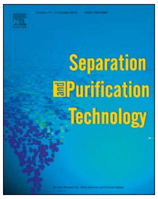
Separation and Purification Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Multilayer system of nanoscale zero valent iron and Nano-Fe/Cu particles for nitrate removal in porous media

Tamer Shubair[a], Osama Eljamal[a,*], Ahmed M.E. Khalil[a,b], Nobuhiro Matsunaga[a]

[a] *Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga, Fukuoka 816-8580, Japan*
[b] *Department of Chemical Engineering, Faculty of Engineering, Cairo University, Giza 12613, Egypt*

ARTICLE INFO

Keywords:
Nanoscale zero valent iron
Nano-Fe/Cu particles
Nitrate removal
Porous media
Multilayer system

ABSTRACT

This work studies the nitrate removal efficiency in porous media using nanoscale zero valent iron (nZVI) and modified surface of nZVI using Cu metal (known as bimetallic nano-Fe/Cu particles) in a multilayer system through an upflow packed sand column. The effect of multilayer and different thicknesses of nZVI/sand and nano-Fe/Cu particles on the nitrate removal performance was investigated. 10 g of nZVI and nano-Fe/Cu particles were introduced in each column with different layers configuration. The initial nitrate concentration was 45 NO_3^-–N mg/L. The distribution of nitrate trapped inside the column was evaluated by measuring nitrate concentrations, not only at the column inlet and outlet, but also at various intermediate sampling ports along the depth of the column. The results showed that the best condition to remove nitrate among nZVI/sand columns was observed when using a single 10-cm high layer of nZVI/sand and more than 97% of influent nitrate was removed. Whereas in (nano-Fe/Cu)/sand columns, the optimum performance was noted when using double 5-cm high layers of (nano-Fe/Cu)/sand and a complete removal was attained (100%). Furthermore, nano-Fe/Cu particles showed better removal efficiency than nZVI for the treatment of nitrate in simulated groundwater. Based on the results obtained, it was concluded that using nZVI in the full length of porous media or using nano-Fe/Cu particles in multilayer porous media could enhance nitrate removal effectively.

1. Introduction

Nitrate contamination of groundwater has become a real environmental and public health alarm worldwide. Excessive nitrate exposure can cause cancer and blue baby disease in infants due to the potential reduction of nitrate to nitrite [1,2]. Due to threats of nitrate contamination, World Health Organization (WHO) and many countries restricted the maximum contaminant level (MCL) of nitrate in drinking water to 50 mg NO_3^-/L and 10 mg NO_3^-–N/L, respectively [3,4]. Nitrate contamination usually originates from chemical fertilizers for agriculture, animal manure, wastewater discharges, fertilizers factories and landfills [5,6].

Several physico-chemical and biological technologies have been proposed for removing nitrate from contaminated water like ion exchange, reverse osmosis, electrodialysis and biological denitrification [7]. However, these processes are relatively expensive and are often limited due to potential of side effect on water quality [6,8]. Therefore, there is a need to explore attractive alternatives for resolving the problem of nitrate-contaminated sites. In recent years, zero valent iron (ZVI) has been employed intensively to remediate soil and groundwater contaminants such as As(III) [9], As(V) [10], Cr(VI) [11], Pb, Ni [12], Cu, Zn [13], PO_4^{3-} [14,15] and NO_3^- [16,17]. Nano-zero valent iron (nZVI) has shown higher reactivity compared with milli – or micro-sized iron for the effective removal of a wide range of contaminants [18,19]. The higher surface reactivity of nZVI is the result of larger surface area due to small size of particles [20,21]. In addition, these particles are nontoxic to aquatic organisms, available and cheap [22].

Recently, many efforts have been recorded to enhance the reactivity of nZVI. Doping the surface of nZVI using another metal (known as bimetallic nanoparticles), such as palladium (Pd), copper (Cu), platinum (Pt) or nickel (Ni) have been effective approach in degradation a variety of contaminants [23,24]. The advantages of bimetallic nanoparticles over nZVI alone are faster reaction kinetics and reduction of formation of toxic intermediates deposited on the surface of nZVI [25]. The increase in reactivity of bimetallic nanoparticles is related to catalytic hydrogenation and electrochemical effects [26].

