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Reduction of nitrate by copper-coated ZVI nanoparticles

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ABSTRACT

Nano zero-valent iron has been shown to be effective for the removal of nitrates from natural wastes and wastewaters. This work studies the application of surface-modified nano zero-valent iron as bimetallic Fe/Cu particles to remove high concentration of nitrates. Dispersed nano-Fe/Cu particles were synthesized by chemical reduction and examined by X-ray diffraction, scanning electron microscopy, and BET surface area analysis. Batch experiments were conducted to investigate the effectiveness of bimetallic particles on the reduction and removal of nitrates. The parameters investigated included the copper content (0.5, 5, 10, and 20% w/w) in zero-valent iron nanoparticles and the initial concentration of nitrates (100, 200, 300, and 500 mg/L). During the experiments, the aqueous solution was analyzed to determine the evolution of NO_3^- as well as NO_2^-, NH_3, and NH_4^+ which were produced as intermediate and final products. Based on the results obtained, it was concluded that the optimum coating rate was 5% w/w copper in nano-Fe/Cu, resulting in more than 80% nitrate reduction in 20 min and complete removal within 1 h.

Keywords: Nano zero-valent iron; Bimetallic nanoparticles; Copper coating; Nitrate reduction

1. Introduction

Nitrogen is one of the essential elements of living organisms, constituting along with carbon, hydrogen, and oxygen almost 96% of their total weight. However, excessive release of nitrogen into the environment can lead to severe environmental problems such as eutrophication. Contamination of groundwater and drinking water by nitrate has become a major environmental concern since nitrates are soluble, and negatively charged, with low sorptivity on soil particles, so that they are easily transferred from the unsaturated zone towards the underlying groundwater bodies. Many studies have shown a high correlation between agriculture and the concentration of nitrates in underground aquifers [1,2]. The extensive use of nitrogen fertilizers is considered as the main nonpoint source of nitrates in groundwater. Septic systems appear also to contribute to nitrates pollution of groundwater. Other sources of nitrates are the leachate from landfills, rainwater runoff, and industrial waste discharges [1,3]. High concentration of nitrates in drinking water can cause severe health issues, such as methemoglobinemia, also known as blue baby syndrome in infants, and cancer when they are reduced to nitrites [3]. Thus, the maximum allowable concentration of nitrate

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nitrogen in drinking water is set at 10 mg/L, equivalent to 44 mg nitrates /L in the USA [4] and 50 mg/L for adults and 15 mg/L for infants in the European Union [5].

Various technologies, including adsorption, chemical reduction, biological denitrification, and ion exchange, have been proposed for the removal of nitrates. However, these methods are either too expensive or require a second phase of treatment. The most commonly used method is the biological denitrification, which is based on the activity of micro-organisms that are able to convert nitrates to nitrogen [6,7]. Although this method is the most widely applied, it has many drawbacks, because it is slow, difficult to control, produces organic residues, and requires constant maintenance and supply of organic substrate [8]. Electrochemical methods for removing nitrate from aqueous solutions have also been studied extensively over the past 30 years. Three different modes of electrochemical reduction of nitrates are known: (1) the addition of electrocatalytic active ions such as VO_3^-, WO_4^{2-}, or cobalt complexes directly in solution, (2) immobilization of the catalyst on the electrode surface, and (3) electrochemical reduction on solid electrodes [9,10]. Physicochemical methods such as ion exchange, reverse osmosis, and electrodialysis effectively remove nitrates from water, but cannot destroy them. This results in the generation of secondary waste streams containing high nitrate concentrations, posing an additional disposal problem [11,12]. Despite these disadvantages, physicochemical methods can be used as a first stage of nitrate removal, especially in cases where biological methods cannot be applied [13,14]. Ion exchange and reverse osmosis are relatively expensive methods of rehabilitation, because they require frequent media regeneration and generate secondary waste [15]. For this reason, their application in wastewater treatment is limited.

