



Nitrate reduction by nano-Fe/Cu particles in packed column

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ABSTRACT

In this work the application of a modified surface nano zero valent iron (NZVI) as bimetallic Fe/Cu particles to remove high concentration of NO_3^- -N through packed sand column has been studied. Dispersed nano-Fe/Cu particles has been synthesized in water mixed ethanol solvent system (1:4 v/v) and described by XRD pattern, TEM and SEM images and BET analyze. Batch experiments have been conducted to investigate the effect of percentage coating of Fe^0 by Cu on the nitrate removal. Research on packed sand column (120 cm length, 6.5 cm inner diameter) has been done under conditions of Nano-Fe/Cu concentration (2, 5, and 8 g l^{-1} of solution), high initial NO_3^- -N concentration (100, 200, and 300 mg l^{-1}) and pore water velocity through sand (0.125, 0.250, and 0.375 mm s^{-1}) in seven sets. Results of batch experiments indicated the efficient coating percentage of Fe^0 by Cu in NO_3^- -N reduction was 2.5% (w/w). In addition, increase of pore velocity of water through packed sand has negative effect on the nitrate reduction rate. In contrast, increasing the injected mass of nano particles and the influent NO_3^- -N concentration would increase the rate of NO_3^- -N reduction. The best condition to reduce NO_3^- -N has been observed at end of sand column as 75% of influent concentration when nano-Fe/Cu concentration = 8 g l^{-1} , high initial NO_3^- -N concentration = 100 mg l^{-1} and pore water velocity through sand = 0.125 mm s^{-1} .

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1. Introduction

NO_3^- -N concentration higher than Maximum Concentration Level (MCL) in drinking water causes significant risk to human health such as blue baby syndrome in infants and the development of cancer when it is reduced in the form of nitrite ([1]; Haugen et al., 2003). In this regards many countries have set standard limit for in drinking water as 10 ppm [2]. Sources of NO_3^- -N include agricultural runoff, landfill leachate, leaking septic tanks, municipal storm water runoff, animal feeding operations and industrial waste [3,4]. Among the existing technologies for removing NO_3^- -N (e.g. ion exchange, reverse osmosis, electro dialysis, and biological denitrification), using of Zero Valent Iron (ZVI) has been attracted thinks of many researchers (e.g., [5,6]). Although in early 1990s, granular ZVI has been first employed in Permeable Reactive Barrier (PRBs) as an electron donor to reduce NO_3^- -N but it did not gain its popularity until the last decade when appeared in the size of nanometer.

Advantages of nano-zero valent iron (NZVI) particles in remediation of NO_3^- -N are due to small size of particles which is resulted in larger specific surface area and higher surface reactivity. In addition,

these particles are non-toxic, ubiquitous, and inexpensive and can be effectively injected to contaminated zones by groundwater ([7], Saleh et al., 2007, [8]).

In spite of NZVI efficiency in reduction of nitrate from water, but it faced critical issues for in-situ applications when injected in porous media. Some of these challenges include strong tendency of aggregation, agglomeration, rapid settlement on the solid phase surface which resulted consolidation, pore plugging and significant loss of porosity and permeability of porous media [9]. In addition, groundwater commonly has relatively high values of ionic strength, which is suitable for the reduction of electrostatic repulsion between nano particles and increase of aggregation [10]. Aggregation can cause reduction of NZVI transport through porous media. Research show that iron nano-particles may travel only a few centimeters in porous media from the injection position under typical groundwater conditions [11]. Johnson et al. [12] discussed that transport of significant mass loading of bare NZVI in porous media without varying large pore velocity through packed medium, mechanical increasing of NZVI, and/or use of amendments to the NZVI, is confronted by serious difficulty.

Many efforts have been carried out to prepare a stable suspension of NZVI by modifying particle surface to enhance the mobility of NZVI in porous media. In this regards promising new synthetic methods are being developed to produce more mobile ZVI nano-particles and reduced sticking coefficients without giving up significant reactivity. Many surface modifier and anionic surface chargers such as polyacrylic acid [13], Non-ionic surfactants such as polyoxyethylene sorbitan monolaurate [14], PV3A [15], starch [16], noble metals [17] and oil [18].

Abbreviations: NZVI, Nano zero valent iron; XRD, X-ray Diffraction; TEM, Transmission Electron Microscopy; BET, Brunauer, Emmett and Teller Method; MCL, Maximum Concentration Level; ZVI, Zero Valent Iron; PRB, Permeable Reactive Barrier; PV3A, Polyvinyl Alcohol-Co-Vinyl Acetate-Co-Itaconic Acid; TCA, Tetra-Chloro-Ethane; DI water, De-ionized water; PV, pore volume; UV-Vis, Ultra Violet-Visible; R_n , Reynolds's number.

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Coating nano- Fe^0 using another metal such as Ag, Pd, Pt, Ni, and Cu named bimetallic nano particles is another efficient approach which has been used in degrading a variety of contaminants (Ruangchainikom et al., 2006). The rate of reduction by bimetallic particles is significantly faster than those observed for Fe^0 alone [19]. The mechanism responsible for this reactivity is related to catalytic hydrogenation and electrochemical effect [20]. In addition, higher stability for the degradation and the prevention or the reduction of the formation and accumulation of toxic byproducts are the advantages of bimetallic nano particles.

Among the surface modifier metals for NZVI, Cu has superiority and known as a mild hydrogenation catalyst (Yang et al., 1997). Fennelly and Roberts [21] have observed that the Fe/Cu system increase the rate of reduction 1,1,1-TCA related to Fe/Ni combination and the bimetallic show a dramatically faster rate than Fe^0 alone. The efficiency of the catalyst used in bimetallic nano particles system reduces during time due to formation of an iron hydroxide layer, which delays reactant contact to the catalyst [22]. Liou et al. [23] has evaluated effects of three metals including Pd, Pt and Cu deposited onto nano- Fe^0 surface to test their reactivity to NO_3^- -N reduction. Their results indicate that the reactivity of three bimetallic nano particles can be ranked as $Cu > Pd > Pt$. Therefore, coating of NZVI by Cu metal enhances the rate of nitrate reduction in aqueous solution and decreases the aggregation and agglomeration of NZVI when injected in porous media.

