Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.817631

52 (2014) 6240–6248
September

Taylor & Francis
Taylor & Francis Group

Performance evaluation of advanced $Fe^{\circ}/Fe^{+2}/Fe^{+3}/H_2O_2$ process in the reduction of nitrate and organic matter from aqueous solution

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Received 6 May 2012; Accepted 30 May 2013

ABSTRACT

Today, global concerns about nitrate and organic matter in water and its adverse impact on health have increased. This study aims to investigate the use of nZVI technology for nitrate reduction and the use of Fe^{2+}, Fe^{3+}/H_2O_2 technology for COD removal, simultaneously. Different factors that influence the reaction of nitrate with nZVI and COD removal were investigated. These included nZVI, Fe^{2+} and Fe^{3+} dosages (1–10 mg/L), initial nitrate concentration, initial solution pH (2–10), H_2O_2 concentration (30–250 mg/L), and treatment duration (10–90 min). At $[Fe^{\circ}] = 2.5$ mg/L, 81–90% nitrate removal efficiencies were observed for initial $[NO^{3-}]$ ranging from 20 to 200 mg/L. At $[Fe^{\circ}] = 1$, 2.5, 5, and 10 mg/L, 22, 26, 39.5, 77.5, and 70% COD removal efficiencies were observed for reaction time 60 min and initial COD 520 mg/L. When the initial pH values were 2, 4, 6, 8, and 10, the nitrate removal efficiency was approximately 82, 93, 68, 60, and 40%, respectively, with nZVI. COD degradation percent at pH 10 is approximately 28%, whereas at pH 6, removal efficiency reaches to 77.6% after 60 min reaction time. Based on the results, the optimum pH for nitrate reduction is 4 whereas for COD degradation is 6. The reduction capacity for nitrate increases with increasing time and nZVI dosage but decreases with the increase in initial concentration of nitrate and pH values.

Keywords: Advanced oxidation process; Nanoscale zero-valent iron; Fe^{2+}/H_2O_2; Reduction of nitrate

1. Introduction

One of the most important parameters for drinking and agricultural water quality is nitrate and organic matter levels. Nitrate is a common surface water and groundwater contaminant that can cause health problems in infants and animals, in addition to eutrophication of the water body [1]. Nitrate originates in surface and groundwater from decomposed human and animal feces, industrial products, such as nitrogenous fertilizers, and agricultural runoff. The annual application of nitrogen fertilizers and other crop management practices provide a considerable source of nitrates that may leach into groundwater [2]. Possible health concerns of nitrate ingestion

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include methemoglobinemia in infants and the potential formation of carcinogenic nitroso compounds [3].

The presence of organic matter in aquatic environments is known to cause severe damage to aquatic life and living organisms; and some organic matter such as PAHs are potential carcinogenic and mutagenic. Furthermore, the presence of organic matter in wastewaters has increased in recent years and their abatement will be a challenge in the near future; and the presence of natural organic matter in water and soil has to be considered when applying remediation techniques aimed at pollutant removal. Thus, its presence in drinking water is a concern and must be removed [4]. Different processes have been reported for nitrate and organic matter removal from water including the use of absorption [5], electrodialysis [6], ion exchange [7], and reverse osmosis [8]. All of them are physicochemical process and their application in large scale is expensive from the economic perspective. Nowadays, researchers have paid more attention to the performance and potential application of nanoscale zero-valent iron (nZVI) due to its high specific surface areas and thus enhanced reactivity [9–11]. nZVI can effectively transform a wide array of environmental contaminants including chlorinated solvents, organochlorine pesticides, PCBs, organic dyes, and inorganic pollutants such as perchlorate, heavy metal ions, and nitrate [12]. Recently, considerable research has been conducted on nitrate reduction and organic matter removal by nZVI due to its larger specific surface area and higher surface reactivity than granular ZVI. However, the application of ZVI reduction in the degradation of nitrate is still limited because it produces reaction intermediates, which require further mineralization to meet local effluent standards [11].

Advanced oxidation processes (AOPs) have proved to be highly effective for the removal of most of the pollutants in wastewater. The Fenton process, which employs Fe^{2+}/H_2O_2, has been used for the treatment of toxic and nonbiodegradable organic matter from wastewater [12,13]. The formation of Fe^{3+} during the Fenton process results in the production of iron sludge because Fe^{3+} precipitates to iron oxyhydroxides particularly at higher pH. The resulting sludge is required to be treated and disposed of properly. Fenton oxidation has been considered as one of the most interesting ways in which electron transfer takes place in the presence of a metal ion. The advantages of this process can be high performance, simple technology, low cost and low toxicity of the reagents, high reactivity for contaminant removal, sufficient mobility within porous media and sufficient reactive longevity [14]. Disadvantages of the Fenton process include production of large amounts of sludge and formation of a high concentration of anions in the treated wastewater. Recently, a few researchers successfully applied the ZVI/H_2O_2 to the treatment of dyes and MTBE [15].