The use of nano zero-valent iron (nZVI) has been considered as an attractive alternative for *in situ* remediation of contaminated sites, due to the small particle size, large specific surface area, and high surface reactivity [16–18]. The nZVI has also the capacity to remain in suspension for long time and can be injected into contaminated zones. Research conducted using ZVI in nitrates solution indicated that nitrite, nitrogen gas, and ammonia are the products of nitrates reduction [18]. Furthermore, it was indicated that different patterns of nitrogen species concentration evolution over time were obtained using nZVI. Most of the studies propose that the main final product is ammonia, which is an undesirable end product [19]. However, some researchers have suggested that the final reaction product is nitrogen gas, which is an ideal product of nitrate reduction [20].

Coating of nanoiron with other metals such as Ag, Pd, Pt, Ni, and Cu has been proposed for treating a number of contaminants in water. Bimetallic nanoparticles have a higher reaction rate compared to those observed for nZVI alone [21,22], but shorter lifetime, possible toxicity, and higher cost. The mechanism responsible for their reactivity is related to catalytic hydrogenation and electrochemical effects [22]. It was indicated that coating of nZVI by copper decreases the aggregation and agglomeration of nZVI, in addition to enhancing the rate of nitrate reduction in aqueous solution [23]. However, the efficiency of the catalyst used in bimetallic nanoparticles decreases during time due to formation of an iron hydroxide layer, which hinders the contact between the reactants and the catalyst [24]. Liou et al. [24] have evaluated the effects of three metals including Pd, Pt, and Cu deposited onto nano-Fe^o surface to test their reactivity for nitrate reduction. Their results indicate that the reactivity of three bimetallic nanoparticles can be ranked as Cu<Pd<Pt. In the present study, the effect of various parameters, including the copper content in nano-Fe/Cu particles and initial concentration, on nitrate reduction was investigated.

2. Materials and methods

2.1. Materials

Chemicals used for nZVI and nano-Fe/Cu particles synthesis include ferric chloride (>99.0%, Merck, Germany), copper (II) chloride (>98.0%, Merck, Germany), sodium borohydride (>98.0%, Alfa Aesar, Germany), NaOH (98%, Panreac, Spain), and ethanol (>99.0%, Merck, Germany). Potassium nitrate (>99.0%, Merck, Germany) was used to prepare nitrates solution whereas hydrochloric acid (37%, Sigma-Aldrich, USA) was used for pH adjustment.

2.2. Synthesis of nanoscale zero-valent iron

The nZVI was prepared based on the borohydride reduction method involving vigorous mixing of sodium borohydride ($NaBH_4$) and ferric chloride ($FeCl_3{\cdot}6H_2O$) at room temperature. The synthesis of nZVI was conducted inside a glove box in a 500 mL flask reactor with a tuneable mechanical stirrer at 500 rpm. The 200 mL of sodium borohydride solution (0.16 M) was introduced to 200 mL ferric iron solution (0.1M) with a flow rate of 18 mL/min using an automatic dosing device (Metrohm, Dosimat 665), for the reduction of ferric iron to nZVI. The entire process was carried out in a nitrogen atmosphere.

The reduction reaction is as follows:

$$\mathrm{Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 \downarrow + 3B(OH)_3 + 10.5H_2} \quad (1)$$

The generated iron particles have been filtered by vacuum filtration through Gelman Sciences filter papers and then washed with DI water and ethanol at least three times. The freshly prepared particles have been dried in an oven for 24 h at 75˚C, in a nitrogen atmosphere.

2.3. Synthesis of bimetallic nano-Fe/Cu particles

Bimetallic particles were prepared by mixing the 1 g-Cu/L $CuCl_2$ aqueous solution of copper with the freshly prepared nZVI particles in vigorous stirrer at ambient temperature according to Zhang et al. [25] and Schrick et al. [26]. After 5 min of redox reaction between the Cu^{2+} and nZVI, the resulting nano-Fe/Cu particles were washed three times with diluted ethanol (3%). The drying process and storage method followed the above description. The redox reaction describing the coating of nZVI with Cu is as follows:

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

The final iron concentration in the solution was 290 mg/L and copper concentration was below the detection limit (<0.1 mg/L).

