# Application of Photo-Fenton Process For the removal of Nitrate from Aqueous Solutions

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## Abstract

**Introduction:** Nitrate is one of the pollutants of groundwater and the great amount of nitrate in drinking water can bring about some hygienic problems such as methemoglobinema phenomena in children. Therefore, this research aims to study the efficiency of photo- Fenton in removing nitrate and investigating the variables affecting it in aqueous solutions.

**Methods and Materials:** This research was carried out in water and wastewater chemistry lab at public health faculty of Hamadan medical science university. The variable parameters in this study included pH( in four ranges 3,5,7 & 11), the concentration of zero-valent iron powder (in four ranges of 10, 15, 20 & 30 g/L)، the concentration of peroxide hydrogen (in four ranges of 5, 10, 15 and 20 ml/L)، contact time (in four ranges 30, 60, 90 & 120 min). , along with the use of UV lamp with overage pressure of 30W and wavelength of 247/3 nm as the source.

**Results:** According to the results from this study, decreasing pH can increase the efficiency of removal. The highest efficiency of removal occurred in pH=3, contact time 120 min, H2O2 of 10 ml/L and iron powder of 30 g/L, which was equal to 98.8 percent.

**Conclusions:** Given the results of this research, photo-Fenton process could be used efficiently for the removal of nitrate from water resources.

**Keywords:** Iron powder, photo Fenton, Batch reactor, advanced oxidation, Nitrate.

## Introduction

One of the most common pollutants of water resources, especially groundwater, is nitrate compounds [1, 2]. Nitrate can enter the water through various resources such as agricultural lands, effluent of wastewater treatment plants and absorbing wells [3,4]. Consuming nitrate-contaminated water can bring about different problems such as symptom of met-hemoglobinema, damage to liver and increase in cancer. The symptom of methemoglobinema appears in children by consuming contaminated water with high concentration of nitrate [5 ,6]. Nitrate in body can convert into nitrosamines that are known as carcinogenic maters. Nitrate is known to produce cardiac and behavioural problems in experimental labs as well [7, 8]. Some specifications such as solubility, possibility of absorption and little deposition of nitrate have resulted in difficulties in removing it from water resources[9]. According to the drinking water standard , the maximum permissible amount of nitrate in drinking water is considered to be 50 ( mg/L) in terms of nitrate[1, 5]. Different processes such as ion exchange, reverse osmosis, biological denitrification and chemical oxidation are used to remove nitrate from aqueous environments. The reverse osmosis and ion exchange processes have not found wide applications due to the lack of complete removal of nitrate and production of waste containing high concentration of nitrate. In nitrification and denitrification processes, the main drawbacks of the systems are high sludge retention time of process and need in addition of organic matters [10]. In recent years, attention has been paid to using advanced oxidation processes to treat water and wastewater pollutants.The major characteristic of these processes is to form hydroxyl radicals with the high oxidation power [11]. Fenon process is one of the advanced oxidation processes that is used to remove varieties of organic and inorganic matters such as fenol, chlorofenol, nitrobenzene and so on. This process can alone transform %40-60 of organic matters into mineral matters [12]. In fenton process, hydroxyl radicals are produced in the conditions of acid (pH=3-5) at the presence of iron catalyst with degradation of hydrogen peroxide, according to the following equation.

Equation (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^0 + HO^-$$

As seen, in this reaction, $Fe^{+3}$ is produced which has low ability to catalyse hydroxyl radical. After UV ray is used in Fenton process, $Fe^{+3}$ is reduced to $Fe^{+2}$, therefore, production of hydroxyl radicals is accelerated, called as photo Fenton process:

Equation (2): $Fe(OH)_3 + hv \rightarrow Fe^{2+} + HO^0$
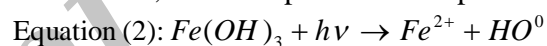
This reaction takes place after reaction (1) and continues with photo radiation [13]. Hydroxyl radicals are the second most powerful oxidizer after fluoride and do not produce by product. Lack of increasing harmful chemicals in the environment to remove nitrate and simplicity of iron removal which was added to the system are the main benefits. On the other hand, compared with the common method, nitrate removal is less costly in this method and it has a greater efficiency. In addition, using sunlight as the radiation source of UV increases the economicity of this method totally. Neverthless , because of high consumption of H2O2 and Fe powder in this method , application of this process is limited for low volume of contaminated water. Liao et al.(2004), used photo Fenton to remove nitrate and investigated the effect of organic matters on efficiency of removal[2]. They also used photo Fenton in removing two commercial colours ( $Ry_{84}$ and $RR_{12}$ ) . In this research, the effect of different parameters on the efficiency of

removal was studied and the greatest efficiency of removing $RR_{84}$ colour at pH=2 and RR120 colour at pH=3 was respectively %100 and % 97 [14]. Ghaly et al (2001) used photo Fenton in the removal of p-chlrophenol with the efficiency of %100at pH=3 [15] .Yong et al.(2004) used iron powder to reduce nitrate and investigated the effect of low pH on removal efficiency . The removal efficacy of low pH increases remarkably at %70 [1]. This researches main objective is investigating the efficiency of photo Fenton in removing nitrate from aqueous solutions

## Methods and Materials

Photo Fenton process was used to remove nitrate from aqueous solutions. In production of photo Fenton, Fero iron, $H_2O_2$ and UV light were used. In this research, the concentration of iron powder was 15, 10, 20 and 30 g/L, that of $H_2O_2$ was 5, 10, 15 and 20 ml/L, contact time was 30,60,90 and 120 min and pH was 3,5,7 and 11.To homogenize the solution, we put all the samples on shaker exposed to UV light with wavelength of 264 nm with UV lamp of average pressure 30w with wavelength of 247/3 nm (Nojan Teb).

First, the solution containing nitrate was obtained from sodium nitrate powder (Merk) synthetically and then the required concentrations were provided. Regarding the existence of four variables in this research, iron powder, H2O2, contact time and pH, we chose three variables fixed and changed a variable to investigate its effect on removal efficiency. Therefore, the efficiency was investigated in 256 cases. In each stage, the solution was sampled 3 times and their average was computed. In batch reactor to regulate pH, we used normal $H_2SO_4$ (Merk).Iron powder had the effective size of 150 μ and purity degree of %98 (Merk). The

batch reactor consisted of a one liter beaker that had a magnetic mixer to homogenize the solution. To determine the removal efficiency in each stage after the sampling, by application of spectrophotometer UV/VIS the values of nitrate in the solution were calculated [16]. The results were analysed by Excel software to compute the mean value and drawing grafs.

## Results

1-the effect of contact time on the nitrate removal efficiency:
The effect of contact time on the nitrate removal efficiency is shown in figure 1. The results showed that with the increase of contact time, the removal efficiency increased, so that in optimal condition, the nitrate removal efficiency changed from % 93 to %98.8 as the time changed from 30 to 120min.

**2- The effect of concentration of $H_2O_2$:**
Different concentrations of $H_2O_2$ on removal efficiency regarding optimal condition (**$NO_3$=100mg/L, $H_2O_2$=10** mL/L , **pH=3, Fe=30** g/L) . As seen in figure 2, the highest removal efficiency has an increasing trend up to concentration 10 mL/L $H_2O_2$ and then decreases so that the maximum efficiency reaches % 98.8.

**3-The effect of pH on removal efficiency:**
In this research, the effect of pH changes in four ranges of 3, 5, 7 and 11 in different concentration of $H_2O_2$, iron powder and contact time were determined . As seen in figure 3, with the increase of pH, the removal efficiency decreases in optimal condition so that the greatest efficiency at pH=3 is %98.8 and the minimum is % 23.6 at pH=11.

**4. The effect of iron powder concentration on removal efficiency:**
In this study, different concentrations of iron powder for 5, 10, 20 and 30 g/L were used

to remove nitrate with different concentration of $H_2O_2$, contact times and pH values.