According to the studies on harmful effects of nitrate in the environment and its impact on human health and also given the advantages of using Fe°, Fe^{2+}, and Fe^{3+}/H_2O_2 as well as successful experiences in this field, the development of this method is intended to reduce nitrate and remove organic matter, simultaneously [16]. Moon et al. showed that $nZVI/H_2O_2$ effectively degraded Orange II [15]. This paper aims to: (1) investigate the use of nZVI technology for nitrate reduction and the use of Fe^{2+} and Fe^{3+}/H_2O_2 technology for COD removal, simultaneously; (2) study how various factors, such as initial nitrate concentration, initial pH, and nZVI dosage, may affect nitrate reduction and COD degradation; and (3) compare nitrate removal in Fe°, Fe^{2+} and Fe^{3+} $/H_2O_2$ processes and nZVI. The findings of this study can provide the basis for further engineering applications and could be useful for treating nitrate from groundwater remediation.

2. Materials and methods

2.1. Materials

All chemicals used in this study were of analytical grade and were used without further purification. Chemicals used in this study include iron chloride $FeCl_3{\cdot}6H_2O$, ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, >99%), H_2O_2, (30% by W/V), NaOH, H_2SO_4, $NaNO_3$, potassium nitrate (KNO_3), acetic acid (CH_3COOH), sodium bro hydrate ($NaBH_4$, >98%), methanol and ethanol 30%, calcium chloride and sodium nitrate all of which were purchased from Merck.

2.2. Preparation of nZVI particles

In this work, nanoscale iron particles were synthesized based on the method reported by Babuponnusami et al. [17]. $FeSO_4{\cdot}7H_2O$ was used to produce nZVI. Synthesis of nZVI particles was performed by the borohydride reduction method. About 10 g of $FeSO_4{\cdot}7H_2O$ was dissolved in 100 mL of 30% ethanol, and then, the pH of the solution was adjusted to 6.8 using 0.1 N sodium hydroxide. About 1.8 g of $NaBH_4$ powder was added incrementally into the solution and stirred for 20 min. Both $FeSO_4{\cdot}7H_2O$ and $NaBH_4$ were dissolved in 30/70 (v/v) ethanol/water. Polyvinylpyrrolidone (1/10, nZVI/PVP, w/w) was then added into the $FeSO_4{\cdot}7H_2O$ solution. The vessel was mechanically agitated, so that the solution was completely mixed. In order to prevent the production of hydrogen gas in solution and accelerate the production of zero-valent iron, solution of $NaBH_4$ (1%) was quickly added into the $FeSO_4{\cdot}7H_2O$ solution with vigorous stirring under nitrogen. Reduction of ferric iron (Fe^{3+}) to Fe° as a result of oxidation–reduction reaction in the presence of $NaBH_4$ was carried out based on the following equation:

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

Here, sodium borohydride was used as the key reductant to reduce ferric ion in $FeSO_4{\cdot}7H_2O$ solution. The above reaction was performed at room temperature and with magnetic stirring. Therefore, nanoscale iron particles synthesized can be easily separated from liquid by filtration and then washed, respectively by deoxygenated deionized water and pure ethanol three times.

The specific surface area of the particles was measured by a specific surface area and a pore size analyzer (ASAP2020M). The specific surface area of the synthesized nZVI was $28.9\,m^2/g$, which was slightly low, but still higher than the values previously reported under the same synthesis conditions. Fig. 1(A) shows the size distribution image of nZVI with the average size of 20–30 nm.

2.3. Experimental procedure

Batch experiments of nitrate removal by nZVI were carried out at room temperature (27 ± 2℃) in 1,000 mL three-necked flasks. For each reactor, 500 mL of nitrate and organic solution was treated with a corresponding amount of freshly prepared nZVI which was realized by pipetting a certain volume from the prepared nZVI. The required amount of iron in the form of Fe°, $FeCl_2$, and $FeSO_4{\cdot}7H_2O$ was added to the aqueous solution and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide was added to the mixture, simultaneously, with pH adjustment to the required value using H_2SO_4 or NaOH. The time at which hydrogen peroxide was added to the solution was considered the beginning of the experiment.

