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Nitrate Removal from Water Using Synthesis Nanoscale Zero-Valent Iron (NZVI)

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Abstract

This study was conducted to investigate chemical reduction efficiency of nitrate by synthesis nanoscale zero-valent iron (NZVI) in aqueous solution, under aerobic condition. TEM image shows synthesis nano zero-valent iron has a size in the range of 40–150nm. Experimental results suggest that the reduction efficiency of nitrate decreased quickly with increasing initial pH value from 4 to 10 increased considerably with the increasing dosage of nanoscale zero-valent iron from 0.25 to 1gl^{-1} and did not vary much with initial nitrate concentration changing from 30 to 50 mg l^{-1} (NO_3-N). With reductive denitrification of nitrate by nano zero-valent iron, the removal rate of nitrate reached 80% in 60 min with nano zero-valent dosage of 1.0gl^{-1} and pH_{in} 4, in room temperature.

Keywords: nitrate, water, iron nanoparticles.

1. Introduction

Nowadays, regarding to increasing demand on safe drinking water, removal of widespread pollutants such as nitrate is creating a significant challenge in water treatment industry. Anthropogenic sources such as nitrogen fertilizer, nitrogen pesticides and industrial waste effluent discharge account for most nitrate contamination of ground and surface waters [1]. Elevated nitrate concentrations in drinking water supplies present a potential risk to public health. In infants NO_3 is reduced to NO_2, which combine with hemoglobin in the blood to form methemoglobin leading to cyanosis in babies under six month old [2]. A research conducted by Mayo Clinic Center in Minnesota also showed that drinking tap water with a high concentration of nitrate would have a higher risk of causing bladder cancer and ovary cancer [3]. Therefore many countries have regulated the concentration of nitrate in drinking water. In the US, EPA established a maximum contaminant level (MCL) of 10mg/L NO_3-N for drinking water [4]. In Iran the regulatory thresholds for NO_3-N in drinking water sources are set as 10mg/L which is equivalent to 44.82 mg/L NO_3. Current technology to remove nitrate from water include ion exchange, reverse osmosis, biological denitrification and chemical reduction [3]. Among different water treatment methods, using nano materials such as nano zero-valent iron as a new method has a good potential for removal of nitrate. Researchers have studied the use of zero-valent iron in halogenated organics, azoaromatic nitroaromatics and the treatment of different kinds of compounds such as inorganic compounds like heavy metals [5]. In recent years, there has been a growing interest in the use of zero-valent

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iron in the treatment of water containing nitrate. Previous studies have demonstrated that nitrate could be completely reduced by metallic iron under anoxic and aerobic conditions; furthermore, the major reduction product was ammonia [6,7]. Nano zero-valent iron in contrast with iron powder have some advantages of high specific surface area, high active surface, easily being sca- tered and so on, which lead to the increasing denitrification rate of nitrate [5]. In this paper, we studied the parameters which affect on the effectiveness of nitrate removal by synthesis iron nano particles. These parameters include pH, dosage of nanoscale Fe° and nitrate concentration. The Purpose of this study is to improve our understanding of denitrifcation condition by nanoscale Fe.

2. Materials and Methods

2.1. Chemicals and materials

The following chemicals were purchased from Merck: $NaBH_4$ (for synthesis), $FeSO_4.7H_2O$ (98%), Methanol (99%), NaOH (99%), H_2SO_4 (98%), KNO_3 (98%). Nitrate reagent (Nitraver 5) was obtained from Hack company.

2.2. Method for nanoscale Fe⁰ synthesis

In a typical synthesis of Fe° Nanoparticles by borohydride reduction, 4.0g of $FeSO_4 \cdot 7H2O$ was dissolved in 200mL of 30% methanol and 70% de-ionized water (v/v). The pH was adjusted to about 6.8 by 3.8M NaOH. Then 1.5 g of $NaBH_4$ powder was dissolved in 10mL de-ionized water and the solution was added incrementally to the mixture in ultrasonic shaker at 25ºC temperature for 45 min After addition of all of the $NaBH_4$ solution the mixture was stirred in jar test for another 45 min and then centrifuged for 15 min at 5000 rpm. The solid particles were washed at least three times with methanol and then dried for 4hr under vacuum condition, and then broken up with a spatula to form a fine black powder and immediately added to the aqueous solution to react with nitrate. The ferrous iron was reduced to zero-valent iron according to the following reaction Eq(1):

$$Fe\,(H_2O)_6 + 3BH_4^- + 3H_2O \rightarrow Fe° + 3B(OH)_3 + 10.5\,H_2 \qquad (1)$$

