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IN-SITU NITRATE REMEDIATION
USING NANO IRON/NICKEL PARTICLES

Originally, the application of nano zero valent iron/nickel (nZVI/Ni) particles for nitrate removal in porous media was studied. nZVI/Ni was prepared and employed in batch and continuous modes. Based on batch experiments, the reaction kinetics was consistent with the adsorption model by the order of 1–1.5. The variation of the kinetics order depends on pH and nickel content. So that highest reactivity was observed for nZVI with 10% of Ni at pH $\leq$ 3. Nitrate remediation in a continuous system was mostly influenced by seepage velocity, quantity and freshness of nZVI/Ni and particle size of porous media. In a batch mode, the maximum nitrate removal was 99% while in a continuous mode it did not exceed 85%.

1. INTRODUCTION

Recently, nano materials have found increasing applications in environmental technologies, including water and wastewater treatment, groundwater and soil remediation [1]. Among remediation agents, nano zero valent iron (nZVI) has received the most attention for effective removal of a wide spectrum of contaminants. The higher reactivity of nZVI is the result of greater total surface area, higher density of reactive sites on the particle surface, and/or more intrinsic reactivity of the surface sites [2]. Iron nano particles have been extensively studied to remediate pollutants such as chlorinated compounds and metal ions [3], nitrates [4], lead [5], carbon tetrachloride, and benzoquinone [6], metalloids such as arsenic [7] and organic compounds [8].

Nitrates are likely the most ubiquitous groundwater contaminants and can occur naturally or originate from artificial sources. Nitrates are very soluble and do not bind to soils; therefore, they have a high potential to migrate to groundwater sources. Using nitrate contaminated groundwater as drinking water may cause serious health prob-

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lems [9]. Ion exchange and reverse osmosis (RO) are the most frequently used treatment technologies for nitrate removal which are expensive *ex-situ* techniques. Recently, *in-situ* technologies like permeable reactive barriers (PRB) have become promising alternatives to *ex-situ* methods owing to their lower operational costs [10].

This study consists of four steps: (1) synthesis of the surface modified nano zero valent iron/nickel (nZVI/Ni) particles; (2) determination of kinetics of NO_3^- removal by nZVI and evaluation of the factors affecting this reaction; (3) study of the effects of flow characteristics on the nitrate removal; (4) the bench-scale modeling of nitrate remediation from groundwater.

2. MATERIALS AND METHODS

nZVI/Ni preparation. Fe/Ni nano particles were prepared *in situ* to prevent more oxidation of nZVI surface. To synthesize the nZVI particles, 1.5 M NaBH$_4$ solution was added slowly at the rate of 1–2 cm^3/min into 1.0 M FeCl$_3$·6H$_2$O aqueous solution at ambient temperature and vigorously stirred at 400 rpm [11]. During this reaction, ferric ions are reduced into black particles with sodium borohydride as shown in the following reaction [12]:

$$4Fe_{(aq)}^{3+} + 3BH_4 + 9H_2O \rightarrow 4Fe_{(s)}\downarrow + 3H_2BO_3 + 12H_{(aq)}^+ + 6H_{2(g)}\uparrow \qquad (1)$$
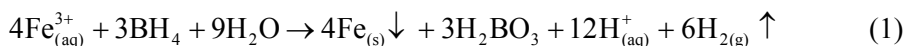
The second metal, nickel (Ni), was deposited on the nZVI by immersing the membrane in a NiCl$_2$·6H$_2$O solution of ethanol/water (90:10 vol. % mixture) under vigorous shaking. This process created core-shell iron nano particles with nickel coating. The deposition occurred via the following reaction [13]:

$$Ni_{(aq)}^{2+} + Fe \rightarrow Ni_{(s)}\downarrow + Fe_{(aq)}^{2+} \qquad (2)$$
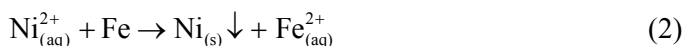
The black precipitates were filtered by vacuum filtration through filter papers and then washed with distilled water and ethanol three times. To characterize the synthesized Fe/Ni nanoparticles, XRD, SEM and DLS were recorded as shown in Fig. 1. X-ray powder diffraction of nano Fe/Ni particles were obtained using a D8 Advanced Bruker diffractometer. A S4160 FE-SEM was used for scanning electron microscopy (SEM) of Fe/Ni particles. Also, dynamic light scattering (DLS) of these nano particles has been achieved by a NanoS(red Badge) model ZEN1600.