2.4. Preparation of aqueous organic and nitrate solution

The aqueous solution of organic matter was prepared by dissolving 325 g of glucose in 1 L deionized water at constant initial COD 520 mg/L. Different concentrations of nitrate in aqueous solution were prepared by dissolving desired quantities of $NaNO_3$ in deionized water and then added to the organic matter solution. Concentrations of 20, 50, 100, 150, 200, and 300 mg NO_3^- nitrate of the stock solution of sodium nitrate was prepared. After 15, 30, 45, 60, and 90 min, some samples were taken periodically and the output of nitrate was studied. Each experiment was repeated three times for process control [18]. After the reaction, 2–3 mL samples were withdrawn from the reactor at different reaction times. The sample was passed from the filter 0.45 µm, and tested for chemical oxygen demand (COD), NO_3, NO_2, and NH_3.

Different factors that influence the reaction of nitrate with nZVI were investigated, including nZVI,

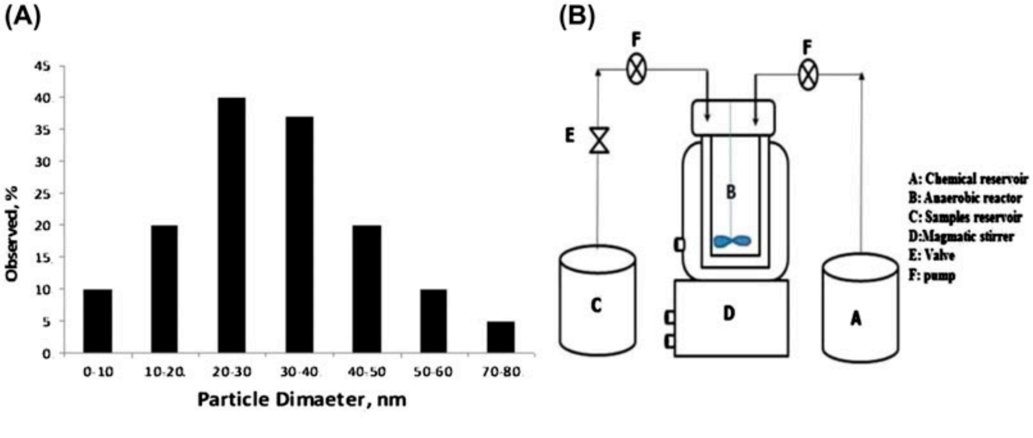

Fig. 1. Size distribution image of nZVI with the average size of 20–30 nm (A) and schematic diagram of the reactor system (B).

Fe^{2+}, and Fe^{3+} dosage (1–10 mg/L), initial nitrate concentration, initial solution pH (2–10), H_2O_2 concentration (30–250 mg/L), and time (10–90 min). Keeping all variables constant and changing only one variable at every stage, the optimal value for the desired parameters was determined [19]. The schematic diagram of process is given in Fig. 1(B).

2.5. Analytical methods

In all experiment, all samples obtained at the top of the reactor, unless otherwise specifically stated, were analyzed after filtration with a 0.45 μm syringe filter. The concentrations of nitrate, nitrite, and ammonium were measured colorimetrically according to the methods 4,500 listed in the 20th edition of the Standard Methods using a UV–Vis spectrophotometer (HACH model DR-5000) with an optical path length of 1 cm. [20]. Chemical oxygen demand (COD) was conducted based on dichromate method (closed reflux, 5220C, colorimetric method), and BOD_5 in accordance to Winkler's method (5210 B) [20]. If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water [16]. The initial pH of the nitrate solutions was adjusted by adding diluted HCl (1 M) or NaOH (0.1 M) and determined by a digital pH meter HACH HQ 40d model. The total iron content was analyzed using a flame atomic adsorption spectroscopy. Ferrous ions were analyzed colorimetrically at 510 nm after forming colored complexes with 1,10-phenanthroline according to the Standard Methods 3500-Fe [20]. Hydrogen peroxide concentration was analyzed by the method described by Sunil and Narayanan [21]. Known amounts of sample were taken in 10 mL standard flasks and to each of this, 1 mL of potassium iodide was added followed by 1 mL of 2-M hydrochloric acid. The mixture was shaken well until the appearance of yellow color and then 0.5 mL of 0.01% toluidine blue indicator solution was added followed by 2 mL of 2-M sodium acetate solution. The contents were made up to the mark and mixed well. Absorbance was measured at 628 nm against reagent blank [21].

Amounts measured by laboratory methods have been recorded and were defined to analyze by statistical tests software SPSS Ver14. First, KS test for the normality of the test data was used and according to the nonnormal data ($p < 0.05$), nonparametric statistical tests were used for data analysis. One-way ANOVA was used to determine whether there is any significant difference between the $Fe^\circ/Fe^{3+}/H_2O_2$ process, pH, and time for nitrate removal (Table 1).