For in situ nitrate removal from groundwater, permeable reactive barrier (PRB) is one of the well-known technologies owing to their effective operation and maintenance costs [27,28]. ZVI PRB has been successfully used to remediate groundwater contaminated with nitrate [29,30]. Several researches have focused on evaluating the behavior and

---

[*] Corresponding author.
E-mail address: osama-eljamal@kyudai.jp (O. Eljamal).

http://dx.doi.org/10.1016/j.seppur.2017.10.069
Received 14 September 2017; Received in revised form 27 October 2017; Accepted 29 October 2017

Please cite this article as: Shubair, T., Separation and Purification Technology (2017), http://dx.doi.org/10.1016/j.seppur.2017.10.069

efficiency of nitrate treatment by ZVI in laboratory scale column. Liu et al. [22] designed an anaerobic two-layer permeable reactive biobarrier to remediate nitrate contaminated groundwater in the presence of ZVI powder. Based on the results of their column experiment, the denitrification efficiency was estimated to be more than 94%. Similarly, Tehrani et al. [31] investigated nitrate removal using nZVI/Ni particles. They concluded that nitrate remediation was mostly influenced by seepage velocity, freshness and quantity of nZVI/Ni and particle size of porous media. Adding that the maximum nitrate removal did not exceed 85% in column experiment. Huang and Zhang [32] observed that adding certain selected cations (Fe(II), Fe(III), or Al(III)) in feed solution can greatly enhance nitrate removal and extending hydraulic retention time, increased nitrate reduction by Fe^0 packed columns. Gandhi et al. [8] studied degradation of nitrate by Fe^0 in columns under different microbial conditions and reported that reactive iron barriers can intercept and degrade nitrate effectively. Tang et al. [29] indicated that ZVI PRB is a potential technique for in situ remediation of soil and groundwater contaminated with nitrate in the alkaline conditions. Jeong et al. [33] investigated the removal efficiency of nitrate by ZVI in packed sand reactor bipolar electrolytic cell. The results showed that more than 99% of nitrate was removed and ammonia was the main final product of nitrate reduction. Hosseini and Tosco [34] assessed nitrate removal in a laboratory bench-scale aquifer system (60 cm length × 40 cm width × 50 cm height) using nZVI and carbon substrates. The results of their study demonstrated that the model has a great possibility for nitrate reduction in-situ contaminated groundwater. Araújo et al. [35] showed that the use of nZVI in PRBs is, indeed, a suitable technique for denitrification with high performance record but the long-term impact of nZVI on the environment and on the human health needs further work. Westerhoff and James [36] studied removal of nitrate under laboratory and field conditions using ZVI packed columns. They reported that nitrate removal ranged from 30% to 90% and also noticed a pH increase, DO decrease, and soluble iron increase during nitrate removal. Despite these studies, sufficient data cannot be found in the literature concerning the removal of nitrate using nanosized ZVI in packed sand column.

Other researchers investigated different nanoparticles to remediate different contaminants. Hu et al. [37] suggested that immobilized Phanerochaete chrysosporium loaded with nitrogen-doped TiO_2 nanoparticles could be a compatible and efficient method for treatment of landfill leachate which includes a variety of pollutants. Wan et al. [38] evaluated sodium dodecyl sulfate stabilized nano-chlorapatite (SDS-nClAP) for Pb immobilization in contaminated sediment. Experimental data indicated that SDS-nClAP was effectively transforming unstable Pb to stable fraction with a 38.3% increase.

In the present article, the main objective of this research was to study the effectiveness of nZVI and nano-Fe/Cu particles for the removal of nitrate in porous media using an upflow packed sand column. To attain this goal, the effect of multilayer system and different thickness layers of nZVI/sand and (nano-Fe/Cu)/sand on the nitrate removal rate was investigated. Nine columns were operated using 10 g of nZVI or nano-Fe/Cu particles in each column under different configurations. Additionally, tenth column was filled with sand only and used as a control column. Nitrate concentration was monitored in the influent, effluent and at different sampling ports along the various depths of the column. To the best of our knowledge, this research is the first study that uses nZVI or nano-Fe/Cu particles in multilayer system in porous media along the length of packed sand column to remediate nitrate contamination. Moreover, by using nZVI or nano-Fe/Cu particles in PRB, a new methodology that is more reactive is opened for the removal of different contaminants in situ.

