

Nitrate Removal from Aqueous Solutions by Magnetic Nanoparticle

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ABSTRACT

Introduction: Due to causing methemoglobinemia, different cancers, and teratogen effects in human nitrate contamination of water resources has become a critical environmental problem. Therefore, the aim of this work was to determine the optimum condition of nitrate sorption onto magnetic nanoparticle.

Materials and Methods: The removal of nitrate from aqueous solutions by magnetic nanoparticles has been studied through using batch adsorption method. X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM) was applied to characterize the synthesized Fe₃O₄. The effect of pH, nano-magnetic, adsorbent dose, initial concentration of nitrate, and contact time were investigated.

Results: According to SEM and TEM images, the adsorbent particles were nanosized and spherical; the sizes were about 20–30 nm. The experiments' results indicated that the optimum adsorbent dose was 750 mg in 1000 ml of solution, with a contact time of 90 min, while the optimum pH was 9. The kinetic models for nitrate adsorption showed rapid sorption dynamics by both first-order kinetic ($R^2 = 0.97$) and second-order kinetic ($R^2 = 0.96$) models. Nitrate adsorption equilibrium data were fitted well to the Freundlich isotherm than Langmuir isotherm.

Conclusion: The results showed that, magnetic nanoparticles can be used as a low cost and efficient adsorbent for removal of nitrate from aqueous solutions.

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Introduction

Agricultural and industrial activities development has caused production of anionic inorganic toxic pollutants such as nitrate. Nowadays, these pollutants in environment have caused public concern about the quality of underground water¹⁻³. Nitrate is produced and

entered into the water resources through industrial processes such as fertilizing, cellophane, pectin, and ammunition making⁴.

The arrival of this anion pollutant into the environment has led to health and environmental problems such as eutrophication and methemoglobinemia diseases in children,

because it combines the resuscitated nitrate to nitrite with blood hemoglobin which impairs oxygen transportation to the tissues⁵. Hence, the World Health Organization (WHO) and the United State Environmental Protection Agency (USEPA) have recommended maximum concentration of nitrate in drinking water, 50 mg /l in terms of nitrogen and 10 mg/l in terms of nitrate^{6,7}.

To remove different forms of nitrogen from aqueous solutions. These methods include ion exchange, adsorption, reverse osmosis, electro-dialysis, denitrification, algal removal, ozonation, and activated carbon filter. Various methods have been reported^{8,9}. Among these processes, the overall adsorption process has been further considered for its ease of operation, design, economic considerations, as well as regeneration of low-cost adsorbents for pollutant removal in recent years⁹. Adsorbents such as activated carbon, zeolite, chitosan, agricultural, and industrial wastes are used in this process^{10,11}.

Magnetic adsorbent nanoparticles have been considered because of their high specific surface, nontoxicity, easy separation by magnet, rapid response, high efficiency, and ability to absorb pollutants in recent years^{10,12-15}. Yavuz et al. in 2010 studied arsenic removal from aqueous solution by magnetic nanoparticles and concluded that arsenite and arsenate are removed in 99% by using Fe_3O_4 ¹⁶. Amin et al. also reported that magnetic nanoparticles can remove more than 94% of benzene from aqueous solution in both aquatic solution and absorption column¹⁷.

Hosseini et al. in a study on absorption of copper from aqueous solutions through magnetic nanoparticles with modified tea wastes reported that tea wastes with modified magnetic nanoparticles are more suitable and effective to remove heavy metals from aqueous solutions¹⁸. In addition Qadri et al. indicated that the maximum adsorption of acridine orange color by Fe_3O_4 is 59 mg/g¹⁹. The aim of this study was to evaluate efficiency of magnetic nanoparticles as adsorbent for the removal of nitrate from aqueous solutions with the influence of variables such as pH, initial nitrate concentration, adsorbent dosage, and

retention time due to high performance of magnetic nanoparticles in removal of environmental pollutants from aquatic environments.

Materials and Methods

This experimental-intervention study investigated how nitrate is absorbed from contaminated water on synthetic and natural samples by using magnetic nanoparticles (Fe_3O_4). This study was conducted at faculty of Health, Isfahan University of Medical Sciences.

To conduct the current research, samples were prepared through synthetic way in water and wastewater laboratory of chemistry in Environmental Health, Department of Health School. Samples were taken at the system's influent and effluent to study the magnetic nanoparticles (Fe_3O_4) in nitrate removal from aquatic solutions and absorption column. Samples were analyzed in chemistry laboratory of Health School in Isfahan University of Medical Sciences. Materials and solutions needed with an analytical reagent grade were purchased from the Merck Company.

Adsorption studies

Absorption experiments were conducted to examine the effect of different factors and nitrate removal efficiency at different initial pH (5, 7, 9 and 11). Erlenmeyer flask of 250 ml were used by adding a certain amount of adsorbent (0.1, 0.5, 0.75 and 1 g/l) and 100 ml of nitrate solution containing different concentrations (50, 100, 250 and 500 mg/l) in this experiment. After sample preparation, sample vials were placed on a stirrer (Orbital shaker, model OS 625) and mixed for 15, 30, 60, and 90 minutes at 240 rpm.