The most information about the mechanism of nitrate reduction by nano Fe^0 or bimetallic type have been obtained from batch experiments [24–26] and limited research have been found that investigated the process of nitrate removal from water by these agents in saturated porous media in the scale of packed column or in-situ application.

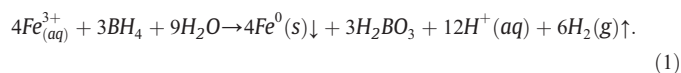
In this regards, the objectives of this study were first, to synthesize dispersed nano Fe/Cu particles that is highly reactive to reduce nitrate and also is mobile when injected in porous media. Second, to evaluate the effect of high initial NO_3^- -N concentration, mass of injected nano Fe/Cu particles, and pore water velocity through packed column sand on the NO_3^- -N removal rate. As far as the previous studies show, no previous work could be found on investigation of high concentrated NO_3^- -N reduction by nano particles of Fe/Cu in the length of packed column sand.

2. Materials and methods

2.1. Synthesizing of the nano- Fe^0 and nano- Fe/Cu particles

Research indicated that synthesizing of the Nano- Fe^0 using reduction of ferric (Fe^{III}) by BH_4^- , resulted as excessive pollution in high concentration of boron in the final products and causes harmful effects to human [27]. In this regards, synthesizing NZVI with low concentration of boron is problematic. To solve this challenge in this study, water mixed solvent (ethanol) system is used instead of water as single solvent for ferric in synthetic step, as described follows.

To synthesize nano- Fe^0 particles, $NaBH_4$ (0.2 M, 99%, Merk) solution (solution has been prepared as 4:1 (v:v) DI water/ethanol) has been added slowly in the rate of 1–2 ml min^{-1} into $FeCl_3 \cdot 6H_2O$ (0.05 M, 99%, Merk) aqueous solution at ambient temperature and vigorous stirrer ~400 rpm according to [28,29]. Using of ethanol during the synthesis step will resulted low concentration of boron in final products (for more information refer to [30]). All aqueous solutions have been de-oxidized using N_2 purged DI water for 20 min. During this reaction, ferric ion (Fe^{III}) has been reduced into black particles by sodium borohydride as the reductant, as shown in the following reaction:



The black precipitates have been filtered by vacuum filtration through Whatman (blue band) filter papers and then, washed with DI

water and ethanol at least three times. The freshly prepared particles have been stored in N_2 purged solution of 10^{-4} M HCl ($pH = 4$). A major advantage of this synthesis method which has once been used by Li et al. [31], is its relative simplicity and un-necessarily special instruments.

Bimetallic nano-Fe/Cu particles (full coating) have prepared by adding the fresh prepared Fe^0 particles into 1 g-Cu/1 $CuCl_2$ aqueous solution in vigorous stirrer and ambient temperature according to Zhang et al. [32] and Schrick et al. [33]. After a few minutes, redox reaction has been occurred between the Cu^{2+} and nano- Fe^0 as follows:



The resulting nano-Fe/Cu particles have been washed twice with DI water and stored in de-oxidized water. The whole above process has been carried out in a nitrogen environment.

2.2. Bench scaled packed sand column

Reduction of NO_3^- -N by nano-Fe/Cu particles have been carried out in bench scaled packed sand column. Uncontaminated sand with non-uniform size (effective diameter $d_{50} = 0.82$ mm) has been used as porous medium. Maximum and minimum diameter of sand particle is equal to 1.2 and 0.2 mm, respectively. The porous medium properties have been estimated as bulk density ($\rho_b = 1.68$ g cm^{-3}), particle density ($\rho_s = 2.67$ g cm^{-3}), and average porosity of packed system ($n = 0.37$). The average hydraulic conductivity has been estimated to be 0.55 $mm\ s^{-1}$ (44.5 m day^{-1}) from permeameter with constant head measurements. The experiments have been performed in a cylinder from plexi-glass with length of 120 cm and internal diameter of 6.5 cm. Sand (with characteristics that mentioned before) has been packed in the cylinder as the homogeneous porous medium. A permeable glass diffuser cover has been placed on top of the sand column to provide a uniform distribution of nano particles in sand (Fig. 1). To pack the sand in the plexi-glass cylinder, layers with 10 cm height have been vibrated after saturation. Sand has been flushed with a 1 mM HCl solution at 10–15 pore volumes (PV) in order to obtain a uniform surface charge in sand.

Before starting each experiment, 10–20 PV of water with certain concentration of NO_3^- -N has been passed through sand column to create a media with uniform concentration of N. On the length of the column, four points (P_1 to P_4) have been considered to sample from contaminant plume. 5 ml of the solution has been withdrawn from sampling points of P_1 to P_4 with a syringe, simultaneously, and then filtered by a 0.2 μm filter paper just before analysis by UV-Vis spectrophotometer for measuring the absorbance values of sample.

To better simulation of groundwater system in the experiments, water which was used in both batch and packed column experiments contained other ions as reported in Table 1. To supply water with a certain concentration of NO_3^- -N (100, 200, and 300 $mg\ l^{-1}$), KNO_3 as mineral source of NO_3^- -N has been added manually in main reservoir as shown in Fig. 1. In all experiment by packed sand column, acidity of the influent water to the sand has been nearly $pH \sim 7$. A reservoir containing NZVI particles suspended in DI water with certain concentration was considered to inject nano particles in beginning of sand. An electromotor with low stirrer was considered in the reservoir of NZVI particles to inject a homogenous rate of nano particles into sand. In addition, to avoid the NZVI oxidation by oxygen in the reservoir before the injection to column, Ar gas has been sparged to solution during the injection time. It is important to keep fresh the NZVI surface during synthesis and also before it injected in any reactive zone [34].