2.4. Characterization of synthesized nanoparticles

To characterize the synthesized nZVI and nano-Fe/Cu particles, X-ray diffraction (XRD) analysis, scanning electron microscopy, and BET measurements were conducted. The XRD analysis was performed using a Bruker D8-Focus powder diffractometer with nickel-filtered CuKα radiation ($\lambda = 1.5405$ Å), 40 kV and 40 mA, and at a scan speed of 1˚ min^{-1}. The size and morphology of the bare nanoiron and nano-Fe/Cu particles were observed by field emission scanning electron microscopy (SEM, Jeol 6380LV). Chemical composition of the nanoparticles was carried out by an Oxford INCA energy dispersive spectrometer (EDS) connected to SEM. The BET surface area of nanoparticles was determined by Quantachrome Nova 1200 series.

2.5. Reduction of nitrates by nano-Fe/Cu

Batch experiments for nitrate reduction were conducted in 500 mL flasks. The flask was filled with 300 mL nitrate solution with a certain concentration (100, 200, 300, and 500 mg L^{-1}) which was contacted with 1.0 g of nano-Fe/Cu particles (with copper concentration 0.5, 5, 10, and 20% w/w). Uncoated nZVI was also tested for its effectiveness on nitrate reduction. The nitrate solution was used without any acidification (initial pH 6.2–7.2). A single test involving the use of pH 2.3 nitrate solution (initial concentration 200 mg/L) and nano-Fe/Cu particles (5% w/w) was also performed for comparison. A mechanical shaker was used for continuous stirring of the solution at 200 rpm and at ambient temperature (25˚C). The solution was purged with nitrogen gas for five minutes and then the flask was sealed. Samples were taken periodically by burette. Concentrations of nitrate and nitrite were determined by means of ion chromatography (DX-120, Dionex Co., Sunnyvale, CA, USA). Ammonium and ammonia were analyzed by using a nesslerization method and a spectrophotometer (SMART SpectroTM). The redox potential of the solution was measured using a KCl saturated Ag/AgCl reference electrode.

3. Results and discussion

3.1. Characterization of synthesized nanoparticles

As shown in Fig. 1, the nZVI particles were spherical with chain network structure and particle size finer than 100 nm (Fig. 1(a)). The nano-Fe/Cu particles produced were also spherical with similar size. According to EDS analysis, the main elements in the nZVI product were Fe and O emanating from the partial surface oxidation of nZVI nanoparticles. The peak at $2\theta = 45^\circ$ in the XRD spectrum of nZVI indicates that the material is metallic iron (Fig. 2) while the weak peaks at $2\theta = 35^\circ$, 65° in the XRD spectrum of nano-Fe/Cu particles indicate the existence of magnetite and/or copper ferrite spinel in the synthesized product, which determines the core-shell structure. The BET surface area of the synthesized nano-Fe/Cu particles (5% w/w copper content) was 34 m^2 g^{-1} in accordance with previous studies [22].

3.2. Nitrates reduction by nano-Fe/Cu

Fig. 3 shows the concentration of nitrate and reduction products during the reduction of 200 mg/L nitrate solution with nano-Fe/Cu particles (5% wt/wt Cu). The results in Fig. 3 are expressed as the ratio C/C_o of the concentration of each compound (C, mmoles/L) in solution to the initial nitrates concentration (C_o, mmoles/L). Ninety-nine percent of nitrates were removed within 1 h and complete removal was attained within 90 min. Nitrite was initially produced

