recommended 50–100 mg L^{-1} as an acceptable level for nitrate (Koparal and Öütveren, 2002; Choi et al., 2009) and the maximum contaminant level (MCL) was set by EPA for nitrate of 10 mg L^{-1} as N. Nitrate is very difficult to be removed by precipitation and adsorption because it is seldom complexed with cations. Conventional drinking water purification processes including flocculation, sedimentation and filtration appear to show no measurable effects for nitrate removal (Paidar et al., 2002; Zhou et al., 2007). Physical and chemical methods such as reverse osmosis, chemical denitrification and electrodialysis have been developed for elimination of nitrate from water (Follett and Hatfield, 2001). However, these nitrate removal processes have various limitations and are particularly not suitable for small communities that suffer nitrate contamination of the groundwater of their wells. To overcome these problems, electrochemical technologies have become studied for the removal of nitrate (Lacasa et al., 2011). Electrochemical methods through the selective nitrate reaction have several advantages: no requirement of chemicals before and after the treatment, production of the fewer amounts of sludge, small area demand and low investment cost (Koparal and Öütveren, 2002). The electrokinetic method is applicable to any electrically charged organic or inorganic species in water. In the electric field, positively charged ions migrate towards the cathode and negatively charged ions migrate towards the anode. The nitrate was attracted towards and concentrated near the anode in the electrical field and it would even retain nitrates with artificial flow (Eid et al., 1999). When the potential is applied, reactions (1) and (2) take place at the anode and cathode with electrolysis of water. If the produced ions are neither removed nor neutralized with other chemical reaction, these reactions lower the pH at the anode and raise it at the cathode (Probstein and Hicks, 1993):

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* Corresponding author. Tel.: +82 2 2220 0411; fax: +82 2 2220 1945.
E-mail address: jooypark@hanyang.ac.kr (J.-Y. Park).

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$$2H_2O + 2e^- \rightarrow H_{2\,(g)} + 2OH^- \quad (1)$$

$$2H_2O \rightarrow O_{2\,(g)} + 4H^+ + 4e^- \quad (2)$$

For electrolysis, there are two different electrode configurations, namely monopolar and bipolar. In the monopolar mode, all the electrodes are alternately tapped by electricity, whereas in the bipolar mode, only the electrodes at both ends are connected to electricity. Bipolar electrodes have been used in industrial reactors for applications such as electrosynthesis and water splitting and also for increasing fuel cell performances (Loget and Kuhn, 2011). The advantages of bipolar electrolysis are that it can pack as many as electrodes in a given space and the ohmic drop is low since the cathode and anode are located in the vicinity. However, these electrodes are limited in operating life because the structure finally agglomerates into a solid mass and clogs of the bed (Hadžismajlović et al., 1996). For efficient bipolar electrolysis, the electrolyte solution should have low electrical conductivity (Juvekar et al., 2009).

In this study, nitrate in a simulated groundwater was treated by the electrochemical method using ZVI packed bed bipolar electrolytic cell. Characteristics of electrolysis were investigated using multiple continuous experiments to find out the better operation parameters such as electrode position, packing ratio and flow rate (retention time). Performance of these reactors was also discussed with electric current consumption and reaction products of ZVI.

2. Materials and methods

2.1. Set-up and procedure

The electrolytic cell is composed of a number of electro-conductive particles packed between two main electrodes, and each particle works as an electrode. ZVI was used not only as conductive particles but also as an electron donor. The silica sand was used as non-conductive particle because it unlikely interferes with the nitrate reduction by ZVI (Huang and Zhang, 2005). Fig. 1 shows the schematic diagram of ZVI packed bed bipolar electrolytic cell. The reactor was made of a cylindrical acrylic resin (8 cm inner diameter, 20 cm height), and the bed volume was 1 L (HRT was 36 min at flow rate of 10 mL min^{-1}). The cathode was placed on the top and the anode was placed on the bottom of the reactor with cork gaskets for keeping water tightness between flanges. To achieve uniform flow in the reactor, the feed solution was injected in upward direction by using a peristaltic pump. To improve flow distribution, spherical glass beads (5 mm diameter) were packed at the bottom of reactor. The simulated groundwater was synthesized based on the compositions of the groundwater in a small community that are polluted with nitrate about 30 mg L^{-1} as N due to stock farming. The main characteristics of simulated groundwater are given in Table 1. All aqueous solutions were prepared using deionized water. The porosity of the silica sand-ZVI mixture bed was measured to be 36%.

Table 1
The properties of simulated groundwater (based on the compositions of the groundwater in stock farming community).

Parameter	Value
pH	6.8–8.0
Electrical conductivity	249–369 μS cm^{-1}
Nitrate	28.5–32.2 mg L^{-1} as N
Temperature	17.3–25.1 °C

2.2. Chemicals and materials

Sodium nitrate ($NaNO_3$ > 99.0%, guaranteed reagent, Junsei) and sodium chloride (NaCl > 99.0%, ACS reagent, Sigma–Aldrich Inc., USA) as electrical conductivity adjustment were used for making simulated groundwater contaminated with nitrate. A peristaltic pump (Easy-load® II, Cole-Parmer Instrument Co.) and tubing (4.8 mm inner diameter, 96410-25, Masterflex®) were used to feed the solution uniformly. Sphere type of ZVI (Fe > 98.4%, 0.6 mm diameter, Sanga Co.) and silica sand (<0.3 mm diameter, Joomoonjin silica sand Co.) were used as packing materials (780 g of silica sand and 1340 g of ZVI were used for each experiment). Direct

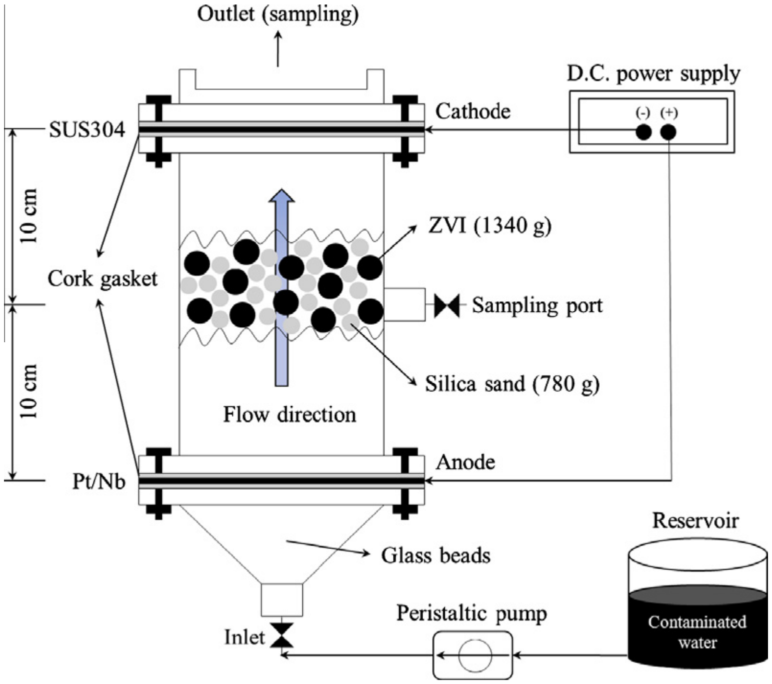

Fig. 1. The schematic diagram of ZVI packed bed bipolar electrolytic cell (not to scale) (reactor volume, 1 L; porosity, 36%; HRT, 36 min at flow rate 10 mL min^{-1}).