Table 1
One-way ANOVA for nitrate degradation at different $H_2O_2/Fe^\circ/Fe^{3+}$, $H_2O_2/Fe^\circ/Fe^{2+}$, pH, time, and nitrate concentration

Parameter	No. of groups	*F*	*P*-value	*F* crit
$H_2O_2/Fe^\circ/Fe^{3+}$	6	3.67	0.009	2.48
$H_2O_2/Fe^\circ/Fe^{2+}$	6	3.14	0.021	2.32
pH	5	2.89	0.012	2.69
Time (min)	5	1.62	0.026	3.55
Nitrate concentration	4	0.098	0.912	3.254

3. Results and discussion

3.1. Fe° concentrations on nitrate and COD removal

Concentrations of 1, 2.5, 5, and 10 mg/L Fe° and concentrations of 20, 50, 100, 150, and 200 mg/L of NO_3 were used to study the kinetic of process. According to this study, 58–98% of nitrate can be removed during the 90 min. Fig. 2(A) presents data obtained for the degradation of the nitrate by different concentration of Fe° at pH 7 and residence time 90 min. At nitrate concentrations of 20, 50, 100, 150, and 200 mg/L, and the Fe° concentration 2.5 mg/L, nitrate removal efficiencies obtained were 90, 89, 84.5, 78.8, and 81.5%, respectively. Therefore, this method can reduce nitrate to an acceptable value (Table 1). COD degradation percent after 60 min reaction time was 22, 26, 39.5, 77.5, and 70 at Fe° 1, 2.5, 5, and 10 mg/L, respectively (Fig. 2(B)).

As expected, the concentration of Fe° strongly influences the kinetics of the nitrate reduction. In Fig. 2(A), the nitrate removal with a dosage of 2.5 mg Fe°/L was 85% at 30 min and 90% at 60 min. On the other hand, as the dosages were 5 and 10 mg/L, the nitrate was completely removed at time of 30 min in either case. In addition, the residual profiles of NO_3^- show no difference for the two dosages of 5 and 10 mg/L, but the difference becomes quite significant as the dosage was reduced from 5 to 2.5 mg/L. Hence, the optimum Fe° dosage of 5 mg/L is recommended in the case of initial nitrate of 50 mg/L. Chen et al. [22] reported that treatment of a 60 mg NO_3 mg/L solution with 6% (w/v) Fe° at pH of 1.0 completely transformed all nitrate to ammonium within 24 h. Han et al. [23] reported that under near-neutral pH, magnetite was the dominant corrosion product as a result of iron–nitrate redox reaction [23]. The reaction was summarized as:

$$\begin{aligned} &NO_3^- + 2.82Fe^\circ + 0.75Fe^{2+} + 2.25H_2O \\ &\quad \rightarrow NH_4^+ + 1.19Fe_3O_4 + 0.50OH^- \end{aligned} \tag{2}$$

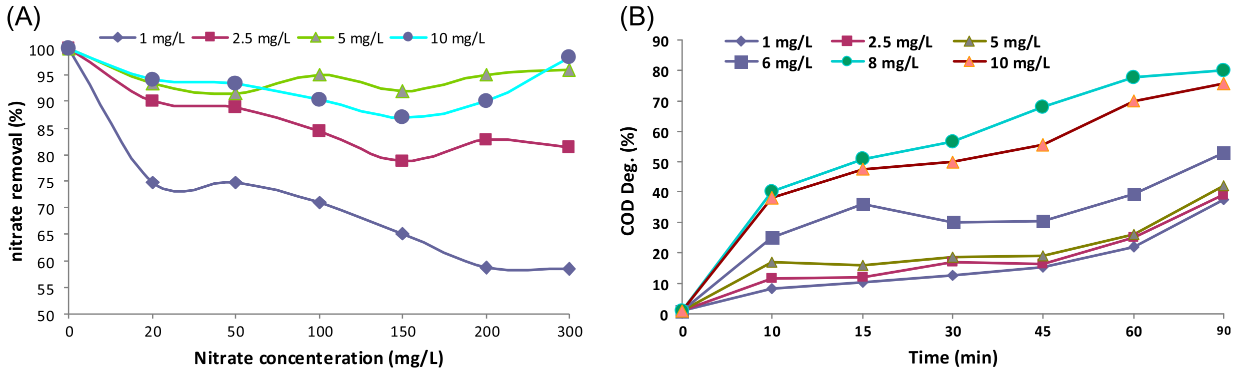

Fig. 2. The effect of Fe° concentrations on (A) nitrate removal as a function of the initial nitrate concentration, (B) COD removed as a function of time (initial pH~7; and initial COD 520 mg/L).