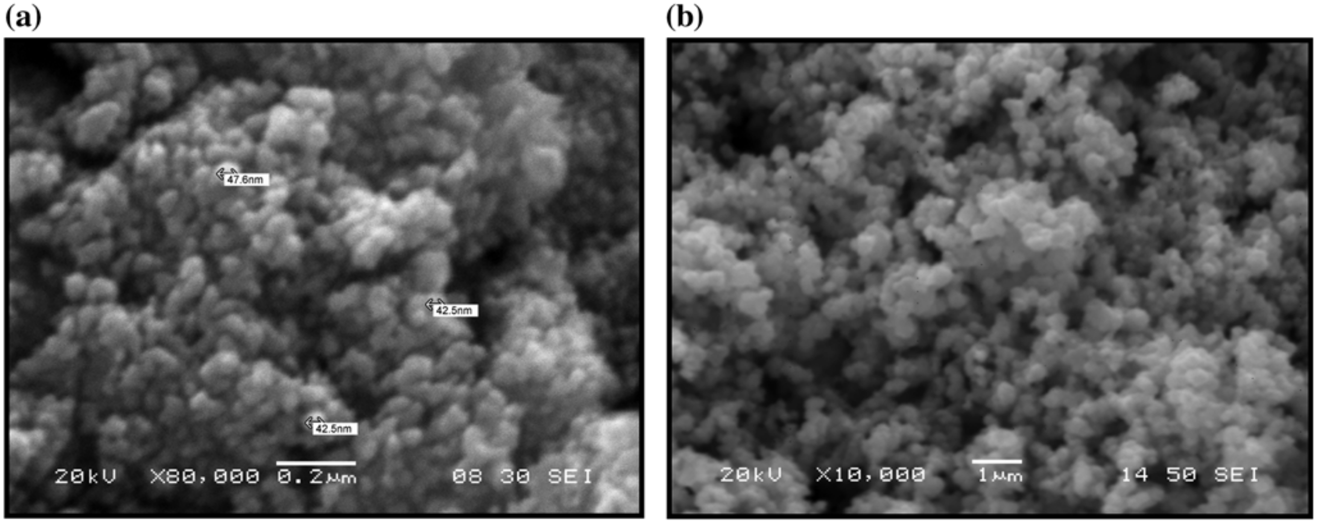

Fig. 1. The SEM image of (a) nZVI and (b) nano-Fe/Cu particles.

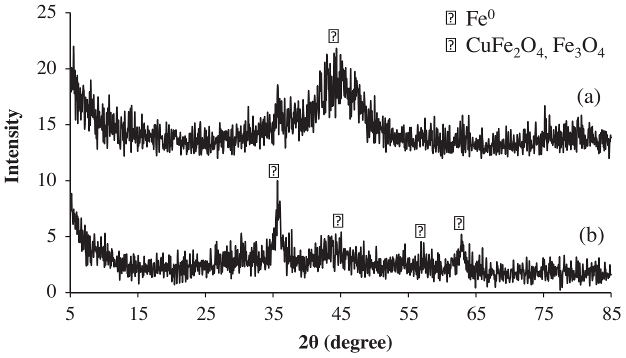

Fig. 2. The XRD patterns of synthesized (a) uncoated nZVI and (b) nano-Fe/Cu particles.

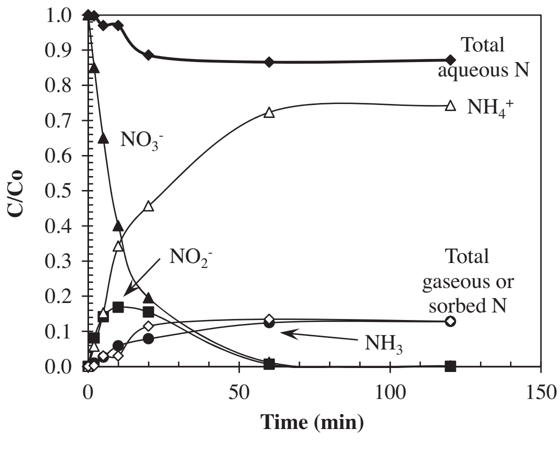

Fig. 3. Normalized concentration of nitrogen species during nitrate reduction by nano-Fe/Cu particles with 5% w/w Cu.

