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Nitrate removal from water using iron nanoparticles produced by arc discharge *vs.* reduction

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ABSTRACT

Methods of fabrication of zero valent iron nanoparticles (FeNps) are found to affect their efficiency in nitrate removal from water. Application of a 50 A/cm^2 current to a pair of iron electrodes, in distilled water, renders FeNps (37 nm) which show twofold efficiency over FeNps (30 nm) produced *via* the reduction of $FeSO_4$ by $NaBH_4$. The approximation of crystallite sizes of FeNps through application of the Scherrer equation to the XRD data suggests a larger size of 39 nm (37 nm by TEM) associated with the more efficient arc fabricated FeNps, compared to the FeNps produced by the reduction (30 nm). On the other hand, scanning electron microscopy (SEM) recommends a higher dispersity for the arc discharged FeNps compared to those produced by $NaBH_4$ reduction. In addition, the XRD pattern of the arc discharge FeNps confirms their purity, whereas Fe_3O_4 appears as an impurity with the reduction product. Higher concentrations of nitrate retards FeNps produced by reduction while exerts less effect on the arc fabricated FeNps. Hence, using the latter brand is recommended for water sources containing higher concentration of nitrate.

1. Introduction

High concentration of nitrate in drinking water is toxic and carcinogenic for human and animals [1,2]. Hence, developing techniques for water remediation, in particular at large scale, is an important and interesting area of research. Nitrate removal frequently involves microbial denitrification, ion exchange, reverse osmosis, electrocatalytic, and chemical reduction processes [3–7]. Microbial reactions are inefficient because of slow progression and require intensive maintenance, such as constant supply of organic substances as electron donors. Nitrate species cannot be removed efficiently by ion exchange and reverse osmosis processes either. Electro-catalytic process often needs high reduction potential to transform nitrate ion into nitrogen gas, for most electrode surfaces. Additionally, higher installation and maintenance costs with the complexity of regeneration of membrane and brine disposal significantly constrain the use of reverse osmosis process [8,9]. The catalytic reduction of nitrate using iron nanoparticles is however suggested as a promising method for the nitrate removal from water without the drawbacks of the conventional methods [10,11]. This method is deemed the most cost-effective option in many studies. Therefore, its innovative applications can often be found for *in situ* groundwater remediation or for the treatment of industrial waste streams contaminated with redox active toxic materials [12–25]. In addition to nitrate, extensive laboratory studies have indicated that FeNps are effective for the transformation of a wide range of common environmental contaminants such as chlorinated organic solvents [26], organo-chlorine pesticides [27], PCBs [28], organic dyes [29], and metal ions such as As(III), Pb(II), Cu(II), Ni(II), and Cr(VI) [30].

Various physical and chemical techniques have been employed to produce FeNps, such as thermal and sonochemical decomposition of iron-containing complexes [31,32], chemical vapor condensation [33], reverse micelles [34], and electro-exploding wires [35]. Using $NaBH_4$ to reduce ferric ion is the most common and traditional chemical reduction method for production of FeNps [17,36,37]. Nevertheless, in this method, in addition to the strong reducing agent, salts of sodium and boron are being added to water that may reduce water quality [16].

Recently, we have developed a modified arc discharge technique for the synthesis of metal nanoparticles [38–42]. The advantages of this technique are its cost effectiveness, purity, uniformity, and rather small size of the nanoparticles. In this paper, we compare and contrast the ability of removal of nitrate from water by arc fabricated FeNps *vs.* those produced by chemical reduction.

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2. Materials and methods

2.1. Modified arc discharged method

Two pure iron rods (99.90%) with diameters of 2.5 mm and length of 30 mm are employed as electrodes: one as a movable anode and the other as a static cathode. The distance between the two electrodes is set at 1 mm with a 45° angle between them. A current of 50 A/cm^2 is passed through water-submerged iron electrodes until explosions occur (1–10 ms). Such rod explosions and fragmentations generally tend to proceed by heating the electrodes followed by their melting, and/or evaporation. Gas bubbles are formed in the water during the arc process due to the plasma vaporization/decomposition of the anode material and water. These escaping gas bubbles act both as a condensing media and as carriers of the final products to the water surface. The cooled metal vapor in water leads to the formation of primary particles by the nucleation mechanism turning into iron nanoparticles dispersed in distilled water. We have monitored parameters like current density, electrode-type and dimension, as well as the medium in which explosions are carried out.