Methods. Potassium nitrate (KNO$_3$) was used as the source of NO_3^- in all experiments. The concentrations of NO_3^-, NO_2^- and NH_4^+ were measured with a UV-VIS spectrophotometer (DR-5000, HACH). KNO$_3$, FeCl$_3$·6H$_2$O, NaBH$_4$, and all other reagents were purchased from the Merck, Germany. In each experiment, predeter-

mined quantities of surface modified nZVI/Ni were added into solution and dispersed by ultrasonic device. The batch experiments were conducted in 200 cm^3 flasks. The continuous mode experiments were done also in two following systems:

• transparent column 55 mm in diameter and 650 mm long filled with glass beads (Fig. 2),

• bench-scale apparatus incorporating two PVC columns 300 mm in diameter and 1250 mm high filled with packed sand (Fig. 3).

Prior to the tests, in the first system, glass beads were soaked with hydrogen peroxide solution for 10 h, washed with deionized water, dried at 105 °C for 24 h, and finally sieved to 1.8–2.2 mm (medium I), 2.8–3.2 mm (medium II) [14]. For the second continuous system, sands were prepared by heating at 500 °C for 24 h to eliminate adsorbed organic matter and sieved to 0.4–0.7 mm (medium III) and to 1–2 mm (medium IV).
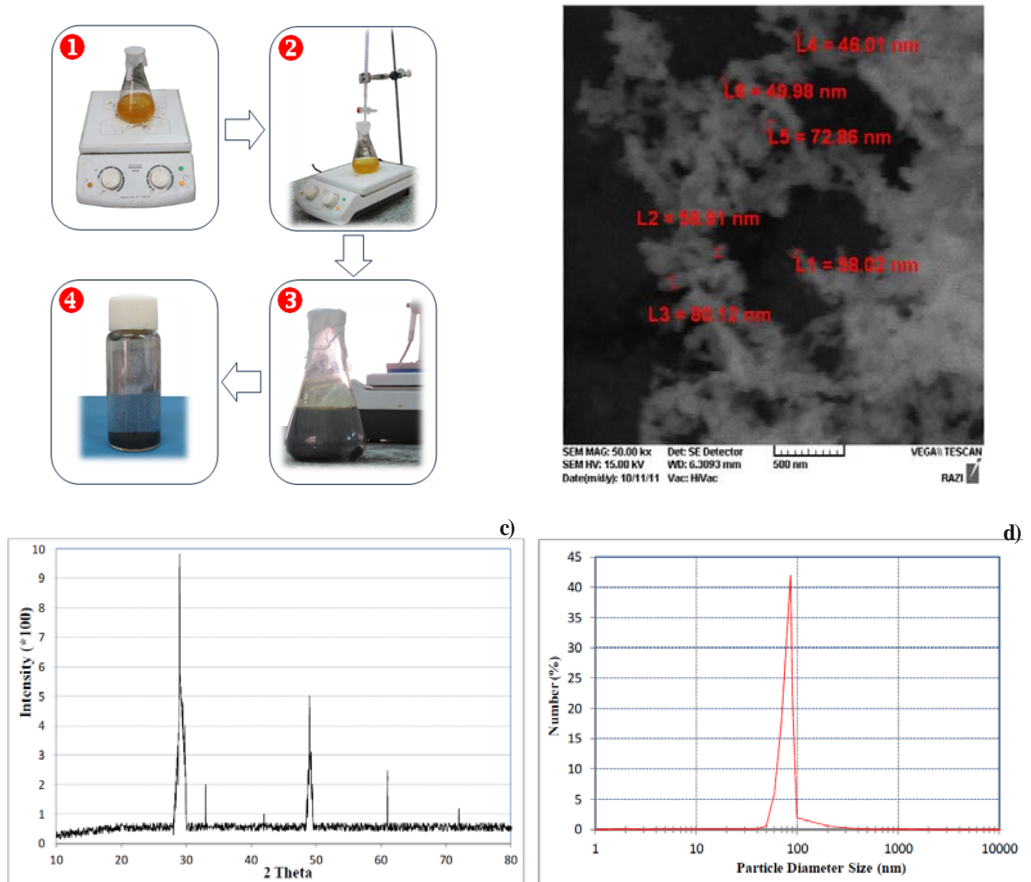