as the main by-product, but its concentration decreased rapidly after the nitrate reduction was almost complete. In the same time, ammonia and ammonium production was observed, according to the following reactions:

$$Fe^0 + NO_3^- + H_2O \rightarrow Fe_2 + NO_2^- + 2OH^- \quad (3)$$

$$5Fe^0 + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + N_{2(g)} + 12OH^- \quad (4)$$

$$4Fe^0 + NO_3^- + 6H_2O \rightarrow 4Fe^{2+} + NH_3 + 9OH^- \quad (5)$$

$$4Fe^0 + NO_3^- + 7H_2O \rightarrow 4Fe^{2+} + NH_4^+ + 10\,OH^- \quad (6)$$

The main nitrogen species remaining in solution is ammonium, corresponding to 74% of the total nitrogen introduced. Ammonia concentration was 7 mg/L corresponding to 12% of the total nitrogen. As seen in Fig. 3, total aqueous nitrogen concentration at 2 h contact time corresponds to 87% of the initial nitrogen concentration. The mass balance difference of 13% may be attributed to the potential production of gaseous nitrogen or ammonia and subsequent emission to the air [18,24], sorption of nitrate/ammonium ion by nanoparticles, and experimental error [24].

3.3. *Effect of Cu content in nano-Fe/Cu on nitrates reduction*

The effect of Cu content in nano-Fe/Cu particles on nitrate reduction is presented in Fig. 4. As seen in this figure, high reduction rates of nitrates were

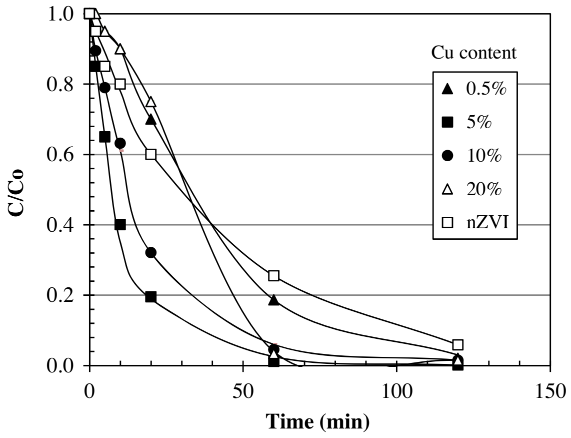

Fig. 4. Effect of time and copper content in nano-Fe/Cu particles on nitrates reduction (initial nitrate concentration 200 mg/L).

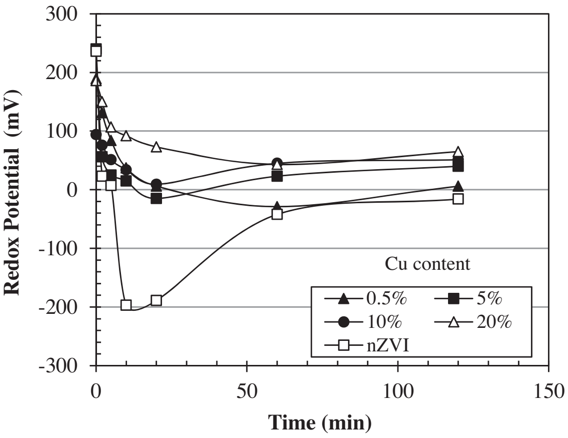

Fig. 6. Effect of reaction time and copper content in nano-Fe/Cu particles on redox potential (initial nitrate concentration 200 mg/L).

obtained in almost all the systems examined. The highest reduction rate was achieved using nano-Fe/Cu particles with 5% copper, and the lowest using pure (uncoated) nZVI. This is in agreement with previous studies [24]. Lower reduction rates were attained at higher Cu content which is attributed to the increased coverage of nano-Fe/Cu surface with copper. More than 80% of the nitrates were reduced with nano-Fe/Cu particles (5% w/w copper) within 20 min and complete removal was attained within 1 h. Using uncoated nZVI, the removal of nitrates was 74.5% within 1 h.

For the same experiments, the pH and redox potential change vs. time for the various Cu contents in nano-Fe/Cu are presented in Figs. 5 and 6, respectively. As seen in Fig. 5, the solution pH increased from 6.2 to higher than 9 in the first 5 min of reaction. The increase of pH is attributed to the reduction of nitrate to ammonia and ammonium and production of hydroxyl anions according to the reactions (5) and (6). The final pH at 120 min reaction time was around 9.6 in almost all the systems with the exception of 20% Cu content which was only 9.1. The increased Cu content in nanoparticles results in increased coverage of their surface with copper leading to the reduction of their reactivity, reduction of the final pH (Fig. 5), and comparatively higher redox potential (Fig. 6). The redox potential of solution significantly decreased from 240 to −30 mV. Even lower values up to −200 mV were measured when nZVI was used for the reduction of nitrates for 10 min, which was progressively increased up to −16 mV at the end of the experiment.