2.2. Chemical reduction method

In a typical synthesis of FeNps by borohydride reduction, 5.0 g of $FeSO_4 \cdot 7H_2O$ (98%, Aldrich) is dissolved in 250 mL of 30% technical grade methanol and 70% deionized water (v/v). The pH is adjusted to about 6.8 by 3.8 M NaOH. Then 2.0 g of $NaBH_4$ powder (98%, Aldrich) is dissolved in 10 mL deionized water and the solution is added incrementally to the mixture, allowing the foaming to subside between increments which finally results in ferric ion (Fe^{3+}) reduction (Eq. (1)). After addition of all of the $NaBH_4$ solution, the mixture is stirred for 45 min and then centrifuged for another 15 min at 5000 rpm. The solid is washed twice with technical grade methanol, effectively substituting methanol for the water in the mixture. The resulting solid is dried for 5 h under N_2 atmosphere and then broken up with a spatula to form a fine black powder.

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

2.3. Characterization of the nanoparticles

The particle size and morphology are investigated by PHILIPS (EM208S, the Netherlands) transmission electron microscopy (TEM) at 100 kV of acceleration voltage and scanning electron microscopy (SEM) of a Holland Philips XL30 microscope with an accelerating voltage of 25 kV. Crystal structures are examined using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (Cu Kα, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2°/min from 10° to 80° (2θ).

2.4. Nitrate removal experiments and analytical methods

Tests are conducted in seven 30 mL polyethylene bottles, in which the synthesized FeNps, 1 mL HCl (0.1 M), and a certain concentration of nitrate solution (0, 5, 10, 15, 20, 25 and 30 mg/L) are placed. Ionic strengths of the solutions are adjusted by KCl (0.001, 0.01 and 0.1 mol/L). Using a buffered solution of 0.2 M acetic acid, the pH is set at 2, 4, 6 or 8. Each bottle is rotated at 200 rpm for 48 h. Nitrate concentration is measured by a HACH Model DR-4000 spectrophotometer according to the 20th edition of Standard Method (1998).

The reaction between the zero valent iron and nitrate is a redox reaction. Oxidation of FeNps results in the formation of metal ions. This makes FeNps a potential reducing agent for many redox labile substances. Nitrite, nitrogen gas and ammonia are possible products of the nitrate reduction. The FeNps, with nano size particles, react with nitrate ions in acidic pH and convert them to nitrogen gas Eq. (2). In contrast, the microparticles of zero valent iron appear to stoichiometrically reduce nitrates into ammonia Eq. (3) [28]:

$$5Fe^0 + 2NO_3{}^- + 12H^+ \rightarrow N_2(g) + 5Fe^{2+} + 6H_2O \qquad (2)$$

$$4Fe^0 + NO_3{}^- + 10H^+ \rightarrow NH_4{}^+ + 4Fe^{2+} + 3H_2O \qquad (3)$$

3. Results and discussion

In this work we have compared and contrasted the most practical methods for the fabrication of FeNps which are known as the arc fabrication and reduction pathways. Other methods such as thermal and sonochemical decomposition of iron-containing complexes [31,32], chemical vapor condensation [33], reverse micelles [34], and electro-exploding wires [35] while interesting, fall beyond the reasonable scope of this manuscript. So, our objective in this work is to compare and contrast the efficiency of nitrate removal from water by two types of iron nanoparticles, produced by arc discharge and reduction methods. We employ the traditional route for the production of FeNps by chemical reduction, using $NaBH_4$ as a strong reducing agent. We also make use of the arc discharge method, known as an effective technique to produce nanosized powders based on vaporization of the metal followed by the condensation and nanoparticle formation.

3.1. Characterization of FeNps produced by arc fabrication vs. reduction

The XRD patterns of FeNps, fabricated by arc discharge method, indicate the formation of pure FeNps, with body centered cubic (bcc) crystals, showing only two lines: (1 0 0) and (2 0 0), at $2\theta = 44.57°$ and 65.21°, respectively (Fig. 1a). In contrast, FeNps produced through chemical reduction appear with some iron oxide (Fe_3O_4) coating (impurity) that possibly is formed in the drying step of the workup. Hence, the XRD patterns for the reduction product show two sets of lines. The first set indicates the formation of FeNps by showing lines (1 0 0) and (2 0 0), at $2\theta = 44.82°$ and 65.16°, respectively. The second set designates the Fe_3O_4 impurity, showing five low intensity lines (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0), at 30.17°, 35.53°, 43.38°, 57.13°, and 62.73°, respectively (Fig. 1b). Using the Scherrer formula [43], arc discharge FeNps (39 nm) appear rather larger than the impure FeNps (30 nm), obtained through reduction by $NaBH_4$.