Fig. 1. Characteristics of synthesized nano Fe/Ni particles with W_{Ni}/W_{Fe} = 10%:
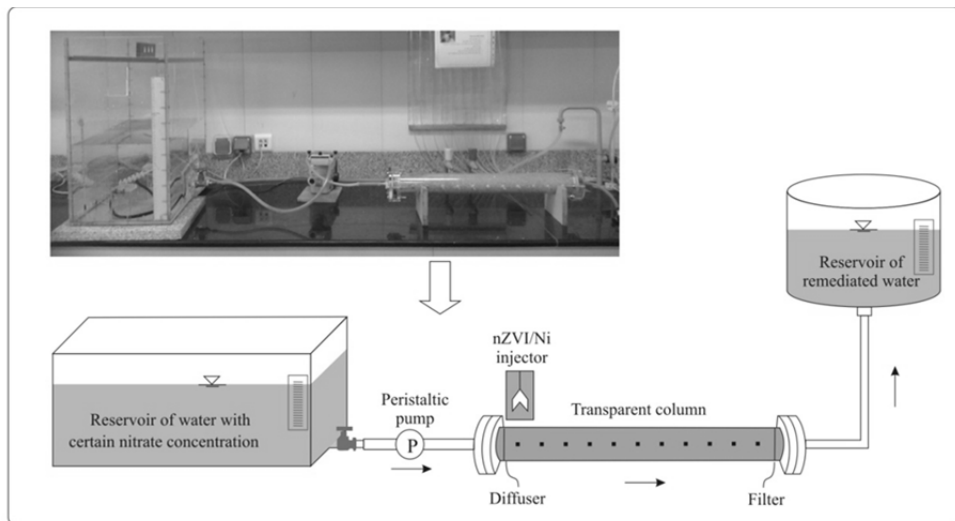a) preparation stages, b) SEM image, c) XRD diagram, d) DLS results

Fig. 2. Photograph and scheme of the laboratory transparent column filled with glass beads

Fig. 3. Photograph of the bench-scale model

3. RESULTS AND DISCUSSION

Batch experiments were conducted to investigate the effect of main parameters, including nickel coating percentage, pH and temperature of the solution. In continuous

tests, lab and bench-scale models were used to simulate *in situ* nitrate reduction in porous media. Details of the experiments are presented in Table 1. At the start of each experiment, adequate distilled water was transmitted through columns to improve packing homogeneity. Influent flow was adjusted with a peristaltic pump. All experiments were performed in triplicate, and the obtained data are expressed as the mean ± standard deviation of three duplicated runs.

Table 1

Experimental design in the present study

Experimenal set[1]			Variable parameter							Controlled conditions[3]
Batch experiments		1-1	controlled pH	2	3	4	5	7		nZVI/Ni 50 mg, C_0 = 100 mg/dm³, 20 °C, 10% Ni
		1-2	temperature	5	10	15	20	30		nZVI/Ni 50 mg, C_0 = 100 mg/dm³, pH 4, 10% Ni
		1-3	Ni coating, %	0	5	10	15	20	30	nZVI/Ni 50 mg, C_0 = 100 mg/dm³, pH 4, 20 °C
Continuous experiments[2]	Transparent column	2-1	nZVI dose, g	1	2	5	10			C_0 = 100 mg/dm³, pore velocity 10 m/d, vertical↑
		2-2	Initial nitrate, mg/dm³	50	100	150	200	300		nZVI/Ni 5 g, pore velocity 10 m/d, vertical↑
		2-3	pore velocity, m/d	5	10	20	40	80		nZVI/Ni 5 g, C_0 = 100 mg/dm³, vertical↑
		2-4	flow direction	horizontal		vertical↓		vertical↑		nZVI/Ni 5 g, C_0 =100 mg/dm³, pore velocity 10 m/d
	Bench-scale	3-1	Initial nitrate, mg/dm³	50	100	150	200	300		nZVI/Ni 8 g, pore velocity 10 m/d, vertical↑
		3-2	nZVI dose, g	2	5	15	20			C_0 = 100 mg/dm³, pore velocity 10 m/d, vertical↑
		3-3	pore velocity, m/d	5	10	20	40	80		nZVI/Ni 5 g, C_0 = 100 mg/dm³, vertical↑