2.3. Preparation of aqueous nitrate solution

Different concentrations of nitrate in aqueous solution were prepared by dissolving desired quantities of KNO_3 in de-ionized water. An initial concentration of 30mg/l NO_3-N (133 mg/l NO_3) was used for studying the effects of pH and dosage of iron nanoparticles, whereas 50mg/l NO_3-N (222 mg/l NO_3) also was used for studying the effect of nitrate concentration on removal effectiveness.

2.4. Experiments for chemical reduction of nitrate by iron

Five hundred milliliter of aqueous nitrate solution of a selected concentration was first put in each of glass beakers for each set of experiments. Freshly prepared nanosized ZVI at arbitrary concentration (1, 0.5 or 0.2g/L) was added to each glass beaker. Chemical reduction of nitrate by nanosized ZVI at ambient temperature, and desired pH(4,7,10) and/or desired nitrate concentrations (30, 50 mg/l) were simultaneously conducted in various glass beakers using a jar test ap-

paratus at a mixing rate of 300 rpm. In each set of experiments the reaction vessels were removed one by one from the jar test apparatus at intervals of 10 min during the 60-min reaction. Periodically, 20ml of the aqueous solution passed through a 0.45 μm membrane filter to separate iron nanoparticles. The concentrations of unreacted nitrate (NO3) were determined by VIS spectrophotometer (VIS DR2800, HACH). The pH value was measured using pH meter (satorius-150).

2.5. Mechanism of denitrification by nanoscale Fe^0

In aqueous systems, zero-valent iron (Fe°) is readily oxidized to ferrous ion (Fe^{+2}) by many substances. under anaerobic condition, H^+ is the only electron acceptor that will be involved in the reaction. Therefore, the overall process of corrosion in anaerobic Fe°–H_2O system is described by the following reaction [6], Eq(2). But Under aerobic conditions dissolved oxygen would play a role of the electron acceptor in the cathodic half-reaction. In this case, the primary reaction yields only OH^- and not H_2 [8], Eq(3):

$$Fe^{\circ} + 2H_2O \rightarrow Fe^{+2} + H_2 + 2OH^- \tag{2}$$

$$2Fe^{\circ} + O_2 + 2H_2O \rightarrow 2Fe^{+2} + 2OH^- \tag{3}$$

The reaction and its mechanisms between nitrate and ZVI is a true redox reaction (Yang and Lee, 2005). Several studies have indicated the final products of chemical reduction of nitrate by ZVI could be N_2 or NH_3 depending on the experimental conditions [6,7,8]. But certainly, the main product of this reaction is ammonium [7], (Eq(4)):

$$4Fe^{\circ} + NO_3 + 7H_2O \rightarrow 4Fe^{+2} + NH_4^+ + 10OH^- \tag{4}$$
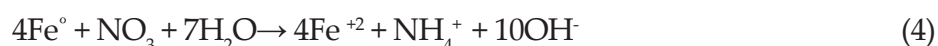
3. Results and Discussion

3.1. Characterization of nanoscale Fe^0

The particle size are determined by PHILIPS (EM208 S, the Netherlands), transmission electron microscopy (TEM) at 100 kV of acceleration voltage. Figure 1, shows TEM image of the synthesized nanoscale Fe°. The particles are spherical with the size ranging from 60 to 120 nm in diameter.
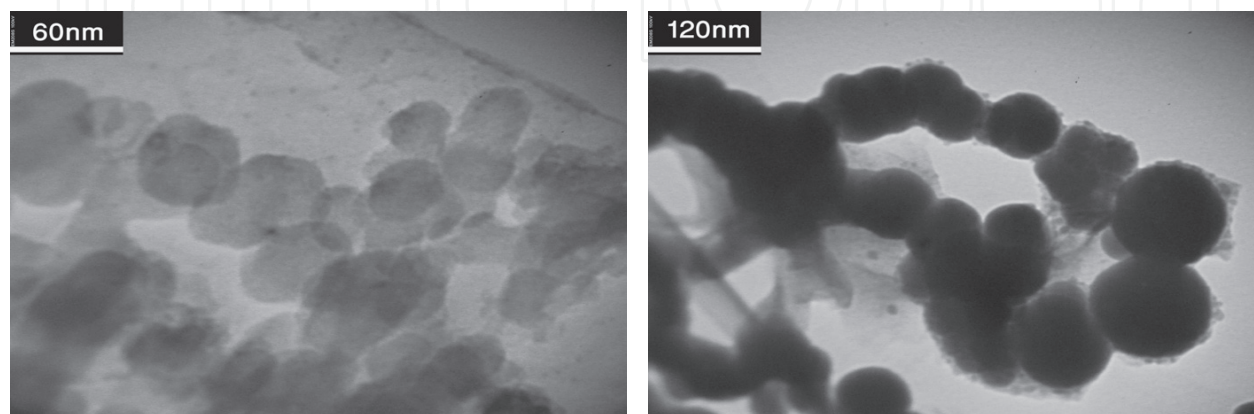