2. Materials and methods

2.1. Materials and chemicals

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99.0%, Junsei Chemical Co., Japan), sodium borohydride ($NaBH_4$, 98.0%, Sigma–Aldrich Inc., USA) and ethanol (99.5%, Wako Co., Japan) were purchased for nZVI synthesis. Potassium nitrate (KNO_3, 99.0%, Wako Co., Japan) was used to make the nitrate solution, while hydrochloric acid (HCl, 35–37%, Wako Co., Japan) was used for pH adjustment. Anhydrous copper chloride ($CuCl_2$, 99.9%, Aldrich Inc., USA) was used to prepare nano-Fe/Cu particles. Sodium sulfate (Na_2SO_4, 99%, Wako Co., Japan), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$, 97%, Wako Co., Japan), sodium bicarbonate ($NaHCO_3$, 99%, Wako Co., Japan) and calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$, 70–79%, Junsei Chemical Co., Japan) were purchased to prepare simulated groundwater. All aqueous solutions including the feed solution were prepared using deionized water and were purged with nitrogen for 20 min for deoxygenation process. Standard sand (As One Co., Japan) was used as porous medium. Maximum and minimum diameter of sand particle was equal to 2 and 0.075 mm, respectively. The sand properties were estimated as bulk density ($\rho_b = 1.3\ g/cm^3$) and average porosity ($n = 0.35$). All chemicals and minerals were used as received without any pretreatment.

2.2. Synthesis of nZVI and nano-Fe/Cu particles

nZVI was synthesized based on chemical reduction of ferric chloride hexahydrate using sodium borohydride as described in the following reaction [39]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \quad (1)$$

In order to make 10 g of nZVI, sodium borohydride solution ($NaBH_4$, 98%, 0.74 M) was added slowly into ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%, 0.15 M) in 5000 mL four-neck glass flask at a rate of 1 L/h using a roller pump. The synthesis was processed under a continuous flow of nitrogen gas to create anaerobic condition. The synthesis was conducted with vigorous stirrer 250 rpm, under temperature 25 ± 0.5 °C using water bath and left for 20 min as aging time to complete the reaction. The resulting black precipitates were filtered by vacuum filtration, washed with deoxygenated deionized water and ethanol three times and then applied immediately in column experiments. Bimetallic nano-Fe/Cu particles were prepared in similar conditions but with addition of $CuCl_2$ to ferric chloride hexahydrate before pumping sodium borohydride. According to Khalil et al. [40], the optimum coating rate in case of nano-Fe/Cu was 5% wt/wt of $CuCl_2$/Fe. The redox reaction between Cu^{2+} and nZVI occurred as follows [41]:

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \quad (2)$$

2.3. Characterization of synthesized nanoparticles

To characterize the nZVI and nano-Fe/Cu particles, their surface morphology was analyzed using a transmission electron microscope (TEM, JEM – ARM 200F, JEOL Co., Japan). X-ray diffraction (XRD, TTR, Rigaku, Tokyo, Japan) was obtained to investigate the crystallinity of nZVI and nano-Fe/Cu particles using Cu/Kα radiation with scanning speed of $2^\circ\ min^{-1}$ and scanning range between 3° and 90°. The particle size of both nanoparticles was determined by a particle size analyzer (SALD-2300, Shimadzu Co., Japan). The Brunauter–Emmett–Teller (BET) specific surface area of nanoparticles was recorded by a specific surface area analyzer (Micromeritics 3Flex, USA).

2.4. Column experiment setup and operation

Column experiments were conducted using a Plexiglas column with a length of 25 cm and an internal diameter of 8.5 cm. The columns were pumped continuously with nitrate synthetic water in an upflow mode using a multiport peristaltic pump (RP-1000, As One, Japan). Four sampling ports were installed along the height of the column at 5 cm (S1), 10 cm (S2), 15 cm (S3) and 20 cm (S4) from the column inlet to