[1]With the exception of set 1-2, all experiments were conducted at ambient temperature, varying from 20 °C.
[2]In all the continuous experiments pH equalled 4 and W_{Ni}/W_{Fe} coating = 10%.
[3]C_0 is the initial nitrate concentration.

3. 1. BATCH EXPERIMENTS

Batch experiments were performed by addition of 50 mg synthesized nZVI/Ni to glass bottles filled with 125 cm³ buffered nitrate solution. Then the bottles were placed in a thermostatic shaker bath at 20±0.5 °C. At given time intervals, 2 cm³ of a sample was withdrawn and filtered through a membrane and concentrations of NO_3^-, NO_2^- and NH_4^+ were measured. This amount of nZVI/Ni provides a stoichiometric Fe/N

ratio of 17.71. Yang and Lee [4] used the ratios of 7.36 and 14.72 (Fe/N) to reduce solution of 150 mg/dm^3 of NO_3^- in batch experiments. They reported that applying the ratio of 14.72 could reduce nitrates from solution after 45 min [4].

Effect of nickel coating on nitrate reduction. The results of microscopic studies suggest that nZVI in aqueous environment mainly consists of zero valent iron and a surface layer of iron oxide [15]. The oxide layer is thought to consist of mixed Fe(II)/Fe(III) oxides near the interface with Fe and mostly Fe(III) oxide near the oxide/water interface [16]. Furthermore, coating nZVI, using other metals such as Ag, Pd, Pt, Ni and Cu is an efficient approach which has been used for degrading various contaminants. The rate of reduction with bimetallic particles is significantly faster than those observed for nZVI alone. The mechanism responsible for this reactivity is related to catalytic hydrogenation and electrochemical effect [17].

In this study, nickel was selected as the surface modifier for nZVI. Mechanisms of nitrate reduction by core/shell nZVI/Ni particles can be described by a general conceptual model presented in Fig. 4. In the figure, aqueous nitrate $(NO_{3\,(aq)}^-)$ is transferred to the boundary layer at the interface of oxidized film and adsorbed later to it as $NO_{3\,(ads)}^-$. Then, it is diffused along the boundary and produces complexes such as $NH_{3(ads)}$, $NO_{2(ads)}^-$ and $NH_{4(ads)}^+$ by delivering electrons originating from the core Fe. Reduction of H_2O in the boundary results in production of H^+. The products in the boundary layer can be resorbed and diffused away from the surface to the solution [18].
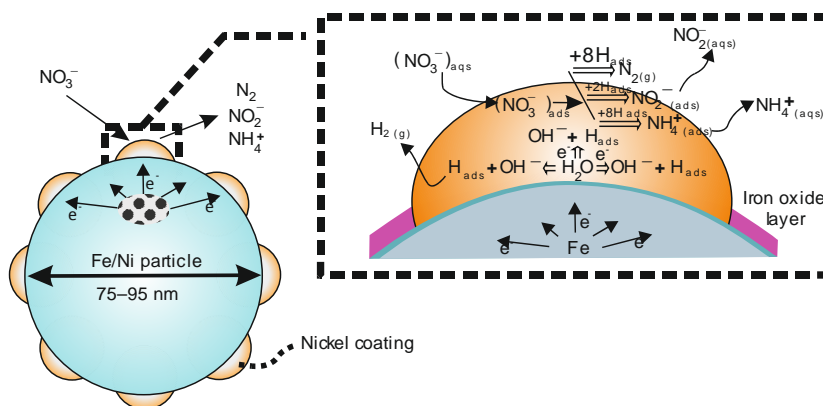

Fig. 4. Schematic representation of nitrate reduction by nZVI/Ni particles [19]