The results (Fig. 2(B)) show that COD degradation percentage increased with the increase in Fe° concentration up to 8 mg/L. Further increase in Fe° concentrations above 8 mg/L did not improve the degradation of COD. This may be due to the direct reaction of $OH^{\bullet}$ radical with metal ions at high concentration of Fe° [24] as in the reaction (3):

$$2Fe^{\circ} + HO^{\bullet} \rightarrow Fe^{2+} + HO^{-} \tag{3}$$

Eq. (3) indicates that Fe°, rather than the surface-complexed Fe^{2+}, is the major electron source, implying that the role of Fe^{2+} is different from some previous studies in which surface-adsorbed Fe^{2+} alone (i.e. without Fe°) or structural Fe^{2+} was found to reduce nitrate [24]. It was clear that the ammonia did not react with nZVI and the removal mechanism could be the ammonia stripping followed by nitrate reduction or H_2O_2/Fe process. Singh et al. hypothesized that iron corrosion by-products (e.g. Fe^{2+}, Fe $(OH)_2$), produced by reactions of Fe° with oxygen, were thermodynamically capable of reducing nitrate to ammonia. Nitrate can be stoichiometrically reduced to ammonium in the presence of iron compounds, and lead to the production of magnetite as an oxidation by-product [19]. The nitrogenous by-product such as ammonium can be removed by Fe/H_2O_2 process.

3.2. Effect of pH on nitrate and COD removal

The aqueous pH and nZVI dosage had major effects on the efficiency of nitrate and COD removal. When the initial pH values were 2, 4, 6, 8, and 10, the nitrate removal efficiency were approximately 63.5, 72, 55.5, 49, and 38% after a reaction of 30 min and 82, 93, 68, 60 and 40%, respectively, after a reaction of 90 min with nZVI. In Fig. 3(A), the effect of pH 2–10 on the decrease in nitrate concentration is presented at retention time of 0–90 min. The efficiency of removal increased with the decrease in the pH up to 4. The nZVI process was more effective in nitrate removal under acidic conditions. In other words, the more the H^+ in the solution, the more easily the reaction occurred and the high the reaction constant was. However, when the initial pH was 10, the removal rate decreased. Fig. 3(B) shows the effect of pH on

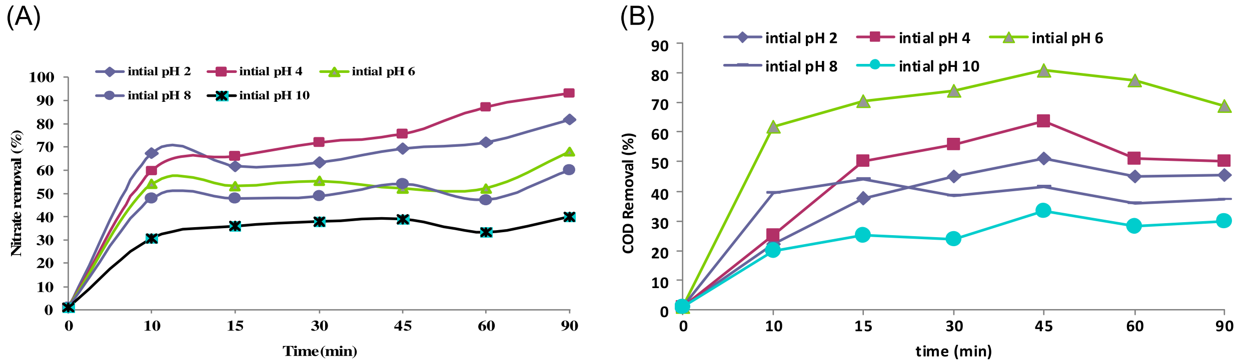

Fig. 3. The effect of the pH reaction on the nitrate (A) and COD (B) removal efficiency by Fe°/H_2O_2 (reaction conditions: nitrate concentration = 100 mg/L; H_2O_2 = 200 mg/L; Fe = 10 mg/L; and temperature = 25°C).

COD degradation. COD degradation percent after 60 min reaction time was 45, 5.5, 77.6, 36, and 28 at pH 2, 4, 6, 8, and 10, respectively (Fig. 3(B)). A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicated that nitrate reduction was significantly affected by pH ($p = 0.012$) (Table 1). Based on the results, the optimum pH for nitrate reduction is 4 whereas for COD degradation it is 6 (Fig. 3(A) and (B)). pH is one of the major parameters influencing the process. Based on numerous studies, it is indicated that control of pH in the range 4–6 can greatly increase the efficiency of the nitrate removal by Fe process [4]. In some groundwater, due to reducing conditions and predominance of anaerobic conditions and lack of O_2, it is possible to use iron nZVI. In this case, it has been suggested that 10–20 mg/L nano-zero iron will be used. Generally, the acidic pH will result in faster reduction of nitrate by nZVI [25].

