

THE APPLICATION OF ZVI BASED IRON-GELS IN REMEDIATION TECHNIQUES

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ABSTRACT

Zero valent iron (ZVI) has been widely used to treat contaminants, like chlorinated hydrocarbons, and it was documented as effective degrading agent of other environmental pollutants. ZVI can reduce halogenated compounds through iron oxidation, however, this process is mainly influenced by the surface of the iron particles. Nano ZVI technology has been developed to maximize the reactive surface of the iron, however, the costs of a treatment process are still quite high and the increased reductive capacity can be toxic. In present work, the combination of the relatively low costs of the traditional ZVI technology and the increased reductive capacity of the nano ZVI technology, avoiding the toxic levels, was tried to be achieved by developing ZVI gels (ZVIG). In up-flow columns filled with the same amount iron (iron powder) in sand (ZVI-P), and gels (ZVIG-A, ZVIG-B), the differences of reduction capacities were determined through nitrate reduction. This process was chosen because of the manageability of nitrate and the fact that ZVI is able to reduce it to ammonia. The column filled with ZVIG-B showed 65 % nitrate reduction from the beginning and maintained this value for 60 days. After the 60th day, a continuous decrease was observed in the efficiency, which reached 10 % after the 160th day. However, ZVIG-A showed 33 % nitrate reduction capacity from the beginning, and the reduction capacity quickly decreased to less than 10 %. After the 15th day, the effectiveness increased rapidly. The same phenomenon could be observed in the ZVI-P column. ZVIG-A could maintain this increased reduction capacity, but the iron powder could not. The nitrate reduction capacity of ZVI-P started to decrease after the 30th day, and it reached 20 % after the 55th day.

INTRODUCTION

Chlorinated hydrocarbons, especially trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC) are produced and utilized in thousands of tons by the industry and agriculture (J.A. Field et al. 2004). These compounds are known as irritable agents and they can be carcinogenic after long exposition time as well. Their degradation in the nature is problematic because of their stability and toxicity. Chlorinated hydrocarbons can accumulate in the soil and can pollute aquifers. Humans can be exposed to them directly via polluted drinking water and via inhaled dust. Since these compounds are drifting in the adipose tissues, it threatens humans indirectly by eating animals exposed to these pollutants.

Biodegradation could be a good solution; however, it requires specific bacterium strains that can completely degrade chlorinated hydrocarbons. However, during biodegradation, toxic intermediates can occur which can be harmful to the surrounding living organisms, such as the bacteria used for the degradation process (Johan E. T. et al. 1997).

Anaerobe abiotic reduction, using zero valent iron is another well-known and favorable process (Comfort S. D. et al. 2001; Shea P. J. et al. 2004). During this process, iron serves as electron donor and the halogenated compounds are the electron acceptors. At the end of the reduction, halogens are switched with hydrogen, and the compounds become less toxic, which makes them more available for the site-born microorganisms. However, this kind of dehalogenisation is connected to the surface of the iron particles, therefore the effectiveness of the reduction depends on the extent of the iron surface. Nano ZVI technology was developed to maximize the reductive surface of the iron. However it had been already documented that the increased reductive capacity can be toxic for *Escherichia coli*, (Changha Lee et al. 2008) and it could be harmful to the site-born bacteria as well. This property is very unfavorable because these bacteria can facilitate the degradation by using the less halogenated hydrocarbons as energy or carbon source and they can also decrease the concentrations of other alternative electron acceptors.

During this study, the different reduction profiles were investigated in constructed up-flow columns via nitrate reduction. This procedure was chosen because nitrate and its reduced forms (nitrite, ammonium) are easier to handle than the chlorinated pesticides. Moreover, it is known that ZVI is able to reduce nitrate to ammonium completely (Yong H. 2004). Therefore, nitrate is an appropriate substrate for the monitoring of the reduction processes.

MATERIALS and METHODS

Up-Flow column studies

Three different column reactors were constructed using 20 ml plastic syringes. The influent was 1 mM KNO₃ and HRT= 1 day. Two of the columns contained two different types of zero valent iron gel (ZVIG-A, ZVIG-B). The third column was filled with sand mixed with 1 g of iron powder (ZVI-P). The amount of iron was the same in each column. Samples were taken every day to determine nitrate and nitrite concentration. Three samples were used for each measurement.