The results showed that increasing iron powder concentration helped to increase
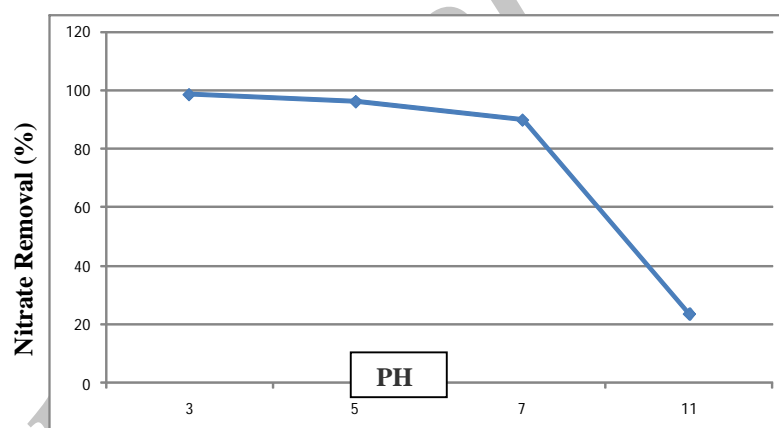
removal efficiency. As seen in **Figure** 4, removal efficiency reached % 98.8 at 30 gr/L iron powder in optimum condition.
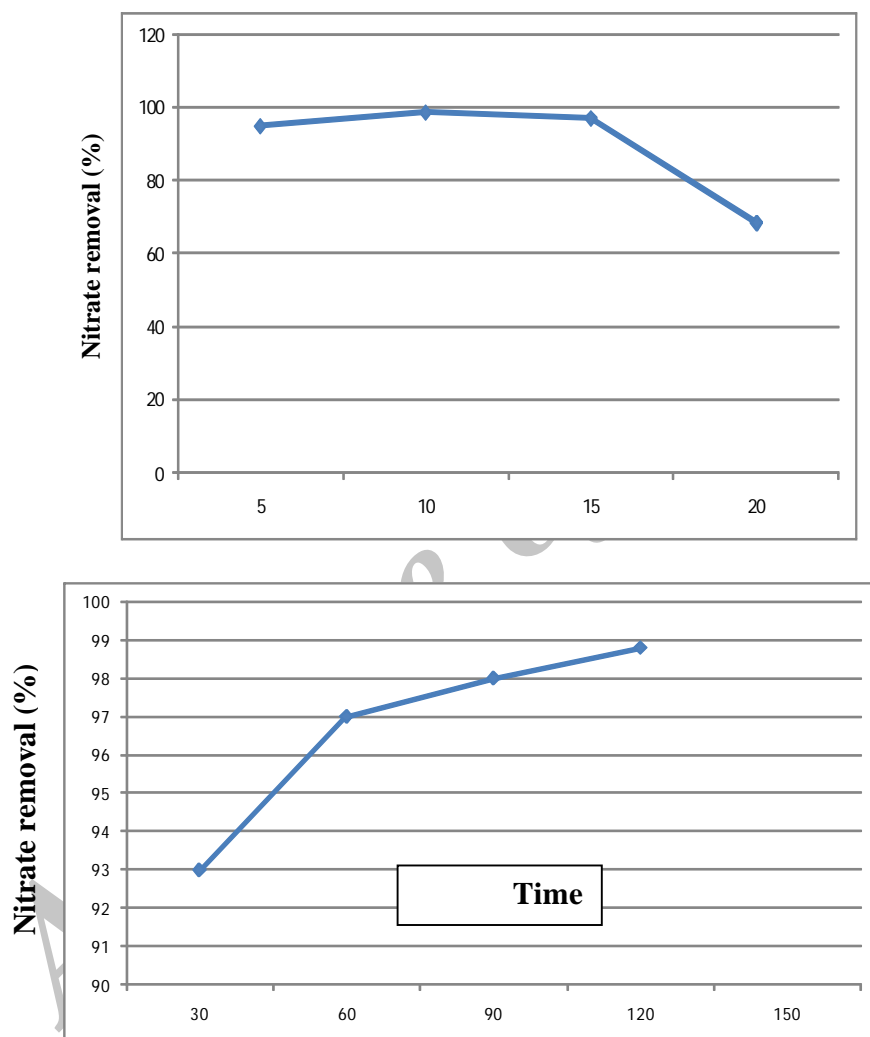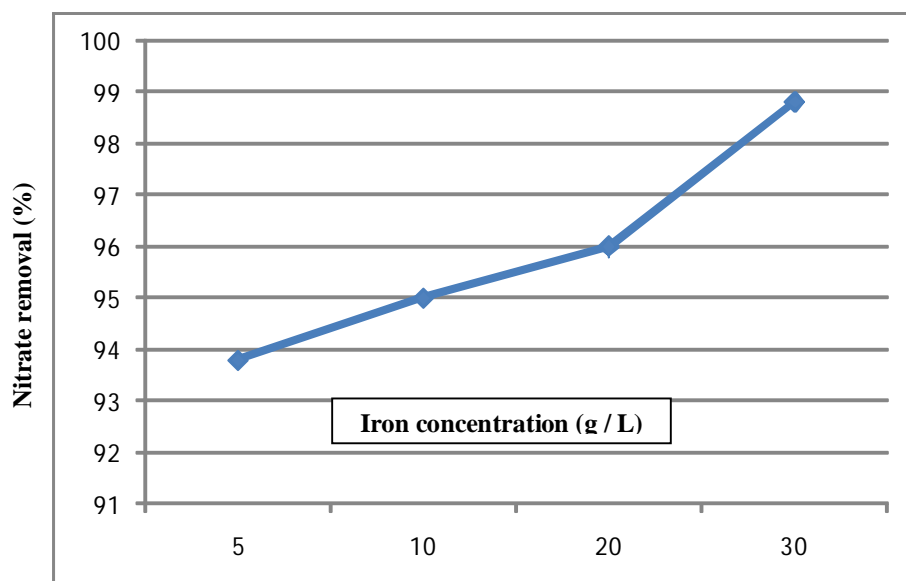