Then, the sample was placed on the magnet for filtration for 2 minutes. Finally, nitrate concentration was measured by spectrophotometer (DR-5000) at a wavelength of 220 nm. All experiments were repeated 3 times and only the mean volume was reported. A control sample with no adsorbent added to it was also applied to ensure that any reduction in nitrate concentrations was only due to absorption on the magnetic nanoparticles and no other factors played role in their concentration decrease.

In all experiments, pH of the solution before and after contact with magnetic nanoparticles for pH_{in} and pH_{out} was recorded by pH meter (EUTECH, Model 1500). pH of samples were adjusted by 0.1 M HCl and 0.1 M NaOH, respectively. The amount of nitrate adsorbed onto magnetic nanoparticles for equilibrium (q_e) was calculated in terms of mg/g and efficiency (%) by the following formulas, respectively:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

In these equations C_0 and C_e (mg/l) are respectively the initial and final concentrations of nitrate, V is the initial volume (liters) of solution, and m is the weight of adsorbent in terms of g/l, respectively.

Data analysis

To determine the effect of pH factors, adsorbent dose, initial nitrate concentration, and contact time on nitrate removal the method designed by software v6 - Design Expert and Orthogonal Taguchi method was performed. In this study, Taguchi method of 4 factors was evaluated in 4 levels. Nitrogen adsorption kinetic and isotherms' results were calculated in optimum conditions of magnetic nanoparticle dosage, contact time, pH, and initiate concentration 0-100 mg/l by using Excel software.

Adsorption isotherms

Adsorption isotherms are equations for describing the equilibrium of adsorbent component between solid and liquid phases. In this study, Langmuir and Freundlich isotherms were evaluated to determine the absorption capacity of magnetic nanoparticles for nitrates and also to identify the absorption nature and adsorption system design. Linear equations of the studied isotherm are examined equations 3 and 4.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad \text{Langmuir equation (3)}$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{Freundlich equation (4)}$$

In these equations q_e and C_e , are respectively the adsorption capacities at equilibrium (mg/g) and

output concentration (mg/l), q_m is the maximum adsorption capacity (mg/g), and b , n , as well as k_f are equations' constants.

Adsorption kinetics

Adsorption kinetics is used to understand absorption mechanisms and effect of contact time on the adsorption better. So, pseudo-first and pseudo-second order simplified models were applied for evaluation of experimental data of nitrate. Kinetic the first and second order pseudo-linear equation is generally presented as the following equation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The first pseudo equation (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The second pseudo equation (6)

Where q_e and q_t are the amounts of nitrate adsorbed (mg/g) at equilibrium and time t (min), respectively, and k_1 (l/min) and k_2 (g/mg min) are the rate constant of first-order and second-order adsorption, respectively.

Results

XRD analysis (Figure 1) on magnetic nanoparticles suggests that Fe_3O_4 nanoparticles form the highest percentage of these compounds, but small amounts of impurities (less than 1.5%) are also observed in these compounds, which mainly consist of Fe_2O_3 . Comparison of the nanoparticles XRD pattern with radiations' standard diffraction showed that the produced product mainly consisted of Fe_3O_4 crystals while other phases such as $Fe(OH)_2$ or Fe_2O_3 are in small amounts. Sharp peaks of this figure show obviously that Fe_3O_4 nanoparticles have high crystalline nature.

TEM images taken from Fe_3O_4 (Figure 2) specifies that the size of these nanoparticles were between 20-30 nm and particles were completely separate and uniform. In addition, SEM image of nanoparticles also shows that the magnetic particles have a size of 20-30 nm and are uniformly distributed.