The scanning electron microscopy (SEM) images of the arc synthesized FeNps portray rather dispersed spheres (Fig. 2a), compared to the more clustered, cloudy nanoparticles produced by the reduction method (Fig. 2b). Fairly strong electromagnetic attraction forces are observed among nanoparticles that are prepared by both methods: arc discharge as well as reduction. One may attribute the higher clustering(s) and more crowded appearance of FeNps produced by the reduction method to their smaller size which renders higher surface/volume ratio giving grounds for higher electromagnetic inter-particle attractions. Of course, the absence of stabilizers, often required in the reduction method, is another cause of the high clusterings. In addition, better control over the explosive power ensures more Lorentzian size distribution in the arc discharge method. The TEM image of the arc fabricated FeNps showed nanoparticles as nearly spherical with the average particle size of 37 nm, confirming the above 39 nm estimation *via* Scherrer's formula (Fig. 3).

3.2. Comparative nitrate removal by two brands of FeNps

We now compare and contrast the abilities of the above two brands of FeNps for removing nitrate from water. FeNps (1.33 g/L)

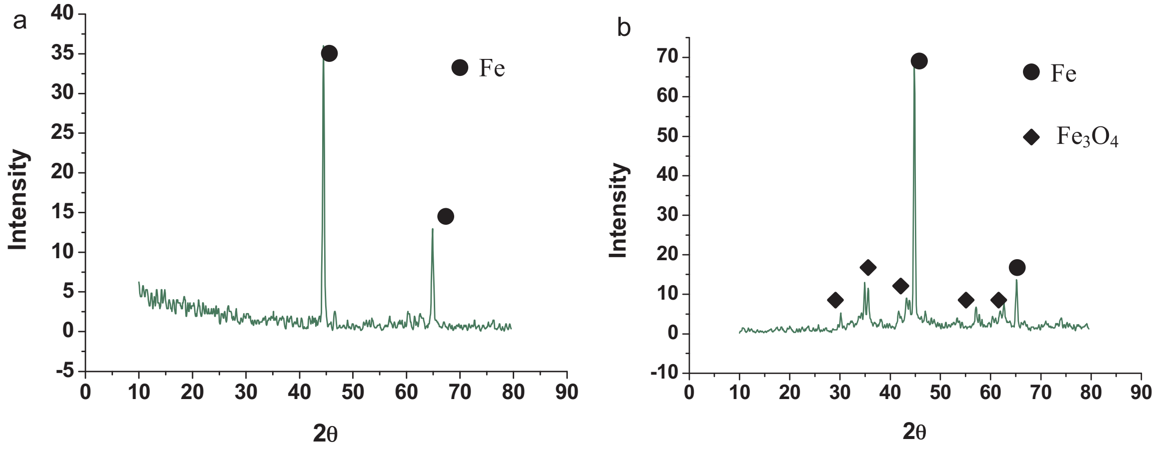


Fig. 1. Comparison of the XRD patterns of the iron nanoparticles produced by arc discharge (a) and chemical reduction (b).