**Figure 1: The effect of time on nitrate removal efficiency in optimal conditions: ( NO$_3$=100mg/L, H$_2$O$_2$=10ml/L, pH=3, Fe=30 g/L)**
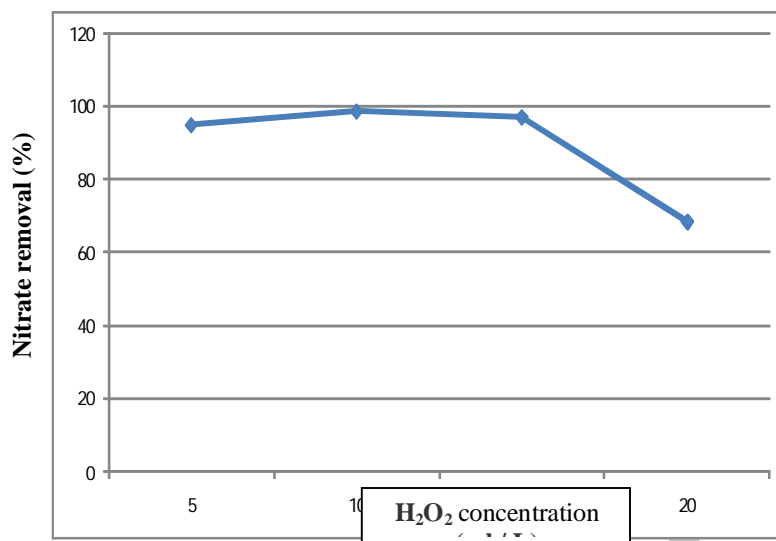
**Figure 2: The effect of hydrogen peroxide concentration on nitrate removal efficiency in optimal (conditions: $NO_3$=100mg/L, $H_2O_2$=10 mL/L , pH=3, Fe=30 g/L)**