The framework of experiments and considered factors and their relationships in this study is shown in Fig. 2. In packed sand column experiments, the effects of initial NO_3^- -N concentrations (100, 200, and 300 $mg\ l^{-1}$), nano Fe/Cu concentration (2, 5, and 8 $mg\ l^{-1}$) and

pore water velocities through packed sand (0.125, 0.250, and 0.375 mm s^{-1} lead to 10.8, 21.6, and 34.2 m day^{-1} , respectively) have been investigated. The selected values of NO_3^- -N and nano Fe/Cu concentration were according to [35]. In order to better simulate the natural groundwater system by this laboratory setup, the selected values of pore water velocities has been due to have Darcy's flow through packed sand. Reynolds's number (R_N) controls this condition. Based on Freeze and Cherry [36] and Bear [37] to meet the Darcy's condition on the flow through porous media, R_N must be less than one.

3. Results and discussion

3.1. Characterization of synthesized nano particles

To characterize the synthesized nano- Fe^0 and nano- Fe/Cu particles, XRD, TEM and BET surface area were recorded. X-ray powder diffraction of both nano particles have been obtained by a D8 Advanced Bruker diffractometer as shown in Fig. 3 (a and d). The localized essential information of iron particles have been viewed with SEM photographs, in Fig. 3 (b and e). It is clearly shown that nano- Fe/Cu particles indicate different morphology in comparison with NZVI particles. Fig. 3 (c and f) presents TEM images of nano- Fe^0 and nano- Fe/Cu particles which have been recorded by a Philips CM 200 kW TEM. Nano- Fe^0 possesses a core-shell formation, in which the shell represents the oxidized part that surrounds the Fe^0 core. The weak peaks of 2-theta = 25, 35, 65 in XRD spectrum (Fig. 3-a) indicate the existence of oxide in the synthesized product. BET surface area of synthesized NZVI has been analyzed by HM Model – 1200 series instrument as 32.6 $\text{m}^2 \text{g}^{-1}$.

Fig. 3 indicates a comparison between the suspension time of synthesized nano- Fe^0 (less than 15 min) and nano- Fe/Cu particles (more than 20 h). The synthesized nano- Fe^0 is generally spherical in form and exists as chain-like agglomeration, while nano- Fe/Cu par-

Table 1

Average water chemistry of water used in this study.

| Parameter | Value |
|---|--------|
| Total dissolved solids (mg l^{-1}) | 563.00 |
| Calcium (mg l^{-1}) | 208.42 |
| Magnesium (mg l^{-1}) | 68.04 |
| Potassium (mg l^{-1}) | 74.30 |
| Chloride (mg l^{-1}) | 78.00 |
| Carbonate (mg l^{-1}) | 0.0 |
| Bicarbonate (mg l^{-1}) | 163.72 |
| Sodium (mg l^{-1}) | 25.87 |
| pH (-) | 6.90 |

ticles have irregular shape and distributed separately. Based on the investigation on the diameter of over 200 nano-particles from TEM images, the nano- Fe/Cu particles relatively have had the diameter size of $70 \pm 3 \text{ nm}$ (see Fig. 3-e).

3.2. Effect of coating percentage of nano- Fe^0 by Cu on the NO_3^- -N reduction

In bimetallic nano-particles, the ratio of incorporated two metals is important for its reactivity and degree of suspension in the direction of pollutant reduction [38].

Various percentages of Cu (0%, 2.5%, 5% and 10% w/w) have been considered onto the surface of nano- Fe^0 particles during the Fe/Cu synthesizing and used for NO_3^- -N reduction in batch experiments.

In this regards, 1000 mg of nano- Fe^0 was deposited by 0.017, 0.85, 0.170 and 0.350 g of Cu, separately. These values lead to 0.5, 2.5, 5 and 10% (w/w) of Cu loading on the Fe^0 . Based on BET analysis, the surface area of synthesized bimetallic nano particles were obtained as 33.3, 35.1, 34.3, and 33.8 $\text{m}^2 \text{g}^{-1}$, respectively. The surface areas of bimetallic nano

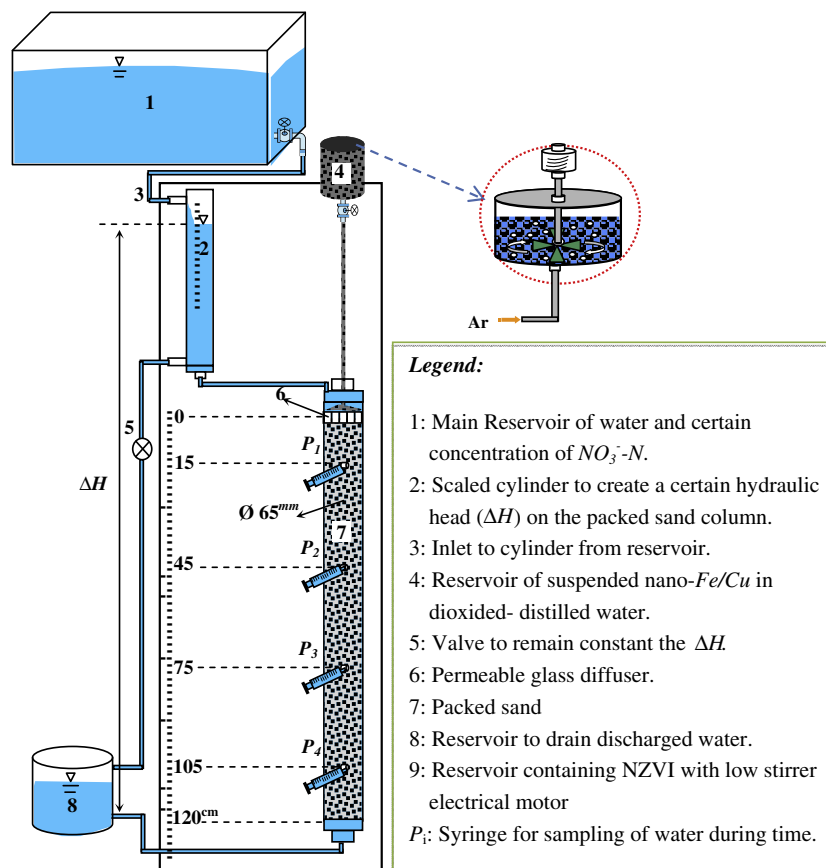


Fig. 1. Laboratory packed sand column setup to investigate the NO_3^- -N reduction by nano- Fe/Cu particles.