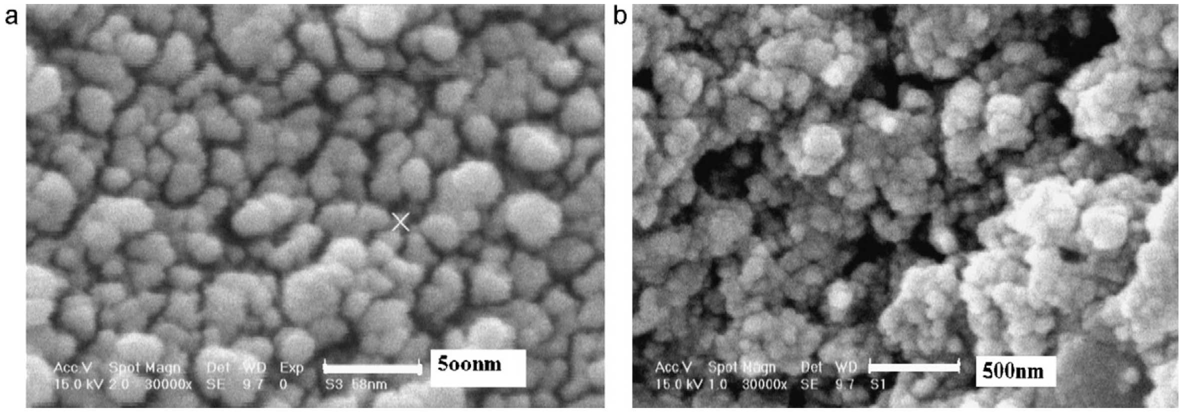


Fig. 2. Comparison of the SEM images of the iron nanoparticles produced by arc discharge (a) and chemical reduction (b).

that are produced by reduction, show the removal of 73% of nitrate from a sample of water containing 5 mg/L of nitrate, at a constant ionic strength of 0.01 M KCl, and with the initial pH of 2. In contrast, under the same exact conditions, arc fabricated FeNps remove 92% of nitrate (Fig. 4). This clearly indicates the higher efficiency of arc fabricated FeNps in nitrate removal from water. Repeating the same experiment under the same conditions demonstrated a linear decrease in the nitrate removal ability of both brands of FeNps as the concentration of nitrate is increased from 5 to 30 mg/L. This effect shows a smaller slope and hence less adverse effect on the arc fabricated FeNps ability of nitrate removal than those produced by reduction. So we may conclude that arc fabricated FeNps are preferred over those produced by reduction, because activity of the former is more immune to higher concentrations of nitrate.

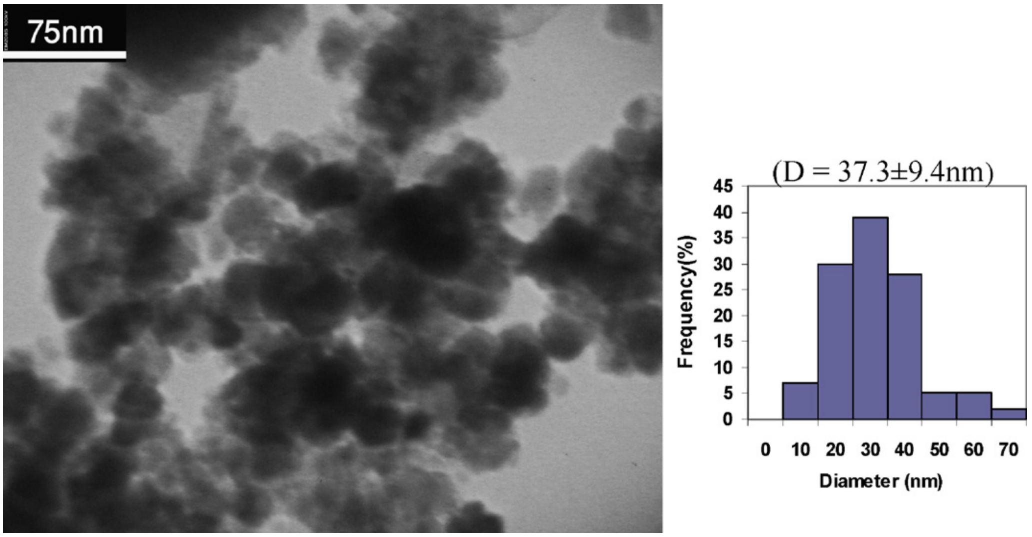


Fig. 3. TEM micrograph and particle size histogram of iron nanoparticles (FeNps) produced by arc discharge.