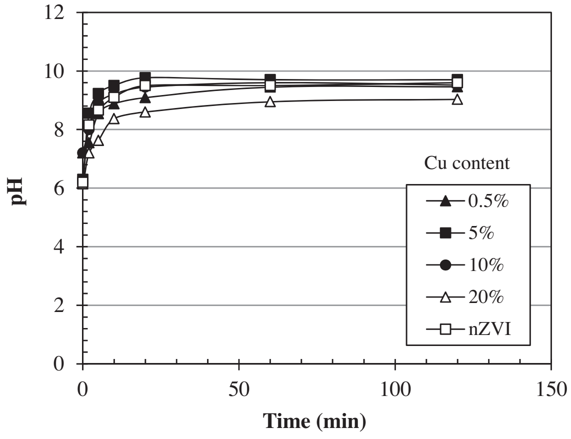

Fig. 5. Effect of reaction time and copper content in nano-Fe/Cu particles on solution pH (initial nitrates concentration 200 mg/L).

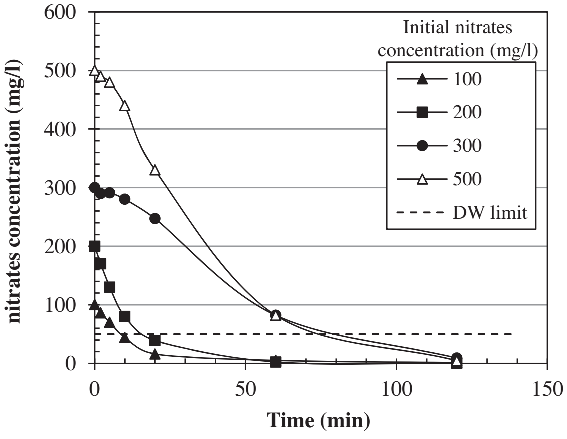

Fig. 7. Effect of time and initial nitrates concentration on nitrates reduction using nano-Fe/Cu containing 5% w/w Cu.

3.4. Effect of initial nitrates concentration

Additional experiments were carried out to evaluate the effect of initial nitrate concentration on nitrate reduction by nano-Fe/Cu containing 5% w/w Cu. The initial nitrate concentrations examined include 100, 200, 300, and 500 mg/L and the results obtained are presented in Fig. 4. As seen in this figure (Fig. 7), the concentration of nitrates was reduced below the EU drinking water limit of 50 mg/L after 10 and 15 min, when the initial concentration was 100 and 200 mg/L, respectively. At the highest initial concentrations investigated, i.e. 300 and 500 mg/L, the time required to reduce nitrates below the EU detection limit was approximately 80 min (Fig. 7).

The results of pH and redox potential vs. time for the various initial nitrates concentration are presented in Figs. 8 and 9, respectively. In the same figures, the pH and redox potential of a test conducted at initial pH 2.3 with initial nitrate concentration 200 mg/L are also presented. As seen in Fig. 8, the pH increased to values above 9 during the initial period of the experiments and subsequently remained constant around 9.6. The pH of the acidified solution also increased and progressively stabilized at less alkaline but still relatively high values, i.e. 8.5 (Fig. 8). The redox potential decreased to values around 0 mV at reaction time 10–20 min depending on the initial nitrate concentration. Then, it slightly increased and subsequently remained constant at around 50 mV values. The same trend was followed in the case of the acidified nitrate solution.