These results show that pH significantly influences the COD degradation. Decrease in COD improvement at pH higher than 4 and lower than 10 may be due to the decrease in dissolved iron, and the decrease in oxidation rate of hydroxyl radical and due to the dissociation and auto-decomposition of H_2O_2 [26,27]. Further, hydrogen peroxide is stable at low pH probably because it solvates a proton to form an oxonium ion (H_3O^+). An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [27]. Therefore, amount of hydroxyl radicals would decrease at low pH, decreasing the degradation of antibiotics intermediate. On the other hand, making acidic conditions causes the continuous removal of sediments from the surface of Fe°. Therefore, the removal efficiency will improve compared to alkaline conditions. Based on Mielczarski et al. oxide and iron hydroxyl layer at pH 4 on the surface of Fe° may be low. The thickness of the oxide layer increases with pH increase, resulting in reduction of the removal efficiency [18]. Due to the production of H_3O_2 ions at pH< 3, hydrogen peroxide became inactivate. At pH less than 3 due to $H_3O_2^+$ ions, it is produced that inactivates H_2O_2. At pH greater than 7, oxidation increases rapidly. This could be due to the decomposition of H_2O_2. So, changing the pH to less than 3 or greater than 8 will adversely affect the removal process. As it can be seen in Fig. 3(B), with increasing pH, the output levels of COD will be added too. The lowest nitrate output is at the initial pH 4. Again, the efficiency is reduced at pH less than 3 due to the production of $H_3O_2^+$ ions. According to Fig. 3(B), retention time of 90 min does not have much impact on COD removal. This is due to the Fe° oxidation by H_2O_2 after 90 min contact time.

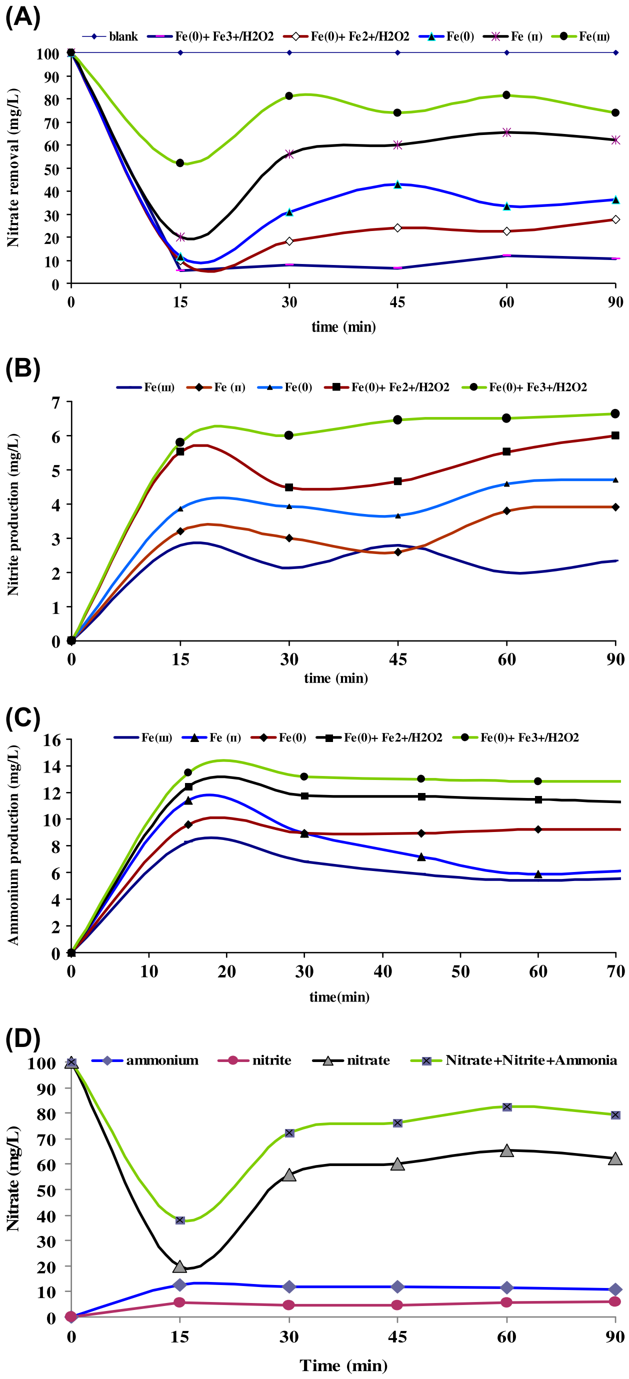

Fig. 4. The effect of iron compounds in the presence of H_2O_2 (Fe^{3+}, Fe^{+2}, Fe°, Fe^{2+}/Fe° /H_2O_2, and Fe^{3+}/Fe°/H_2O_2) for nitrate removal (A); nitrite (B); ammonium production (C); and nitrate concentration (mg/L) and major product formation (D). Initial nitrate concentration was 100 mg/L at 0–90 min, Fe 10 mg/L, 200 mg/L H_2O_2, and pH 7.