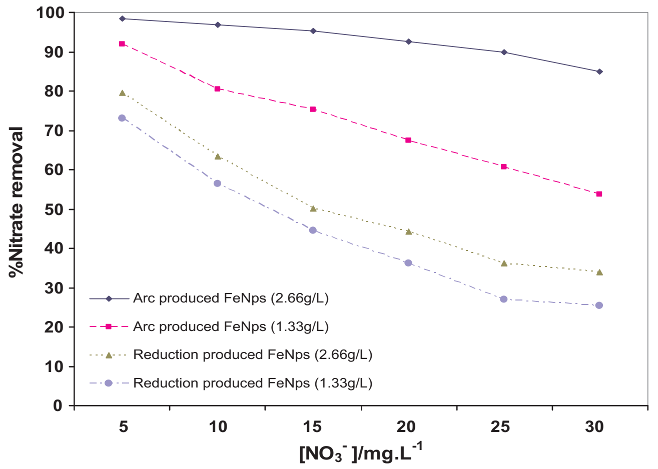
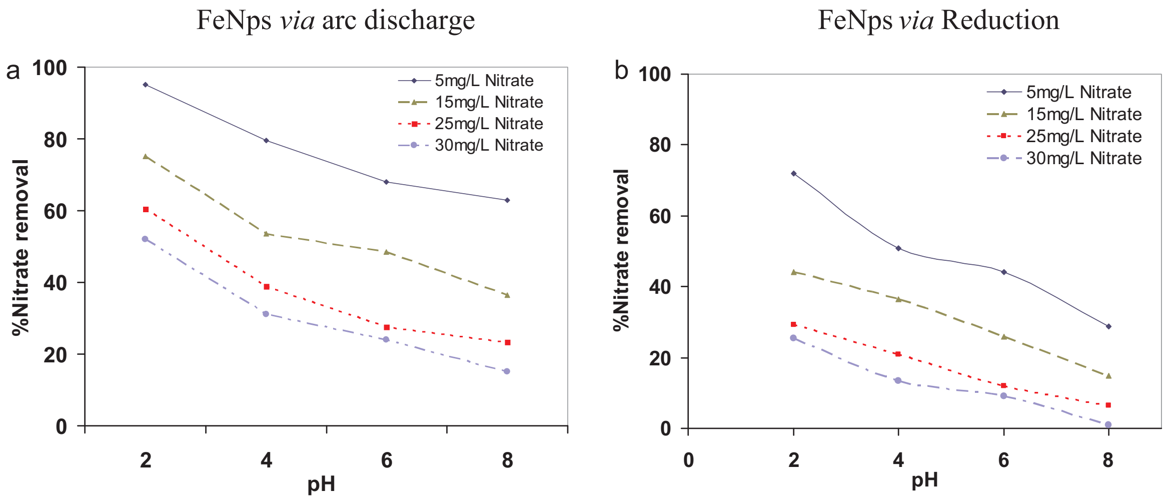


Fig. 4. Nitrate removal from water (0.01 M KCl, pH = 2) by two brands of FeNps (obtained *via* arc discharge *vs.* chemical reduction) each with two concentrations 1.33 and 2.66 g/L, after 24 h.

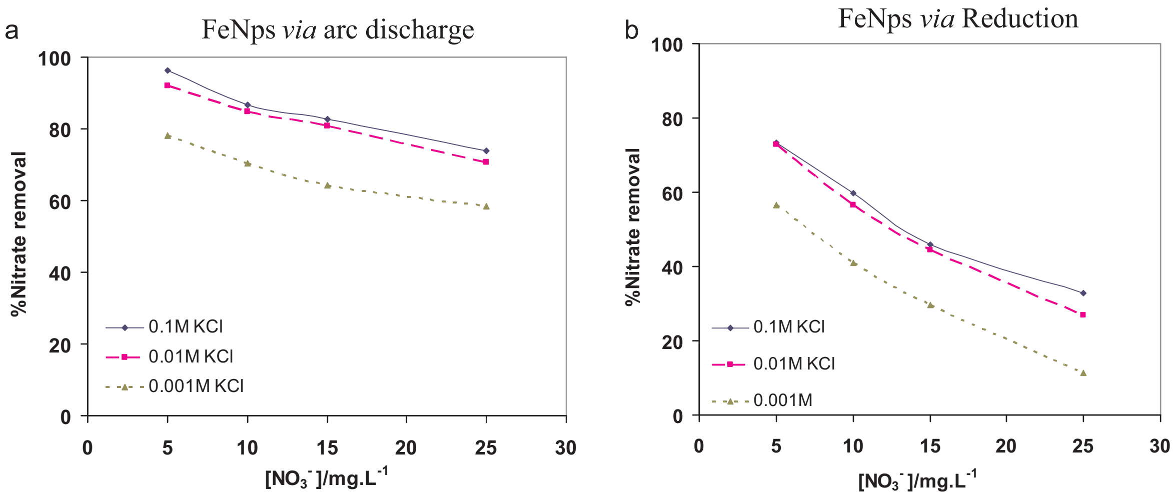
Doubling the concentration of both brands of FeNps increases their percent nitrate removal from water. This effect is more pronounced for arc fabricated FeNps especially at higher nitrate concentrations in water. For example doubling the concentration of FeNps (produced by reduction) from 1.33 g/L to 2.66 g/L, increases its nitrate removal ability, from a sample of water containing 30 mg/L nitrate, from 26 to 34% – an increment of 8%. In contrast, under similar conditions, doubling the concentration (from 1.33 g/L to 2.66 g/L) of the arc fabricated FeNps increases its nitrate removal ability from 54 to 85% (an increment of 31%). Based on these increments, the impact of doubling the concentration of arc fabricated FeNps compared to those produced by reduction is almost four times. Furthermore, we compared nitrate removal from water (0.01 M KCl, pH = 2) by arc fabricated FeNps at four concentrations (0.66, 1.33, 2.0, and 2.66 g/L) where the increase in the FeNps parallels with the increase in nitrate removal (Fig. S1).