**Figure 3: Effect of pH on the nitrate removal efficiency in optimal conditions: ( $NO_3$=100mg/L, $H_2O_2$=10 mL/L, pH=3, Fe=30 g/L)**

**Figure 4: The effect of iron concentration on nitrate removal efficiency in optimal conditions: (**
**NO$_3$=100mg/L, H$_2$O$_2$=10mL/L, pH=3 ,Fe=30g/L)**

## Discussion

Contact time is an important parameter in chemical reactions. This time can have an optimal contact time or equilibrium time. The equilibrium time is the time in which the removal efficiency of pollutant reaches to approximately maximum value(17,18,19).In another word, if contact time is greater than that of equilibrium, the process is not economical as increase of removal efficiency is very little. In the present study, in the photo fenton process, the removal of pollutant has an increasing trend in terms of time( figure **1** ) .Although in contact time 120 min, the efficiency of removal is very high, the reaction has not reached to equilibrium.Therefore, in this process, the contact time can be considered more than 120min. Increasing the contact time in this system leads to the use of active level of iron powder which results in more production of free electrons and the removal efficiency reached 98.8 at optimal condition; yet, increasing contact time resulted in the increase of removal efficiency while it was

not economical and thus contact time120 min was considered. The results from the study of Liao CH et al.(2004) had similarity with those of our research in that increasing contact time caused an increase of the removal efficiency [2]. The results of Suzuki et al (2012) study confirm this statement[20]. The results also showed that increasing H$_2$O$_2$ concentration to 10 ml/L leads to the production more of hydroxyl radicals; therefore, the efficiency of removal process increases.Increasing the concentration of H$_2$O$_2$ greater than the value mentioned leads to the production of inactive radicals and the efficiency of removal process decreases ( figure2), [17,21].In ZVI/UV/ H$_2$O$_2$ process , the increase of initial concentration of H$_2$O$_2$ increases the process efficiency. In Liao CH et al. (2004) study , increasing H2O2 concentration increases the efficiency of Nitrate removal thorough zero-valent Iron powder [2]. The results of Gernijak et al. (2006) study confirm this statement [22].The

results of investigating effect of pH on nitrate removal efficiency showed that increasing pH from 3 to 11 decreases the nitrate removal efficiency from %98.8 to % 23.6 [figure 3]. The major mechanism in this process is the production of hydroxyl radical. In acid environment, more hydroxyl radicals are produced [15]. On the other hand, reduction of pH leads to an increase in $H^+$ ions to the reaction environment. In aqueous environments, zero-valent iron changes in to 2-valent iron by losing 2 electrons and then turns in to 3-valent iron by losing one electron to leave the environment as deposit. 3-valent iron does not have the ability to produce electron and causes the process efficiency to reduce through setting deposit on zero valent iron [18]. With the reduction of pH and increase of $H^+$ ion, 3-valent iron is oxidized to two-valent iron when it takes electron from hydrogen ion, which produces hydroxyl radicals. (eq.1), and the cycle continues if the hydrogen ion exist [19 ,20, 21]. Huang Cp et al (1998) used iron powder to reduce nitrate and investigated the effect of low pH on reducing nitrate by iron powder. They observed that removal efficiency in low pH (2-4.5) increases remarkably to %70 [12]. In this research, the effect of iron concentration on nitrate removal efficiency was studied (optimal condition). In Contact time of 120 min, pH=3 and $H_2O_2$ = 10 ml/L, increasing the initial concentration of iron powder from 10 to 30 mg/L increases the removal efficiency from %93.8 to %98.8. [figure 4].According to equation (1), increasing 2-valent iron ions leads to an increase in hydroxyl radicals which are powerful oxidizing factors. This justifies the increase of the removal efficiency of nitrate with the increase of iron powder concentration, which has been obtained in Choes et al (2004) study in which increasing iron

powder concentration leads to the increase of removal efficiency of nitrate[21]. The results of Gernjak et al (2006) confirm this conclusion [22].