To investigate the effect of nickel coating, solutions of 0.4 g/dm^3 nZVI/Ni of various nickel contents were used for nitrate reduction. The residual concentration of nitrate as a function of reaction time is shown in Fig. 5a.
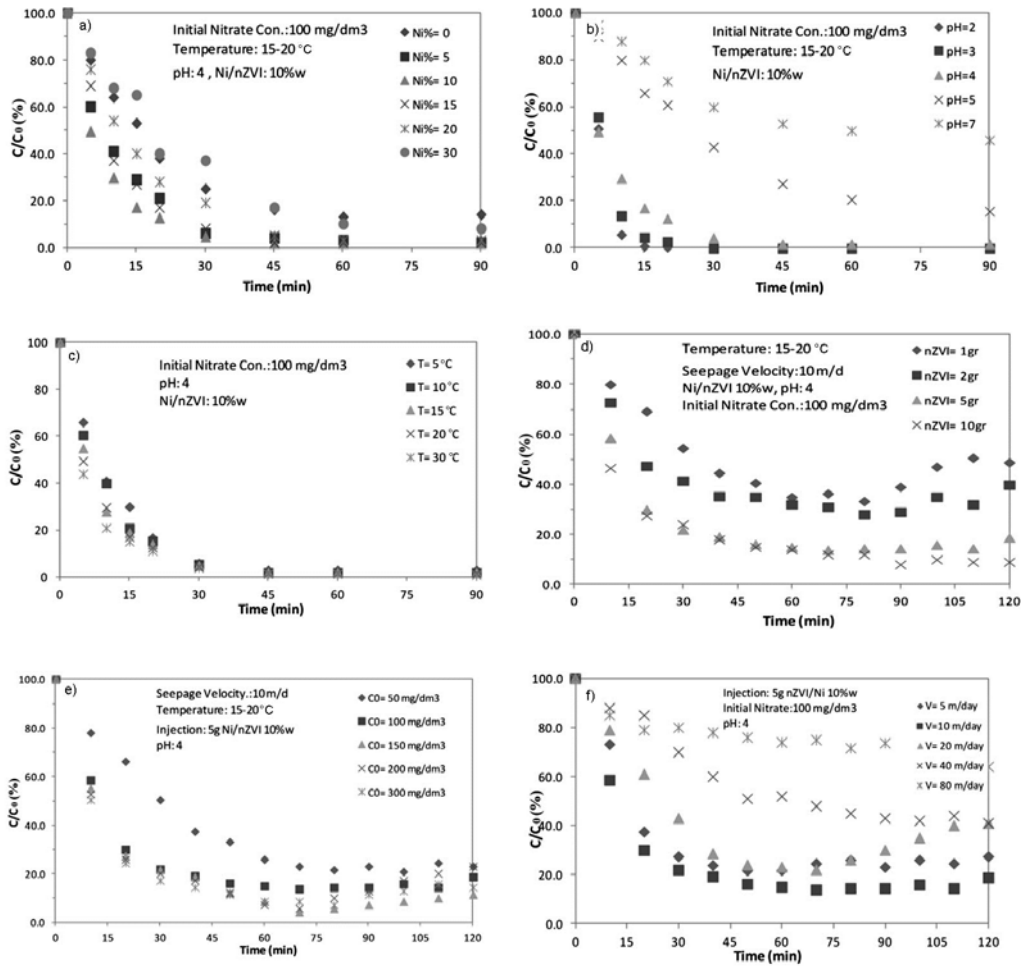
Fig. 5. Time dependences of nitrate reduction rate, batch experiments: effect of coating percentage of nZVI by Ni (a), effect of pH (b) and temperature (c) on the nitrate removal; column experiments: removal of nitrates at various iron injection doses (d), and initial concentrations, and effect of seepage velocity (e)

Determined coefficients of the kinetic equation

$$-\frac{d\left[\text{NO}_3^-\right]}{dt} = k\left[\text{NO}_3^-\right]^n \tag{1}$$

are given in Table 2. They refer to the following conditions: nZVI/Ni – 50 mg, $C_0 = 100$ mg/dm^3, $T = 20$ °C, pH = 4. The catalyst coating of nZVI was found to significantly affect the nitrate reduction. Moreover, the results indicate that the best loading of nickel on the nZVI is 10% ($W_{\text{Ni}}/W_{\text{nZVI}}$).