Increasing the pH from 2 to 8 causes an approximately linear decrease in the ability of both brands of FeNps for removing nitrate from water containing different concentrations of nitrate (Fig. 5). Also, we measured the change of pH during each nitrate removal experiment and found in all systems, pH increases with increasing time. So, the initial pH of 2, 4, 6, and 8 increases finally to 5.48,


FeNps *via* arc discharge

FeNps *via* Reduction

Fig. 5. Effects of pH on the % nitrate removal by two brands of FeNps (1.33 g/L) from water (0.01 M KCl; (5–30 mg/L) NO_3^-), after 24 h: (a) FeNps by arc fabrication and (b) FeNps by reduction.


FeNps *via* arc discharge

FeNps *via* Reduction

Fig. 6. Effects of nitrate concentrations on its % removal by two brands of FeNps (1.33 g/L), from water with three ionic strengths [KCl]s, at pH = 2, after 24 h: (a) FeNps fabricated by arc ion and (b) FeNps produced by reduction.

6.25, 7.83, and 9.26, respectively. These phenomena may be rationalized by considering the consumption of [H^+] through removal of [NO_3^-] illustrated by Eq. (2) [28], and/or the release of hydroxyl group and the increase in solution pH suggested by Eqs. (4) and (5) [22]. Hence, regardless of the brand of FeNps employed, in order to remove higher % of nitrate one must maintain a lower pH of the aqueous solution.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (4)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + H_2 + 4OH^- \quad (5)$$

FeNps (1.33 g/L) that are fabricated by arc discharge show an increase in nitrate removal by 78, 92, and 96% from a sample of water containing 5 mg/L of nitrate, when the ionic strengths are increased by 0.001, 0.01, and 0.1 M KCl, respectively (Fig. 6a). When the same experiment are repeated under similar conditions for FeNps (produced by reduction), lower nitrate removals are observed but with the same trend (Fig. 6b). In addition, changing the nitrate concentration from 5 mg/L to 30 mg/L produces similar trend for both brands of FeNps.

Hence, increase in ionic strength of solutions has a direct relationship with the nitrate removal, in a way that increasing in the concentration of KCl increases nitrate removal regardless of the initial concentration of nitrate in the solution and/or the brand of FeNps employed. Evidently, the increase in chloride ion in solution induces pitting corrosion of the FeNps surface, which may enhance surface reactivity or increase the reactive area of the FeNps for NO_3^- reduction to occur [44]. Nevertheless, increasing of the ionic strength reaches its upper limit at 0.01 M KCl which we employed throughout our experiments. In all of our experiments, about 76% of nitrate is reduced after 12 h, above 90% after 24 h, and approximately 100% after 72 h. Hence, we choose a period of 48 h for comparing the nitrate removal from water by our two brands of FeNps.

4. Conclusion

In this study pure FeNps are fabricated through a novel modified arc discharge method. The efficiency of FeNps, for the removal of nitrate from water appears twice that of rather impure Fe nanoparticles, produced through reduction of $FeSO_4$ by $NaBH_4$. FeNps fabricated by arc discharge are free from extraneous impurities, as no chemicals are used in the process of their preparation. So between the reduction method *via* $NaBH_4$ and arc discharge for fabrication of FeNps the latter method is recommended for the refinement of water sources containing higher concentrations of nitrate.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.10.077.

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