3.3. Effect of Fe/H_2O_2

At the time of 90 min, and initial concentration of nitrate 100 mg/L and pH 7, nitrate removal efficiency for Fe^{3+}, Fe^{2+}, Fe°, $Fe^{2+}/Fe^{\circ}/H_2O_2$, and $Fe^{3+}/Fe^{\circ}/H_2O_2$ will be 10.5, 27.6, 36.5, 62.3, and 74% (the concentration of iron compounds is 10 mg/L), respectively. In Fig. 4, the effect of iron compounds in the presence of H_2O_2 (Fe^{3+}, Fe^{2+}, Fe°, $Fe^{2+}/Fe^{\circ}/H_2O_2$, and $Fe^{3+}/Fe^{\circ}/H_2O_2$) for nitrate removal and nitrite and ammonium production at 0–90 min and pH 7 can be seen.

In Fig. 3(A), the effect of iron compounds in the presence of H_2O_2 to remove nitrate at different retention times and pH 7 is shown. In this study, to increase the effect of hydrogen peroxide, iron catalyst was applied so that the following reaction takes place [2]:

$$NO_3^- + 4Fe^{\circ} + 10H^+ \leftrightarrow NH^{4+} + 4Fe^{2+} + 3H_2O \qquad (4)$$

$$NH_4^+ + 4Fe^{2+} + H_2O_2 \rightarrow Fe(OH)_2^+ + HO^{\bullet} + N_2 \qquad (5)$$

Hence, $HO^{\bullet}$ radicals are produced during the reaction. This reaction will be capable of the nitrate reduction to $Fe(OH)_2$ and N_2 gas [28]. Initially, nitrate is reduced by nZVI to NH_4^+ and then the produced NH_4^+ is oxidized by two electron transfers between the particle surface and the H_2O_2 (Eq. (2)). Fe^{2+}/H_2O_2 oxidants were responsible for the oxidation of NH_3 and nitrogenous compounds into N2 gas. According to the literature, typical values of Fenton reagent ratio are in the range between 1:5 and 1:25 [29]. The optimal operating parameters for nitrate removal by Fe/H_2O_2 process were: $Fe/H_2O_2 = 1:15$, nZVI = 10 mg/L, and pH 4.

As it can be seen, Fe° (10 mg/L) alone has a greater impact on nitrate removal than Fe^{+2} and Fe^{+3}. With the addition of H_2O_2, the nitrate removal increases. More concentration of Fe° makes more nitrate removal efficiency. The theoretical usage of iron needed to completely reduce the entire nitrate in the system is 10 mg/L. Fig. 4(A) and 4(D) shows that the rate of nitrate removal was proportionally dependent on iron type. It has been found that the nitrate was better removed by $Fe^{3+}/Fe^{\circ}/H_2O_2$ process when excess iron (10 mg/L) was utilized. In the Fe^{3+}/H_2O_2 case (10 mg Fe/L, 200 mg/L H_2O_2), certain amount of nitrate was left in the system after the available Fe is consumed. Nitrate accounted for only 10% of the initial nitrate concentration at the end of the reaction by $Fe^{3+}/Fe^{\circ}/H_2O_2$ system ($t > 90$ min). In the study conducted by Rodríguez et al. (2009), the 10 mg/L concentrations of iron compounds also selected [30]. According to Fenton's chemistry, if a reaction is carried out in a high pH condition, the iron forms a precipitate, $Fe(OH)_3$, which decomposes H_2O_2 to O_2. Also, if pH is too low, Fe^{3+} is reconverted to Fe^{2+}. Both cases lead to reduced reaction rate by decreasing the starting reagents [9]. In the control run with no addition of nanosized ZVI, no removal of nitrate was found over the time period of a typical experiment. According to the study conducted by Jiang et al. nitrate removal efficiency reached to 93% at dose of 50 mg/L Fe^{2+} [31]. As confirmed by the nitrate measurement, 80% of nitrate was removed within 15 min in the $Fe^{+2}/Fe^{\circ}/H_2O_2$ system and Fe removal efficiency was 30%. The recovery of nitrite ranges from 3.5 to 13.5% and ammonium ranges from 35.5 to 60.6%, and the ammonium concentration ranges from 9 to 28.8 mg/L as shown in Fig. 4(B) and 4(C).