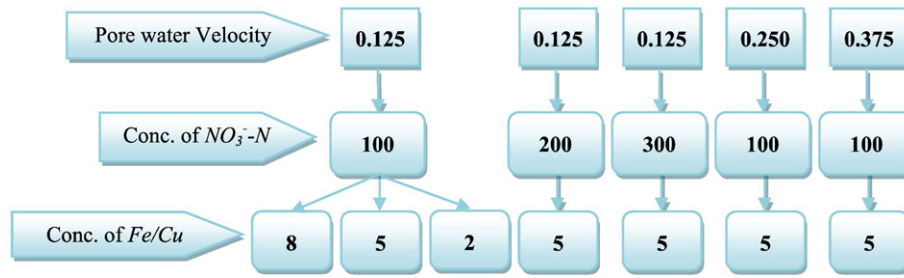


Fig. 2. Framework of this study and factors investigated in NO_3^- -N removal in packed column experiments.

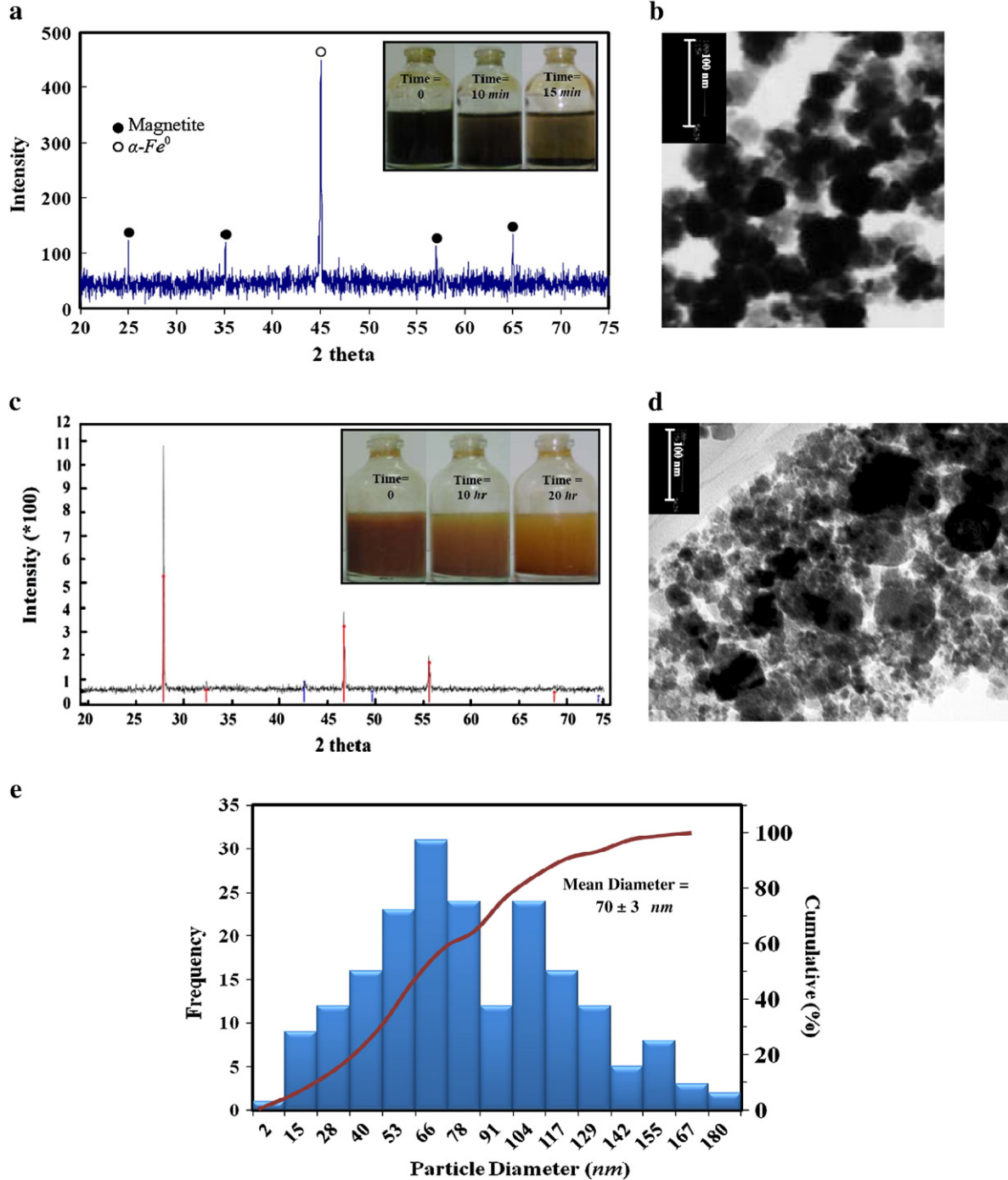


Fig. 3. XRD patterns of synthesized (a) uncoated Fe^0 and (c). TEM image of (b) fresh uncoated Fe^0 and (d) fresh Fe/Cu particles. Histogram of particles distribution for fresh Fe/Cu particles (e). In all cases Fe/Cu particles was coated by 10% w/w Cu loading on Fe^0 .