Parameters of kinetic equation (Eq. (1) for nitrate reduction with
nZVI/Ni for various Ni coating percentages

W_{Ni}/W_{Fe} [%]	k [min^{-1}]	n	R^2
0	0.03	1.33	0.94
5	0.02	1.56	0.99
10	0.10	1.23	0.97
15	0.04	1.31	0.96
20	0.91	1.14	0.91
30	0.07	1.03	0.80

[1]Controlled conditions: nZVI/Ni – 50 mg, C_0 = 100 mg/dm^3,
T = 20 °C, 10% Ni.

Effect of pH on nitrate reduction. Alkaline conditions are not favorable to chemical reduction of nitrate with nZVI because iron hydroxide precipitates at high pH values [20]. Hence, in this study, only low pH values, ranging from 2 to 7 were selected. As shown in Fig. 5b, pH played an important role in chemical reduction of nitrates. At pH 5, after 90 min, ca. 85% of nitrate was degraded, while a complete removal of nitrate was obtained after 45 min at pH 4 and even lower. At the beginning, nitrate concentration was rapidly decreased but no more reduction was obtained after 60 min. As seen in Table 3, the order of this reaction was around 1.1. Furthermore, the rate coefficients for pH 2–5 were estimated as 0.67, 0.35, 0.1 and 0.09 min^{-1}, respectively.

Parameters of kinetic equation (Eq. (1))
for nitrate reduction with nZVI/Ni at various pH[1]

pH	k [min^{-1}]	n	R^2
2	0.67	1.00	0.90
3	0.35	1.06	0.93
4	0.10	1.23	0.99
5	0.09	1.88	0.93
7	0.001	1.05	0.80

[1]Controlled conditions: nZVI/Ni – 50 mg, C_0 = 100 mg/dm^3,
T = 20 °C, 10% Ni.

Effect of temperature on nitrate reduction. The kinetic energy and molecule velocity increases with temperature and for endothermic reactions, the rate of reaction increases with temperature. The rate of nitrate reduction with nZVI/Ni was measured at various temperatures. The results are shown in Fig. 5c. and Table 4. The reduction rate at 5 °C was 0.09 min^{-1}, and it took 40 min to remove ca. 90% of the initial nitrate, whereas the reduction rate at 30 °C was 0.1 min^{-1} and 90% of nitrates were reduced

after 30 min. Therefore, it seems that the temperature ranging from 5 to 30 °C has no significant effects on the removal efficiency and after ca. 90 min, similar nitrate concentrations for all samples were observed.

Table 4

Parameters of kinetic equation (Eq. (1))
for nitrate reduction with nZVI/Ni at various temperatures [1]

T [°C]	k [min^{-1}]	n	R^2
5	0.09	1.21	0.94
10	0.10	1.18	0.97
15	0.10	1.22	0.96
20	0.10	1.23	0.97
30	0.10	1.25	0.95

[1]Controlled conditions: nZVI/Ni – 50 mg, C_0 = 100 mg/dm^3, 10% Ni, pH = 4.

3.2. CONTINUOUS EXPERIMENTS

Lab model (transparent column). As given in Table 1, effects of nZVI/Ni injection dose, nitrate initial concentration and seepage velocity have been evaluated in a transparent column. pH of solutions was adjusted by adding 0.1 M HCl.

The effect of various dosages of nZVI/Ni (1, 2, 5 and 10 g) was investigated. These values were selected according to batch experiment, previous studies and some pre-tests. Other parameters such as initial concentration of NO_3^- and seepage velocity were fixed as 100 mg/dm^3 and 10 m/d, respectively. As seen in Fig. 5d., the more nZVI/Ni injected, the more nitrate removed. Furthermore, for Fe/Ni injection of 5 g, the maximum nitrate removal rates at P1, P2 and P3 (located at the distances of 100, 300 and 450 mm from the beginning of the column) have been measured as 12%, 79% and 86%, respectively. Thus, it seems that the shorter contact time leads to lower nitrate reduction.