Table 2
The effects of H_2O_2 concentration (mg/L) on nitrate removal by Fe^{3+}/H_2O_2, Fe^{2+}/H_2O_2, and Fe°/H_2O_2 process

H_2O_2 concentration (mg/L)	Nitrate removal (%)			COD removal by Fe° (%)
	Fe^{3+}	Fe^{2+}	Fe°	
30	56	66.4	48	52
50	55.8	64.5	45.5	62
100	54	67.5	57.5	75
150	63.5	72.4	84.8	79
200	74	84.8	92	91

Both ammonium generation and nitrite recovery increase with increasing retention time (min). Fig. 4(D) shows the mass balance of nitrogenous species under the condition of pH 7 when using 10 mg/L nZVI and 200 mg/L H_2O_2 as a reducer. It can be seen from Fig. 4 (B) and 4(C) that the amount of nitrite and ammonia increased with the decrease of nitrate. The concentration of ammonia increased continuously during the experiment. The summation of remaining nitrate, nitrite, and ammonia decreased at the beginning of the reaction, and then increased gradually. This was in very good agreement with the finding by Chen et al. in a similar study using ZVI [32]. In the first place, the nitrate was degraded to nitrite and then nitrite was converted to ammonia. However, it is possible that there are other nitrogenous species generated (e.g. N_2, NO, N_2O, and N_2H_4) in the system. It is possible that other unmonitored nitrogen gas species such as N_2 (27), N_2O, and N_2H_4 might have been formed and volatilized under the vigorous flow condition, and other unstable nongaseous intermediates, i.e. ammonium nitrite (NH_4NO_2) and ammonium nitrate (NH_4NO_3)

were formed at shorter retention times and were reduced to the final ammonium product at longer retention times. Most of the reports have indicated NH_4^+ as the end product of nitrate reduction by Fe°, although different end product such as N_2 gas has also been reported [33].

3.4. Effect of H_2O_2 concentration

Hydrogen peroxide (H_2O_2) has a high content of effective oxygen, low cost, and safe storage method; is very easy to use; and above all, has no adverse effect on the environment [28]. Table 2 shows the effect of H_2O_2 concentration on nitrate removal by the simultaneous Fe/H_2O_2 process. When H_2O_2 was applied with nZVI, the nitrate removal efficiency improved (Fig. 3(B)). The nitrate removal efficiency increased with H_2O_2 concentration until it reached 200 mg/L, where the nitrate removal efficiency began to decrease. This effect was partially associated with the scavenging nature of H_2O_2 toward $HO^\bullet$ radicals when it was applied in excess. Table 2 shows that the effects of H_2O_2 concentration (mg/L) on nitrate removal by Fe^{3+}/H_2O_2, Fe^{2+}/H_2O_2, and Fe°/H_2O_2 process.

4. Conclusion

In this study, the application of nZVI (Fe°) synthesized in the laboratory and operational parameters on the reduction of COD and nitrate was investigated. Fe°, Fe^{2+}, Fe^{3+}, and H_2O_2 reaction was evaluated in order to achieve an efficiency of COD and nitrate removal.

COD degradation was 52–91% by H_2O_2/Fe°/Fe^{3+} simultaneous processes in 60 min. COD degradation percent after 60 min reaction time by H_2O_2/Fe°/Fe^{3+} simultaneous process was 45, 5.5, 77.6, 36, and 28 at pH 2, 4, 6, 8, and 10, respectively. When the processes were conducted simultaneously (Fe°/Fe^{3+}/H_2O_2), the nitrate removal efficiency was 75% after 60 min. Complete reduction of nitrate could be achieved within 90 min with nZVI 10 mg/L, H_2O_2 200 mg/L, and the initial nitrate concentration 100 mg/L at pH 7. The reduction capacity for nitrate increases with increasing time and nZVI dosage, but decreases with the increase in the initial concentration of nitrate and pH values.

Heterogeneous Fe^{3+}/Fe°/H_2O_2 system has proven to be an efficient and rapid process for the reduction of COD and nitrate under neutral pH conditions, which is superior to alone nZVI, alone H_2O_2. At the initial pH 7, first-order reduction kinetic of ammonium production was observed, which was composed of Fenton reaction on or near the nZVI surface and the initial pH of solution that effect ammonium production rate. The Fe/H_2O_2 systems may be applied as an attractive alternative for removing COD and nitrate from water. Based on the experimental results, it was determined that Fe/H_2O_2 process can effectively reduce COD and nitrate under optimal conditions and this method can be used for the removal of similar compounds. More work is needed to handle the eventual loss of catalytic activity and the recovery of catalyst for water remediation, which may form the basis of effective application for environmental treatment.

Acknowledgments

This paper is approved by Arak University of Medical Sciences coded 573. We appreciate the research deputy of the University, Mr Changizi Ashtiyani, and management of research projects, Mr Hekmat po, for project funding and all those who without their cooperation, this study was not possible.

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