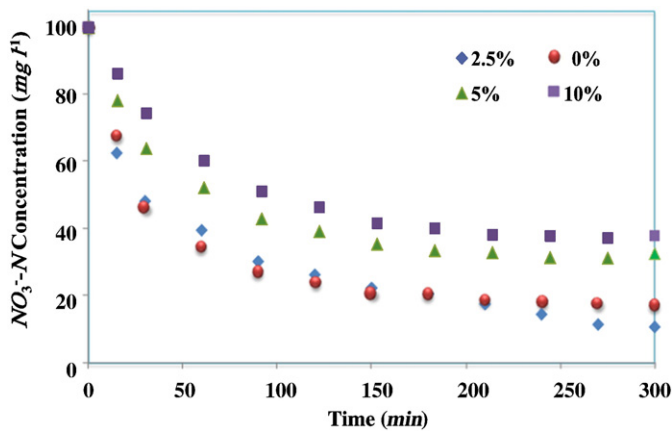


Fig. 4. Effect of coating percentage of Fe^0 by Cu on the NO_3^- -N removal (in all cases, the initial concentration NO_3^- -N and Fe/Cu concentration were equal to 100 and 1000 $mg\ l^{-1}$, respectively).

particles were higher than one for bare NZVI ($32.6\ m^2\ g^{-1}$). In Fe/Cu system, higher deposition of Cu on the Fe^0 surface (10% w/w) decreases the specific surface area of bimetallic particles and decreases the degree of nano particles dispersion. Liu et al. [39] reported that the best efficiency of Fe/Cu bimetallic to reduce the nitrate from water has been obtained when the loading of Cu on the Fe^0 equal to 5% (w/w).

Batch experiments have been conducted in 50 ml bottles. Initial NO_3^- -N concentration for all solutions has been $100\ mg\ l^{-1}$, and mass of injected nano particles for all of cases have been equal to 1000 mg which lead to the stoichiometric ratio of Fe/N is equal to 10. Fig. 4 illustrates the changes in normalized NO_3^- -N concentration (C/C_0) as a function of the reaction time and various percentages of coated nano- Fe^0 by Cu. Values of NO_3^- -N reduction have been observed as 60%, 62%, 82% and 89% by applying bimetallic nano Fe/Cu particles with coating 10%, 5%, 0% and 2.5%, respectively. Results indicate that surplus amount of Cu on the surface of nano- Fe^0 (more than 2.5% w/w) has led to Cu particles agglomeration that has caused negative effect on the reactivity of nano- Fe^0 particles.

Recorded values of reduced NO_3^- -N by bare NZVI and Fe/Cu (with 2.5% w/w) were close together during the reaction time. But, at the end of reaction time (after 200 min) coating of nano- Fe^0 by Cu as 2.5% (w/w) has been more efficient than bare nano- Fe^0 in NO_3^- -N reduction. This may be due to formation of an oxide film on the surface of bare NZVI particles and the reduction of lifetime longevity of these particles after they contact NO_3^- -N. As a practical opinion, stability and reactivity are

both important necessities for reductant agents to treat environmental problems. Therefore, in packed column test the bimetallic nano-Fe/Cu particles with loading of 2.5% (w/w) of Cu has been synthesized and used.

The mechanism NO_3^- -N reduction by bimetallic Nano Fe/Cu particles has been illustrated as conceptual model in Fig. 5. Coating metal can assist electron better transformation of from core (Fe^0) to reduce the contaminant (NO_3^-). Aqueous nitrate (NO_3^-) is transferred to the boundary layer at the interface of Cu and water and then adsorbed to it as NO_3^- ads. NO_3^- ads is diffused along the boundary and produced complex forms as NH_3 ads, NO_2 ads and NH_4^+ ads by give electrons from the core and H^+ from reduction of H_2O in the boundary. The products in the boundary layer can be desorbed and diffused away from the surface into the solution. While in reduction process by bare NZVI, iron oxide shell is mainly unsolvable in natural groundwater conditions ($pH \sim 8$) and protects the bared surface of ZVI core from rapid oxidation but decrease the reduction rate of NZVI in longer period [40].

3.3. Effect of Fe/Cu concentration on NO_3^- -N reduction in packed sand column

As discussed in Fig. 4, the effect of Fe/Cu concentration, initial NO_3^- -N concentration, and pore velocity through porous media have been evaluated on the NO_3^- -N degradation in the length of packed sand column. In this section, the effect of Fe/Cu concentration of 2, 5, and 8 $g\ l^{-1}$ of solution are investigated (these values have been selected according to previous studies and some pre-tests). Other parameters such as initial NO_3^- -N concentration and pore velocity have been fixed equal to $100\ mg\ l^{-1}$ and $0.125\ mm\ s^{-1}$, respectively.

Concentration of 2, 5 and 8 $g\ l^{-1}$ of nano-Fe/Cu particles lead to stoichiometric ratio of Fe/N as 20, 50 and 80, respectively. Yang and Lee (2005) used the stoichiometric ratio of 7.36 and 14.72 (Fe/N) to reduce the NO_3^- with concentration of $150\ mg\ l^{-1}$ in batch experiments. They reported that applying the ratio of 14.72 could reduce all of NO_3^- from solution after 45 min. Analyzed samples in four points of P_1 to P_4 during the experiment time (250 min) are shown in Fig. 6.

Results shown in Fig. 7 can be summarized as following:

- Maximum percentage of NO_3^- -N removal from water when Fe/Cu concentration = $2\ g\ l^{-1}$ (Fig. 6-a) at points of P_1 to P_4 have been observed as 8%, 38%, 52% and 60% of influent nitrate concentration. Different rates of NO_3^- -N reduction in four points of P_1 to P_4 could be due to location of these sampling points from beginning of sand. As illustrated in Fig. 4, points of P_1 and P_4 are located in the distances of 15 cm and 100 cm from beginning of sand. Here, the less contact time of nano particles with nitrate at point P_1 compared to point P_4 leads to less nitrate reduction.

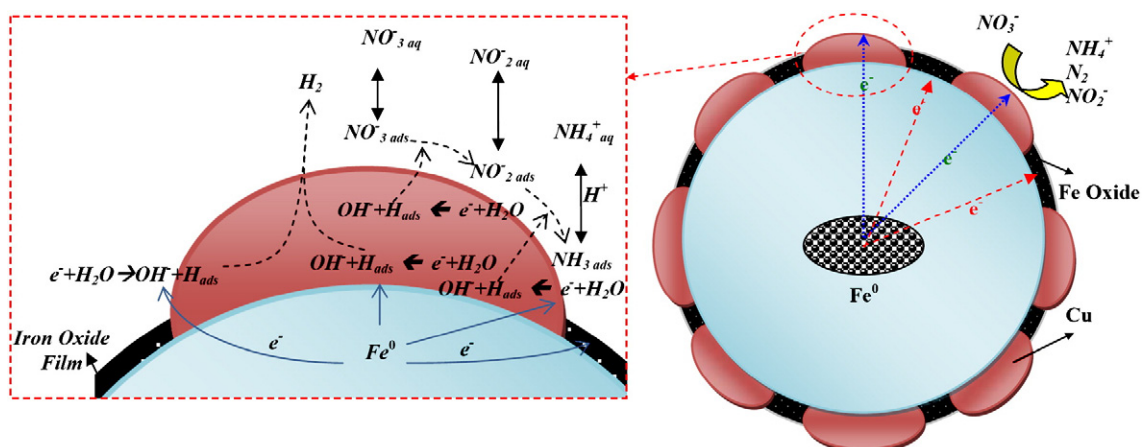


Fig. 5. Conceptual model of NO_3^- -N reduction by bimetallic nano Fe/Cu particles.