Fig 1. TEM images of synthesis nanoscale Fe° particles

3.2. Effect of Fe⁰ dosage on nitrate reduction by nanoscale Fe⁰

Fe° dosage is a significant variable parameter in nitrate reduction by nanoscale Feº. Since the denitrifcation of nitrate by Feº involves reaction at the metal surface, it was anticipated that the quantity of metal surface area should strongly influence the efficiency of nitrate reduction. In this study we used three different dosage of nanoscale Feº (0.2, 0.5, 1 g/L). As shown in figure 2, with the dosage increasing, the removal efficiency of nitrate become higher and higher, In 0.2g/L Feº dosage, after 60 min nitrate removal efficiency reached 57%, then increasing Fe dosage of 0.2 to 0.5, cause increasing efficiency to 70% ,and finally in 1g/L dosage after 60min, nitrate removal reached near 80% . Therefore with increasing Feº concentration, metal surface area also increased, and efficiency of nitrate reduction will be increased [2,7,9].
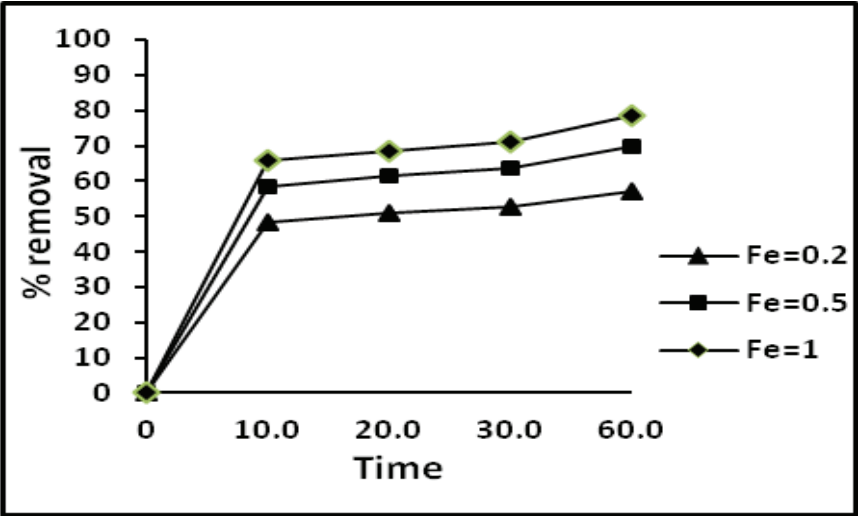

Fig 2. Effect of Fe° dosage on nitrate reduction by nanoscale Fe°, T=20°C, pHin= 4, C_0=30mg/l NO_3-N, stirring at 300rpm