When initial nitrate concentration varied in the range of 50–300 mg/dm^3, nitrate degradation with nZVI/Ni was evaluated. The nZVI/Ni dosage and seepage velocity were fixed at 5 g and 10 m/day, respectively. The results (Fig. 5e), indicate that for initial concentration of 200mg/dm^3, the maximum nitrate removal rates at P1, P2 and P3 were 16%, 85% and 91%, respectively. Also, for initial nitrate concentration of 300 mg/dm^3, removal rates were 16%, 90% and 94%, respectively. These can be summarized as: increasing initial nitrate concentration improved the reduction efficiency.

The seepage velocities were adjusted to 5, 10, 20, 40 and 80 m/day. These values have been chosen in order to have better conformity of experimental setup with

groundwater flow based on the Reynolds criterion. It was observed (Fig. 5f) that seepage velocity of 10 m/d yielded the maximum removal rate. Any variation, increasing or decreasing of the seepage velocity, had a negative effect on the nitrate removal. Apparently, higher seepage velocities enhance the mobility of nano particles through media and reduce the contact time and thus, reduce the remediation.

Bench-scale model. The bench-scale model was designed based on the batch and transparent column consequences. The nZVI/Ni injected in the bottom center of the column form a permeable reactive zone which reduced inlet nitrate. This configuration is fit to study the effect of groundwater ionic strength, porous media type, seepage velocity, initial nitrate concentration and nZVI/Ni dosage.

The results revealed that nitrate reduction through sand materials is lower than glass beads. In addition, increasing seepage velocity has a negative impact on the nitrate remediation. Also, increasing the amount of nZVI/Ni and initial NO_3^- concentration enhances nitrate removal. In all of bench-scale runs, the best nitrate remediation efficiency was about 65%.

4. CONCLUSIONS

The application of Fe/Ni nano particles for NO_3^- remediation was studied in the batch mode, transparent column and Bench-scale model. Our findings suggest that nitrate can be successfully reduced by these nano particles. Therefore, nZVI/Ni has a good feasibility for *in situ* NO_3^- remediation.

Batch experiments indicated that pH is an important parameter. Increasing of the pH value within the solution reduced nitrate removal rate, while in acidic conditions, kinetics coefficients were directly related to pH with $R^2 > 0.90$. However, solution temperature within the range of 5–30 °C had a minor effect on the removal rate. In addition, the catalyst coating of nZVI was found significantly affecting the removal efficiency. Indeed, nickel coating on the nZVI as 10% (W_{Ni}/W_{nZVI}) yielded the highest reactivity. Furthermore, it seems that nitrate reduction by nZVI/Ni could be described by the first or pseudo-first order kinetic model. Several previous studies reported that chemical reduction of nitrates with iron particles could be described by the similar order kinetics [21]. The final products of this reaction could be N_2, NO_2^- and NH_4^+. The product percentage is a function of nZVI dosage as well as its quality, contact time, and rate of mixing. By increasing the aforementioned parameters, the percentage of NO_2^- ions could be reduced below 5% and the major final product would be inert N_2 which is emitted to the atmosphere. In addition, NO_2^- ions are unstable, mostly converted to stable NO_3^-.

Transparent column tests revealed that increasing the seepage velocity through porous media had a negative effect on the removal efficiency. Increasing the amount of nano particles dosage that injected through the column increased the efficiency of NO_3^- reduction.

In the Bench-scale model, natural water with similar conditions to the groundwater flow was used that outcomes confirmed the results of experiments in a batch and transparent column but with lower efficiency. Nitrate removal efficiencies in groundwater were probably lower than under laboratory conditions, larger nZVI/Ni dosage and more time were required to achieve the acceptable remediation. Therefore, it can be recommended that for real remediation projects with nZVI, an initial bench-scale modeling by natural water and sand material are necessary. Finally in this work, high performance of the joint use of bench-scale modeling and batch system for groundwater remediation has been confirmed.

REFERENCES

[1] HASHIM M.A., MUKHOPADHYAY S., SAHU J.N., SENGUPTA B., *Remediation technologies for heavy metal contaminated groundwater*, J. Environ. Manage., 2011, 92, 2355.

[2] CUNDY A.B., HOPKINSON L., WHITBY R.L.D., *Use of iron-based technologies in contaminated land and groundwater remediation. A review*, Sci. Total Environ., 2008, 400, 42.