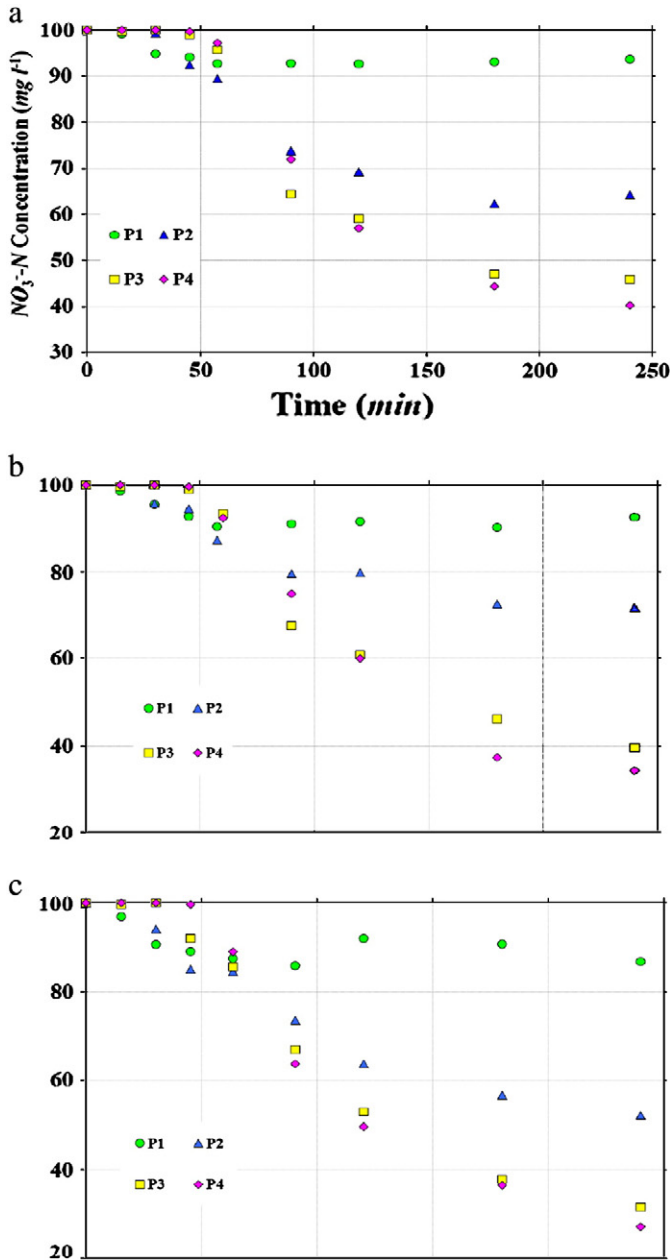


Fig. 6. Reduction of NO_3^- -N in packed sand column: effect of Fe/Cu concentration: (a) 2 g l^{-1} , (b) 5 g l^{-1} and (c) 8 g l^{-1} . In three cases, initial NO_3^- -N concentration and flow velocity were 100 mg l^{-1} and 0.125 mm s^{-1} , respectively.

- In situation where the injected Fe/Cu concentration equal to 2 g l^{-1} (Fig. 6-b), the maximum percentage of nitrate removal from water at points of P_1 to P_4 have been recorded as 10%, 30%, 60% and 64% of influent nitrate concentration.
- At Fig. (6-c) that injected Fe/Cu concentration equal to 8 g l^{-1} , the maximum percentage of nitrate removal from water at points of P_1 to P_4 have been recorded as 17%, 46%, 69% and 73% of influent nitrate concentration.
- Increasing the injected reductant agents (Fe/Cu particles) enhance the maximum percentage of nitrate removal at four points of P_1 to P_4 . The optimum condition to reduce nitrate was observed at point P_4 as 73% of influent concentration.
- In three conditions of injected nano- Fe/Cu concentration ($2, 5$, and 8 g l^{-1}), rate of nitrate degradation in points of P_3 and P_4 at the end of experiment time are close together. It may be because of retention of nano particles (due to aggregation, filtration, settling and sticking) by solid phase through the sand in distance of beginning to P_3 .

3.4. Effect of initial nitrate concentration in packed sand column

Additional experiments have been carried out to evaluate the efficiencies of NO_3^- -N degradation by nano- Fe/Cu in conditions of higher initial NO_3^- -N concentration (e.g., 200 and 300 mg l^{-1}). In these series of experiments, the injected Fe/Cu concentration and pore water velocity have been fixed as 5 g l^{-1} and 0.125 mm s^{-1} , respectively. Reduction of higher concentrations of NO_3^- -N with nano- Fe/Cu during time intervals and four sampling points of P_1 to P_4 have been shown in Fig. 7. Results shown in Fig. 8 can be summarized as following:

- Maximum percentage of nitrate removal from water when NO_3^- -N concentration = 200 mg l^{-1} (Fig. 7-a) at points of P_1 to P_4 have been observed as 12%, 39%, 54% and 58% of influent nitrate concentration.
- At Fig. (7-b) that initial NO_3^- -N concentration equal to 300 mg l^{-1} , the maximum percentage of nitrate removal from water at points of P_1 to P_4 have been observed as 15%, 55%, 65% and 67% of influent nitrate concentration.
- Enhancement of influent NO_3^- -N concentration to the packed sand has increased NO_3^- -N reduction rate during time and the length of column. As NO_3^- -N concentration increases while other ion concentrations are constant, the rate of NO_3^- absorbance to the Cu surface increases (as described in Fig. 5). On the other hand, the presence of other ions with different valence (e.g., Na^+ , Ca^{2+} and Cl^-) in influent water to sand column affects rate of NO_3^- -N reduction. Two valent ions such as Mg^{2+} and Ca^{2+} in the solution reduced the NO_3^- -N removal rate, but the Cl^- has inverse effect. These results have consistency with the results reported by Gandhi et al. [41] and Wang et al. [27].