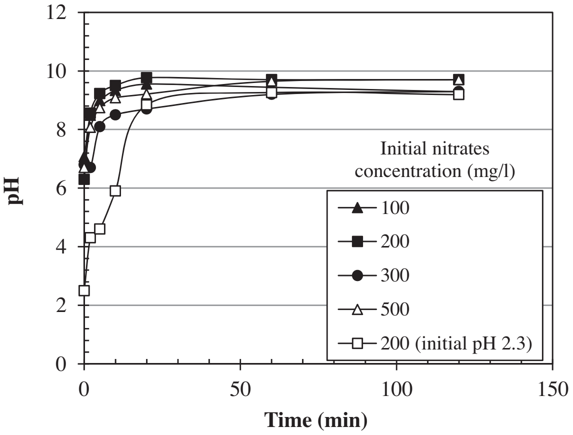

Fig. 8. Effect of time and initial nitrates concentration on solution pH (5% w/w Cu content).

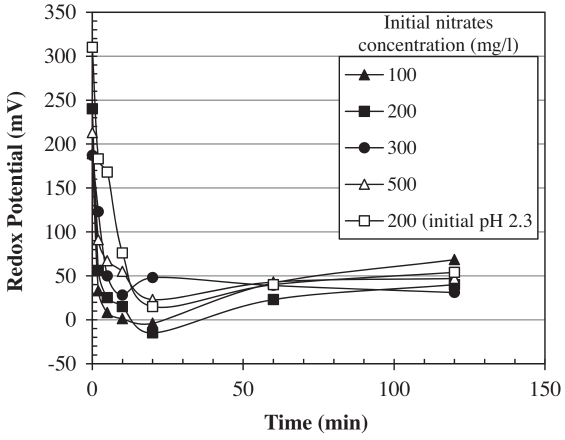

Fig. 9. Effect of time and initial nitrates concentration on redox potential (5% w/w Cu content).

3.5. Evaluation of kinetic data

A variety of kinetic models for nitrates reduction by nZVI have been reported including a pseudo first-order kinetic model and higher or lower apparent reaction order models. The pseudo first-order kinetic model, most widely used for nitrate reduction by nZVI, was employed in this study to determine the reaction rate of the bimetallic systems examined. According to this model, the reaction rate is proportional to nitrate concentration, as given in the following equation:

$$\frac{dC_{NO_3}}{dt} = -k_{obs}C_{NO_3} \tag{7}$$

where k_{obs} (h^{-1}) is the observed first-order rate coefficient. Integration of Eq. (7) results in

$$C_{NO_3} = C_0 e^{-k_{obs}t} \tag{8}$$

where C_0 is the initial nitrate concentration. Observed first-order rate coefficientes were calculated from regressions of $ln(C_{NO_3}/C_0)$ vs. time (t). Regression was performed for either all the data of each experiment, or initial data-sets up to a certain reaction time. It was seen that the initial reaction rates up to 20 min reaction time were almost constant; then, they change significantly mainly due to the high pH values obtained from the reduction of nitrates to ammonium and ammonia. The results of k_{obs} values obtained are presented in Table 1.

As seen in the table, the k_{obs} value of nitrate reduction by nZVI was determined to 1.52 h^{-1}, similar to the values reported in the litterature [18,24]. The k_{obs} value of nitrate reduction in the presence of bimetallic nanoparticles increases by increasing Cu content up to 5% w/w, reflecting the increased reactivity attained by increasing copper content. The highest value, i.e. 5.03 h^{-1}, was obtained using nano-Fe/Cu containing

Table 1
Observed pseudo first-order rate coefficient of nitrate reduction with nZVI and nano-Fe/Cu

Reductant	Initital nitrate concentration (C_o, mg/L)	k_{obs} (for 20 min) (h^{-1})	Correlation coefficient (r^2)
nZVI	200	1.52	0.986
nano-Fe/Cu (0.5% w/w)	200	0.97	0.930
nano-Fe/Cu (5% w/w)	200	5.03	0.995
nano-Fe/Cu (10% w/w)	200	3.26	0.987
nano-Fe/Cu (20% w/w)	200	0.80	0.962
nano-Fe/Cu (5% w/w)	200 (initial pH 2.5)	4.45	0.999
nano-Fe/Cu (5% w/w)	100	5.32	0.994
nano-Fe/Cu (5% w/w)	300	0.55	0.952
nano-Fe/Cu (5% w/w)	500	1.12	0.930

Cu 5% w/w. Slightly lower k_{obs} value ($4.45\,h^{-1}$) was recorded when nitrate solution was intitialy acidified (pH 2.5). Further increase of Cu content in nano-Fe/Cu particles resulted in decrease of k_{obs} value due to the increased coverage of nanoparticles surface with copper and, therefore, reduction of their reactivity.