[3] RANGSIVEK R., JEKEL M.R., *Removal of dissolved metals by zero-valent iron (ZVI): Kinetics, equilibria, processes and implications for stormwater runoff treatment*, Water Res., 2005, 39, 4153.

[4] YANG G.C.C., LEE H.-L., *Chemical reduction of nitrate by nanosized iron: kinetics and pathways*, Water Res., 2005, 39, 884.

[5] XI Y., MALLAVARAPU M., NAIDU R., *Reduction and adsorption of Pb^{2+} in aqueous solution by nano-zero-valent iron. SEM, TEM and XPS study*, Mater. Res. Bull., 2010, 45, 1361.

[6] ZHANG X., DENG B., GUO J., WANG Y., LAN Y., *Ligand-assisted degradation of carbon tetrachloride by microscale zero-valent iron*, J. Environ. Manage., 2011, 92, 1328.

[7] KIM K.-R., LEE B.-T., KIM K.-W., *Arsenic stabilization in mine tailings using nano-sized magnetite and zero valent iron with the enhancement of mobility by surface coating*, J. Geochem. Explor., 2012, 113, 124.

[8] FAGERLUND F., ILLANGASEKARE T.H., PHENRAT T., KIM H.J., LOWRY G.V., *PCE dissolution and simultaneous dechlorination by nanoscale zero-valent iron particles in a DNAPL source zone*, J. Contam. Hydrol., 2012, 131, 9.

[9] POPOVICH D.M., MCALHANY A., *Practitioner care and screening guidelines for infants born to chlamydia-positive mothers*, Newborn and Infant Nursing Reviews, 2004, 4, 51.

[10] LI L., BENSON C.H., LAWSON E.M., *Modeling porosity reductions caused by mineral fouling in continuous-wall permeable reactive barriers*, J. Contam. Hydrol., 2006, 83, 89.

[11] PENG S., WANG C., XIE J., SUN S., *Synthesis and stabilization of monodisperse Fe nanoparticles*, J. Am. Chem. Soc., 2006, 128, 10676.

[12] LEE C., JEE Y.K., WON I.L., NELSON K.L., YOON J., SEDLAK D.L., *Bactericidal effect of zero-valent iron nanoparticles on Escherichia coli*, Environ. Sci. Technol., 2008, 42, 4927.

[13] LIEN H.-L., ZHANG W.-X., *Nanoscale Pd/Fe bimetallic particles: Catalytic effects of palladium on hydrodechlorination*, Appl. Catal. B: Environ., 2007, 77, 110.

[14] KANEL S.R., NEPPOLIAN B., CHOI H., YANG J.W., *Heterogeneous catalytic oxidation of phenanthrene by hydrogen peroxide in soil slurry: Kinetics, mechanism, and implication*, Soil Sediment Contamin., 2003, 12, 101.

[15] MARTIN J.E., HERZING A.A., YAN W., LI X.Q., KOEL B.E., KIELY C.J., ZHANG W.X., *Determination of the oxide layer thickness in core-shell zerovalent iron nanoparticles*, Langmuir, 2008, 24, 4329.

[16] SUN Y.P., LI X.Q., CAO J., ZHANG W.X., WANG H.P., *Characterization of zero-valent iron nanoparticles*, Adv. Colloid Interface Sci., 2006, 120, 47.

[17] O'CARROLL D., SLEEP B., KROL M., BOPARAI H., KOCUR C., *Nanoscale zero valent iron and bimetallic particles for contaminated site remediation*, Adv. Water Res., 2013, 51, 104.

[18] ZHANG X.Y.W., *Subcolloidal Fe/Ag particles for reductive dehalogenation of chlorinated benzenes*, Indus. Eng. Chem. Res., 2000, 39, 2238.

[19] HOSSEINI S.M., ATAIE B., KHOLGHI M., *Nitrate reduction by nano/Fe/Cu particles in packed column*, Desalination, 2011, 276, 214.

[20] HUANG Y.H., ZHANG T.C., *Effects of low pH on nitrate reduction by iron powder*, Water Res., 2004, 38, 2631.

[21] CHOE S., CHANG Y.Y., HWANG K.Y., KHIM J., *Kinetics of reductive denitrification by nanoscale zero--valent iron*, Chemosphere, 2000, 41, 1307.