Measurement of nitrate concentrations

100 µl of 5 gl⁻¹ Na-salicylate was added to the samples, and then they were mixed. The water content of the samples was totally vaporized. After vaporizing, 100 µl c.c. sulfuric acid was added. Then they were diluted with 3 ml distilled water and incubated at room temperature for 10 minutes. After this, 700 µl 10 N sodium hydroxide was added. After complete dissolution, the optical densities were measured with HACH Lange DR5000 spectrophotometer at 410 nm wavelength. Concentrations were determined using a calibration curve.

Measurement of nitrite concentrations

To 5 ml sample, 100 µl 1 % sulfanilamide (90 ml distilled water, 10 ml c.c. HCl, 1 g sulfanilamide) reagent was added. After a thorough mixing and 5-minute incubation at room temperature, 100 µl of 0,1 % NAD (100 ml distilled water, 0,1 g N-naphthyl-ethylenediamine-dihydrochloride) reagent was added. After total dissolution of the reagents, the optical densities were measured at 540 nm wavelength with HACH Lange DR5000 spectrophotometer. Concentrations were determined using a calibration curve.

RESULTS

Different reduction profiles of the three different fillings (ZVIG-A, ZVIG-B and ZVI-P) could be determined during a long-term experiment. The results showed significant variance in the nitrate reduction capacity depending on time as shown on Fig. 1.

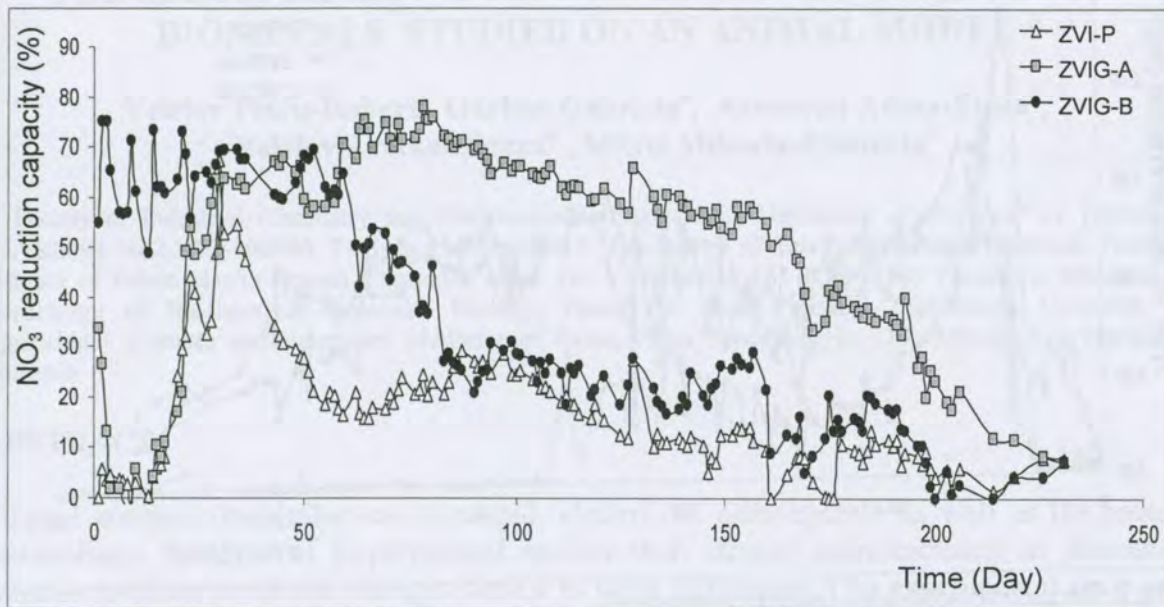


Fig. 1. Reductive activities (Nitrate reduction)

The column filled with ZVIG-B showed 65 % nitrate reduction from the beginning and maintained this value for 60 days. After the 60th day, a continuous decrease was observed in the efficiency, which reached 10 % after the 160th day. However, ZVIG-A showed 33 % nitrate reduction capacity from the beginning, and the reduction capacity quickly decreased to less than 10 %. After the 15th day, the effectiveness increased rapidly. The same phenomenon could be observed in the column filled with iron powder mixed with sand. ZVIG-A could maintain this increased reduction capacity, but the iron powder could not. The nitrate reduction capacity of ZVI-P started to decrease after the 30th day, and it reached 20 % after the 55th day. Then in the following period, it slowly decreased to less than 10 %. In case of the column filled with ZVIG-A, the reduction capacity started to decrease only at the 80th day and declined to less than 10 % from the 226th day.