The initial nitrate concentration significantly affects the k_{obs} values obtained. At the lowest nitrate concentration values examined (100 and 200 mg/l), the respective k_{obs} values recorded were high, i.e. 5.32 and $5.03\,h^{-1}$, respectively. Lower k_{obs} and respective correlation coefficient values were found for initial nitrate concentration 300 and 500 mg/L (0.55 and $1.12\,h^{-1}$ respectively). However, these low initial reaction rates increase at retention time higher than 20 min. A significant lag phase in the onset of nitrate reduction was also reported [27] using microscale zero-valent iron for nitrate reduction.

The value of surface normalized rate coefficient, k_{SA} ($L{\cdot}m^{-2}{\cdot}h^{-1}$), was calculated by dividing the k_{obs} value by the surface area concentration, ρ_α ($m^2{\cdot}L^{-1}$) of nano-Fe/Cu (Cu content 5% w/w) according to the following equation

$$k_{SA} = \frac{k_{obs}}{\rho_a} \tag{9}$$

ρ_a was calculated by taking into account the nZVI concentration in solution (3.33 g/L) and BET surface area of the synthesized nano-Fe/Cu particles (34 $m^2{\cdot}g^{-1}$), the corresponding value being $113.3\,m^2\,L^{-1}$. Moreover, the surface normalized rate coefficient, k_{SA}, was determined to $1.34\,L\,m^{-2}\,h^{-1}$, which is lower than the values reported in the literature for nZVI. This difference was attributed to the one order of magnitude higher concentration of nano-Fe/Cu in solution used in this study (3.33 g/L compared to 0.35 g/L used by Liou et al. [24]) and the fact that iron and copper play different roles in the reduction process. Direct comparison of nZVI and nano-Fe/Cu k_{SA} values could only be made if individual surface areas of bimetallic particles are distinguished [24].

4. Conclusions

Bimetallic nano-Fe/Cu particles with variable Cu content (0, 0.5, 5, 10, and 20% w/w) were synthesized and used at relatively high rates (3.33 g/L) to reduce nitrates in aquatic solution (100, 200, 300, and 500 mg/L). The nZVI and Fe/Cu particles synthesized in this study have a particle size finer than 100 nm. The BET surface area of nano-Fe/Cu containing 5% w/w Cu was $34\,m^2\,g^{-1}$ and the main phases identified by XRD analysis are magnetite and copper ferrite spinel. The results of nitrate reduction indicate that 5% w/w Cu in nano-Fe/Cu particles is the most effective content to reduce nitrates, as it exhibits the highest nitrate reduction rate. More than 80% of the nitrate was reduced within 20 min and complete nitrate reduction was attained within 1 h. The main reduction products are dissolved ammonium and ammonia. Based on nitrogen mass balance calculations, 13% w/w of the initial nitrogen was either emitted to the air in the form of ammonia or nitrogen gas, or sorbed by nano-Fe/Cu nanoparticles. Increase of the copper percentage in nano-Fe/Cu to 20% w/w resulted in a decrease of nitrate reduction rate due to the increased coverage of nZVI surface by copper. Nitrate reduction by nano-Fe/Cu leads to an increase in solution pH to values around 9.6. The increase of the initial nitrate concentration from 100 to 500 mg/L resulted in significant increase of the treatment time required to reduce nitrates concentration below the EU detection limit from 10 to 80 min. The pseudo first-order kinetic model was fit to experimental data resulting in first-order rate coefficient k_{obs} values $1.52\,h^{-1}$ for nZVI and $5.03\,h^{-1}$ for nano-Fe/Cu containg Cu 5% w/w. The observed first-order coefficient decreased at lower or higher than 5% w/w Cu content in nanoparticles and for initial nitrate concnentration higher than 300 mg/L.

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