3.3. Effect of pH value on the reduction of nitrate by nanoscale Fe⁰

In this study three different pH value (4, 7, 10) were employed to study the effects of pH on nitrate reduction efficiency by nanoscale Feº. Figure 3, shows the effect of initial pH value on the reduction of nitrate. The removal efficiencies of nitrate decreased with the increasing initial pH value. When the initial pH was 4, about 80% of nitrate was reduced in 60 min, while the removal efficiencies decreased to 70% and 64%, when the initial pH values were 7 and 10, respectively. This suggests that the reduction of nitrate could be well performed in acidic conditions. In fact, the reduction of nitrate proceeded on the surface of iron particles, lowing pH, would dissolve away ferrous hydroxide and other protective layers at the surface of nanosized Feº yielding more fresh reactive sites for chemical reduction of nitrate. Therefore, Based on the experimental results obtained, in general, the efficiency of nitrate removal by nanosized ZVI increases as the system pH decreases. This finding is in accord with that of reported by Yang et al , Chen et al and Zhang et al [2,5,10].
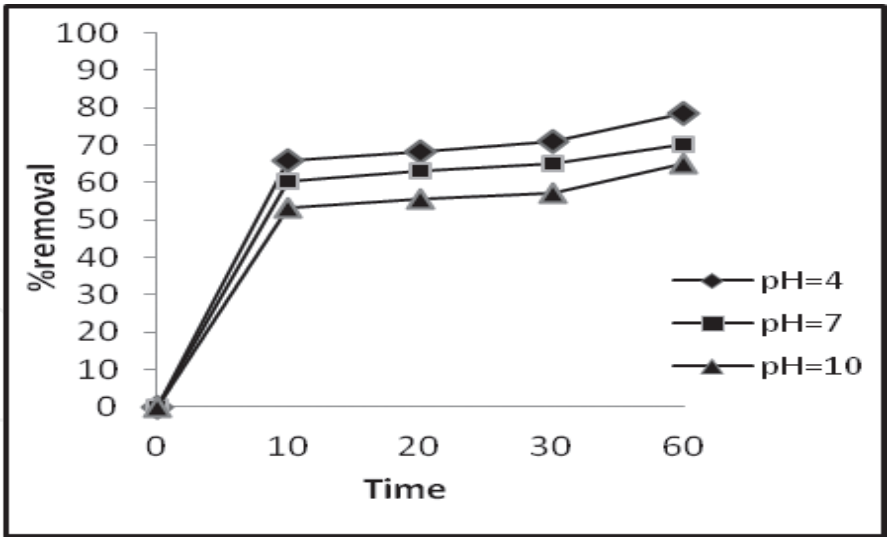
Fig 3. Effect of initial pH on nitrate reduction by nanoscale Fe°, T=20°C, Fe°= 1g/L, C_0=30mg/l NO_3-N, stirring at 300rpm

3.4. Effect of NO_3- concentration on nitrate reduction by nanoscale Fe^0

Two different initial nitrate concentrations (30, 50 mg/L NO_3-N) were employed to study the denitrification efficiency by nanoscale Fe°. Figure 4, shows the effect of nitrate concentrations on the nitrate removal by nanoscale Fe° at initial acidic pH. The removal efficiency of nitrate for 30, 50 mg/L NO_3-N reached 78.3% and 79.98 respectively after60 min. Though the final removal efficiencies of nitrate for different initial nitrate concentrations were close to each other, the final efficiency increased with the increase of the initial nitrate concentration. This finding is in accord with Alowitz et al and Liou et al [11,12].
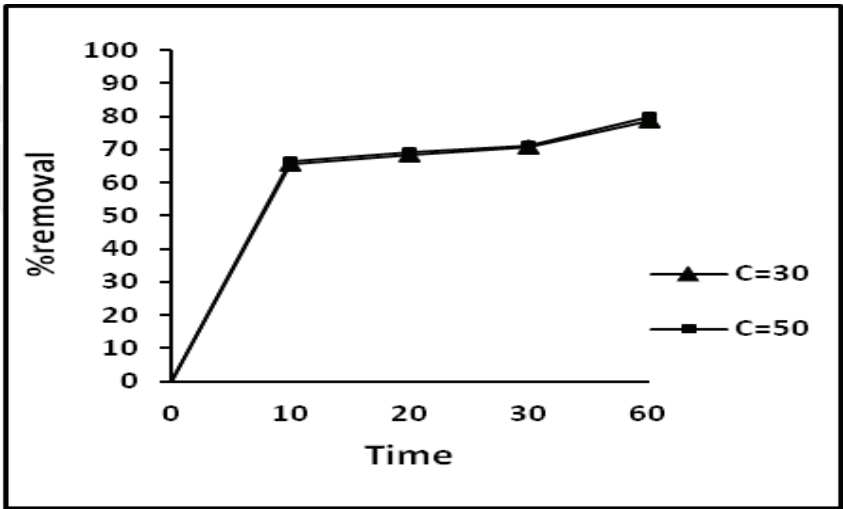

Fig 4. Effect of NO3–N initial concentration on nitrate reduction by nanoscale Fe°, T=20°C, Fe°= 1g/L, pH_{in}=4, stirring at 300rpm

4. Acknowledgements

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