## Conclusions

The results obtained from this research, showed that by increasing the contact time, initial concentration of $H_2O_2$ and initial concentration of iron powder and the removal efficiency of nitrate increases. The maximum value of nitrate removal at pH=3 Contact time=120min, $H_2O_2$=10 ml/L and iron powder 30 g/L was obtained. Increasing $H_2O_2$ concentration from 10 ml/L reduced efficiency. Also, increasing contact time to more than 120 min didn't have remarkable effect on the removal efficiency. Finally, nitrate concentration can be reduced to the suitable level in aqueous solutions.

## References

1-Huang Yong  H ,Zhang Tian C. Effects of low pH on nitrate reduction by iron powder .J Wat. Res. 2004 ;38(11):2631-2642
2 -Liao Chih-Hsiang, Kang Shyh-Fang, Hsu Yu-Wei. Zero-valent iron reduction of nitrate in the presence of ultraviolet light, organic matter and hydrogen peroxide. J. Wat. Res 2003; 37(17): 4109-4118.
3-Garron Anthony, Epron Florence.  Use of formic acid as reducing agent for application in catalytic reduction of nitrate in water. J. Wat. Res. 2003;39(13): 3073-3081.
4-Westerhoff Paul, James Jennifer.  Nitrate removal in zero-valent iron packed columns. J. Wat. Res. 2003; 37(8): 1818-1830.
5-Tada Keijiro, Shimazu Katsuaki. Kinetic studies of reduction of nitrate ions at Sn-modified Pt electrodes using a quartz crystal microbalance. J. Electroanalytical Chemistry 2005 ;577(2): 303-309.
6-WHO. Guidelines for drinking water quality.1998; Volume 1, Third Edition .
7-PEKDEMİR Turgay.  Drinking water denitrification in a fixed bed packed biofilm reactor. Turkish J. Eng. Env. Sci.1998; 22: 39-46.
8- Park Ho Il, Kim Dong kun, Choi Yong-Jin, Pak Daewon.  Nitrate reduction using an electrode as direct electron donor in a biofilm-electrode reactor. Process Biochemistry 2005; 40(10):3383-3388.

9-Andrzejewski Rzemysaw, Kasprzyk-Hordern Barbara, Nawrocki Jacek N-nitrosodimethylamine (NDMA) formation during ozonation of dimethylamine-containing waters. J. Wat. Res 2008;42(4): 863-870.

10-Prasanna Dash Barada, Chaudhari Sanjeev. Electrochemical denitrification of simulated ground water. J. Wat. Res 2005; 39(17):4065-4072 .

11-Ayyasamy PM, shunthi K. Two-stage removal of nitrate from grand water using biological and chemical treatments.J. Biosc. and Bioeng.2007;104(7):129-134.

12- Huang Chin-Pao, Wang Hung-Wen, Chiu Pei-Chun. Nitrate reduction by metallic iron. J. Wat. Res. 32(8):2257-2264.

13- Merzouki M, Bernet N, Deigenès J-P, Moletta R, Benlemlih M . Biological denitrifying phosphorus

removal in SBR: effect of added nitrate concentration and sludge retention time Water Science & Technology 2001;43(3):191-194 .

14–Neamtu M,Yediler A,Siminiceanu ll,Kettrup A.Oxidation of commercial reactive Azo dye aqueous solution by the photo-Fenton and Fenton-like processes.J.photochem.and photobio.2003;161(1):87-93.

15-Ghaly M Y,Hartel G,Mayer R,Haseneder R.Photochemical oxidation of p-chlorophenol by UV/H2O2 and photo-Fenton process.A comparative study.Water Management 2001;21(1):41-47 .

16-APHA,Standard method for the examination of water and wastewater . 20 end 2005.

17-Wakeford C A,Blackburn R,Lickiss P D,Effect of ionic strength on the acoustic generation nitrite, nitrate and hydrogen peroxide 1999;6(3):141-148.