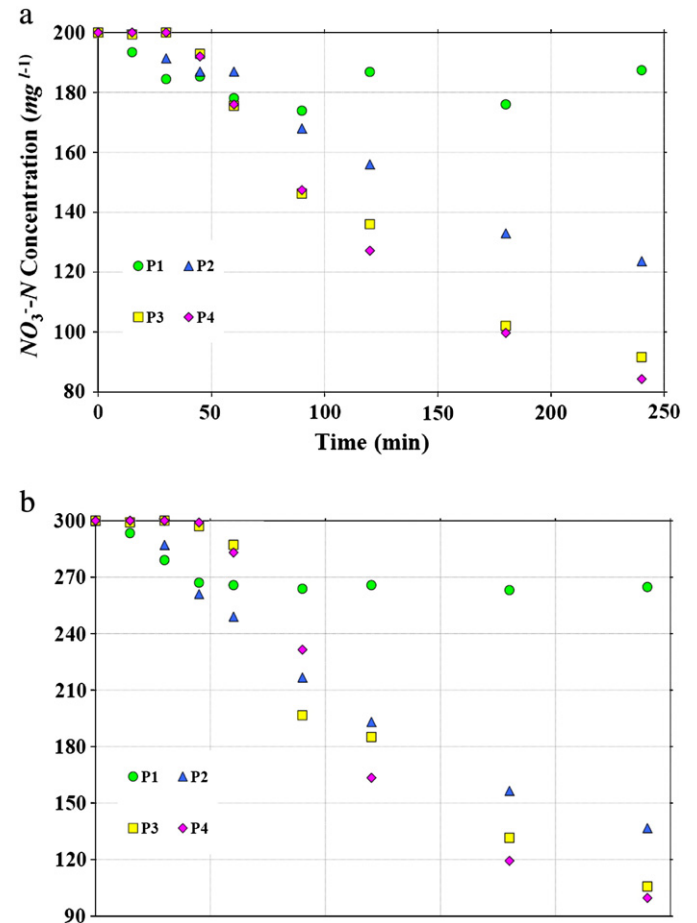


Fig. 7. Effect of initial NO_3^- -N concentration on the reduction of NO_3^- -N in packed sand column: a) 200 mg l^{-1} , b) 300 mg l^{-1} . Used parameters were Fe/Cu concentration was 5 g l^{-1} and flow velocity was 0.125 mm s^{-1} .

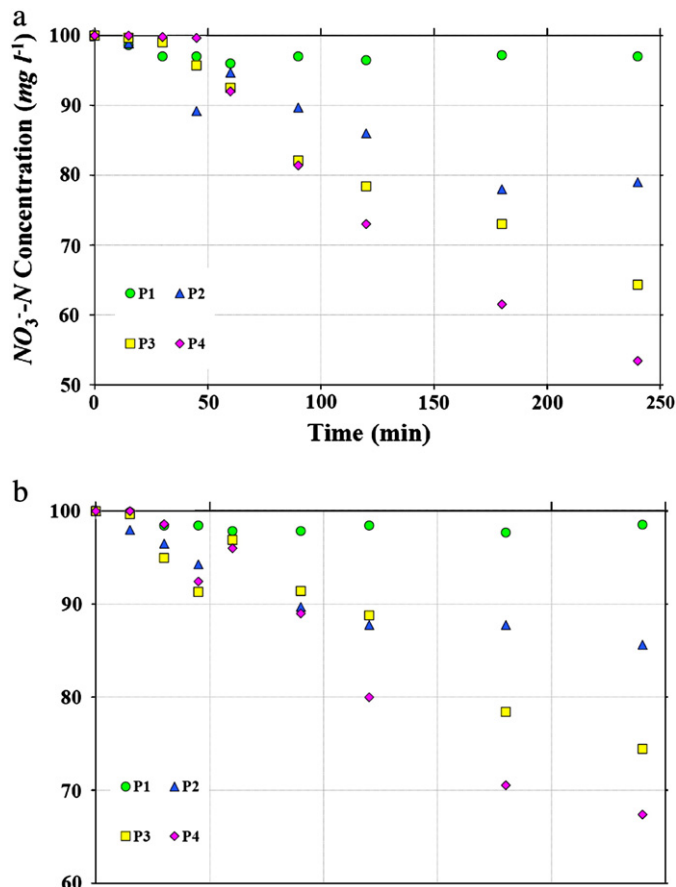


Fig. 8. Effect of pore water velocity on the reduction of NO_3^- -N in packed sand column: a) 0.250 mm s^{-1} , and b) 0.375 mm s^{-1} . Used parameters were Fe/Cu concentration = 5 g l^{-1} and initial NO_3^- -N concentration = 100 mg l^{-1} .

3.5. Effect of pore velocity of water through packed sand column

Another factor that had important effect on NO_3^- -N reduction in packed sand was pore velocity of water. Considering three pore velocities in this study, 0.125 , 0.250 , and 0.375 mm s^{-1} have been based on R_p criterion in order to have better conformity of experimental setup with natural groundwater system. In this set of experiments, Fe/Cu and initial nitrate concentration have been considered as 5 g l^{-1} and 100 mg l^{-1} , respectively. Recorded data about the effect of pore velocity of water on NO_3^- -N degradation by nano- Fe/Cu particles during time and four points on the length of column (P_1 to P_4) are illustrated in Fig. 8.