Nitrite concentrations were also measured in the effluent (Fig. 2.) because this information was important to determine the reductive power of each column and to clear whether nitrate is reducing to nitrite or further. High level of nitrite concentrations should be avoided because it can cause methaemoglobinaemia (Clement A. Finch, 1948).

It was found that NO_2^- -N concentration was low in all of the columns compared to the influent NO_3^- -N concentration. However, it seems that both columns filled with ZVIG were more efficient in nitrite reduction than iron powder itself. In columns filled with ZVI-P, nitrite concentration was higher (almost reached 2.5 mg l^{-1}) while nitrite concentrations measured in the effluent of columns filled with iron gel did not reach 2 mg l^{-1} during the experiments. This indicates that the reduction was faster on the surfaces of the iron particles in the gels than in case of the iron powder, which resulted in less nitrite accumulation.

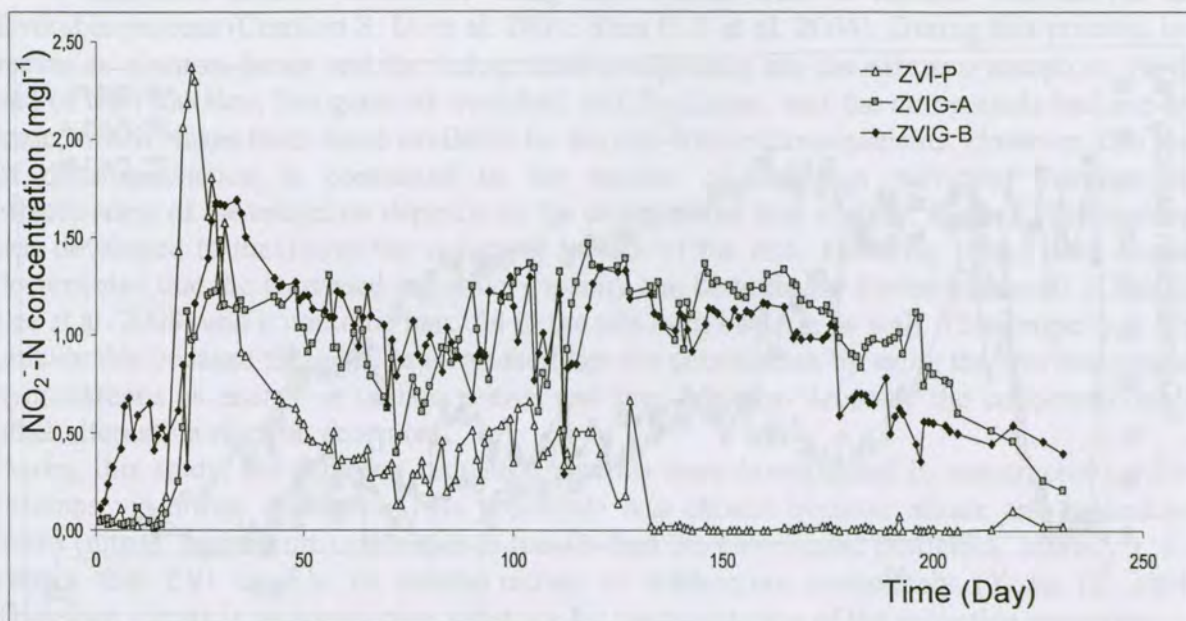


Fig.2. Reductive activities (Nitrite reduction)

CONCLUSIONS

- Due to the increased reductive surface, reduction capacities of iron gels were increased compared to the same amount of iron powder.
- Results showed that ZVIG-A and ZVIG-B iron gels had different nitrate reduction profile. ZVIG-B showed high level reductive capacity from the beginning of the experiment, while ZVIG-A reached the nitrate reduction maximum later, but could maintain it for a longer time than ZVIG-B.

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