Results shown in Fig. 8 can be summarized as following:

- Considering pore water velocity through packed sand column equal to 0.250 mm s^{-1} (Fig. 8-a), result to maximum percentage of nitrate reduction at points P_1 to P_4 as 3%, 22%, 36% and 46% of influent nitrate concentration, respectively.
- When pore water velocity through sand is equal as 0.375 mm s^{-1} (Fig. 8-b), the maximum percentage of nitrate removal from water at points of P_1 to P_4 have been observed as 2%, 15%, 25% and 33% of influent nitrate concentration, respectively.
- Results indicate that increasing the pore velocity of water through packed sand has had negative effect on the rate of NO_3^- -N removal during time in four sampling points. Higher pore velocity enhances the mobility of nano particles through sand and reduces the contact time of nano-particles with nitrate and so, reduces the rate of nitrate removal.

The maximum nitrate reduction rate (C/C_0) in packed column sand for seven sets of parameters values used in this study (initial NO_3^- -N

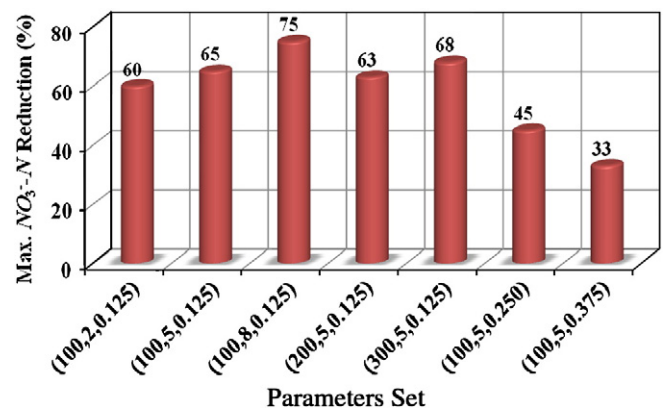


Fig. 9. Maximum NO_3^- -N reduction in packed column sand for different values of parameters. (Parameters set in horizontal axis refer to initial NO_3^- -N concentration (mg l^{-1}), nano Fe/Cu concentration (g l^{-1}) and pore water velocity (mm s^{-1}), respectively).

concentration, Fe/Cu concentration and pore water velocity) are summarized in Fig. 9.

The maximum and minimum percentages of NO_3^- -N removal from water at end of sand column have been observed as 76% (influent nitrate concentration = 100 mg l^{-1} , injected nano- Fe/Cu particles = 8 g l^{-1} and pore water velocity = 0.125 mm s^{-1}) and 33% (influent nitrate concentration = 100 mg l^{-1} , injected nano- Fe/Cu particles = 5 g l^{-1} and pore water velocity = 0.375 mm s^{-1}), respectively.

3.6. Life time of nano- Fe/Cu particles to reduce nitrate

To evaluate the life time (aging) of nano- Fe/Cu particles to reduce a certain concentration of nitrate, a batch experiment has been conducted. Two types of nano- Fe/Cu particles (coating: 2.5% w/w) have been used: freshly synthesized and a week-air exposed nano particles. Two types of nano particles with same dose (100 mg) have been used to reduce 50 ml of NO_3^- -N (100 mg l^{-1}). Recorded data during reaction time has been shown in Fig. 10 as colored points.

Recorded data show that the rate of reaction for week-air exposed nano particles (maximum $C/C_0 = 40\%$) is less than fresh one (maximum $C/C_0 = 90\%$). It is due to the aged nano particles gave up some reactivity compared to fresh one due to formation of oxide shell. Sohn et al. [26] evaluate the aging of NZVI on nitrate reduction. They used four types of iron nano particles: freshly synthesized iron, 3 days air-exposed iron, 1 month air-exposed iron, and 2 months air-exposed iron. Obtained results indicated that the reaction rate for 3 days air-exposed iron is less than fresh iron, but no significant

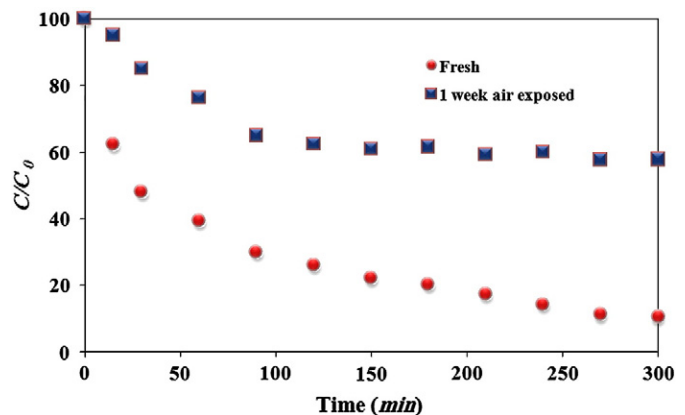


Fig. 10. Effect of life time of nano- Fe/Cu particles on nitrate reduction.

difference has been observed for rate of reaction between three types of air exposed nano particles.

4. Conclusion

In this study, bimetallic of nano-Fe/Cu particles have been synthesized and used in packed sand column experiments to reduce NO_3^- -N through packed sand column. Batch experiment has been used to obtain the best percentage of Cu loading on the Fe^0 surface. Results of batch experiment indicated that loading of Cu on the Fe^0 as 2.5% (w/w) is able to reduce nitrate and travel through sand. In packed sand column, the effects of high concentrated nitrate, injected nano-Fe/Cu particles and pore water velocity have been investigated. Results shown increasing the pore velocity of water through packed sand had negative effect on the NO_3^- -N reduction. Increasing the injected mass of nano particles increases the rate of NO_3^- -N reduction. Enhancement of influent NO_3^- -N concentration has increased the NO_3^- -N reduction rate in length of sand column. The best conditions in NO_3^- -N reduction through packed column has been obtained as 75% of initial concentration in which Fe/Cu concentration was 8 g l^{-1} , initial nitrate concentration as 100 mg l^{-1} and pore water velocity was 0.125 mm/s .

This research considered a few effective parameters on NO_3^- -N reduction process through saturated porous media. Further investigations are required to more investigation on ionic strength of groundwater, environmental effects of NZVI and extending field application.

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