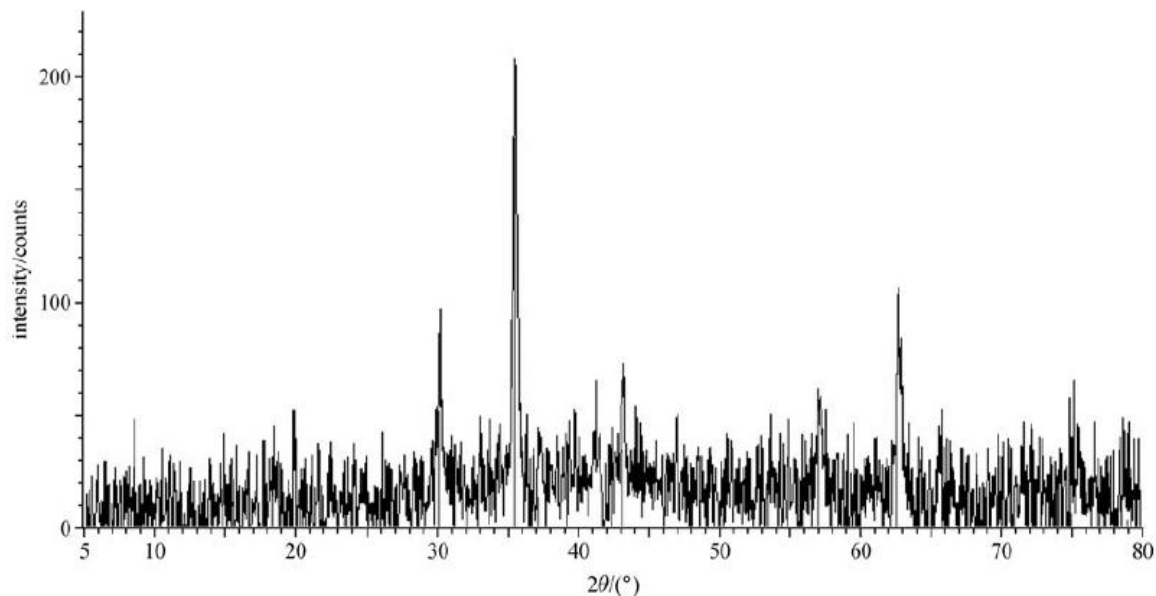


Figure 1: XRD image related to Fe₃O₄ magnetic nanoparticles

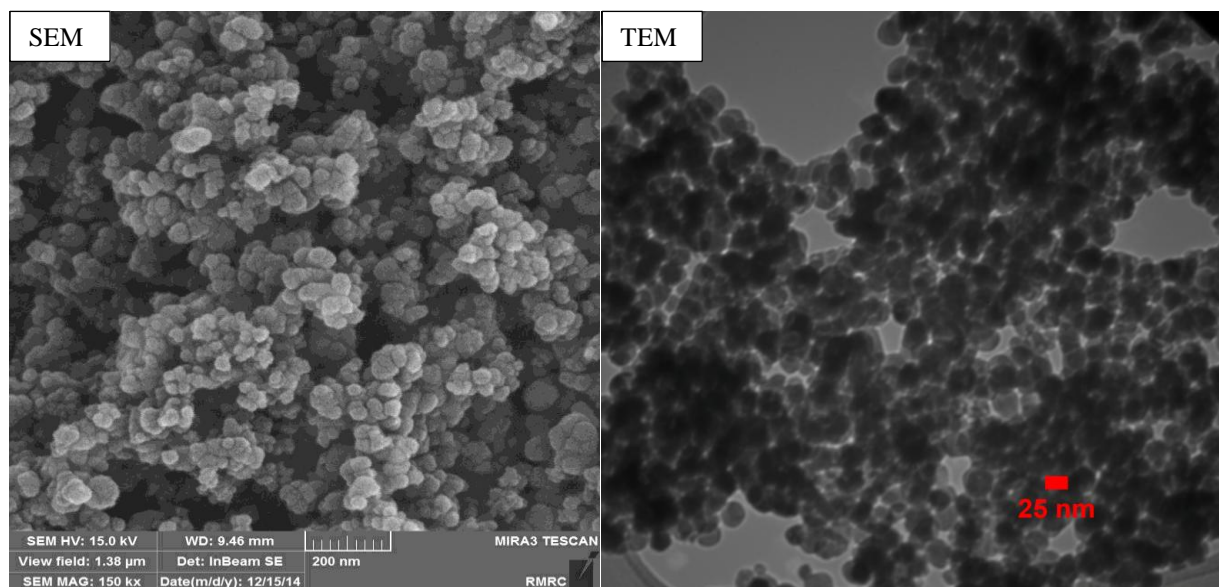


Figure 2: TEM and SEM images of Fe₃O₄ magnetic nanoparticles

The removal and nitrate adsorption by magnetic nanoparticles are tabulated in table 1. Figure 3 shows the nitrate removal in different input concentrations, different doses, contact time, and pH to determine the optimum conditions for nitrate removal by Fe₃O₄ magnetic nanoparticles.

Statistical calculations were conducted to define the isotherms and kinetics adsorption to determine the most appropriate isotherms and kinetics in optimum conditions and at different

levels of input concentration and contact time. The results of these calculations are shown in table 2. Table 3 represents the comparison between magnetic nanoparticles and other studied adsorbents in the efficiency of nitrate removal.

Table 3 represented the comparisons in *q_e* of this study with various adsorbents such as activated carbon (AC) and Sepiolite reported in the literature.

Table 1: Nitrate removal by Fe₃O₄ magnetic nanoparticles in a variety of conditions

Experiment stages	Factors				Results	
	Nitrate concentration (mg/l)	Nanoparticles concentration(g/l)	Time (min)	pH	Efficiency (%)	q _e (mg/g)
1	500	0.75	60	9	86	573.33
2	100	1	60	7	81	81
3	500	0.1	90	5	32	160
4	50	0.5	30	9	82	82
5	50	0.75	90	7	78	52
6	250	1	90	9	84	210
7	500	1	30	11	83.6	418
8	50	1	15	5	8	4
9	100	0.1	15	9	84	840
10	100	0.5	90	11	84	168
11	500	0.5	15	7	85	850
12	100	0.75	30	5	11	14.66
13	250	0.1	30	7	83	2075
14	250	0.5	60	5	27	135
15	250	0.1	60	11	85	2125
16	50	0.1	60	11	85	425

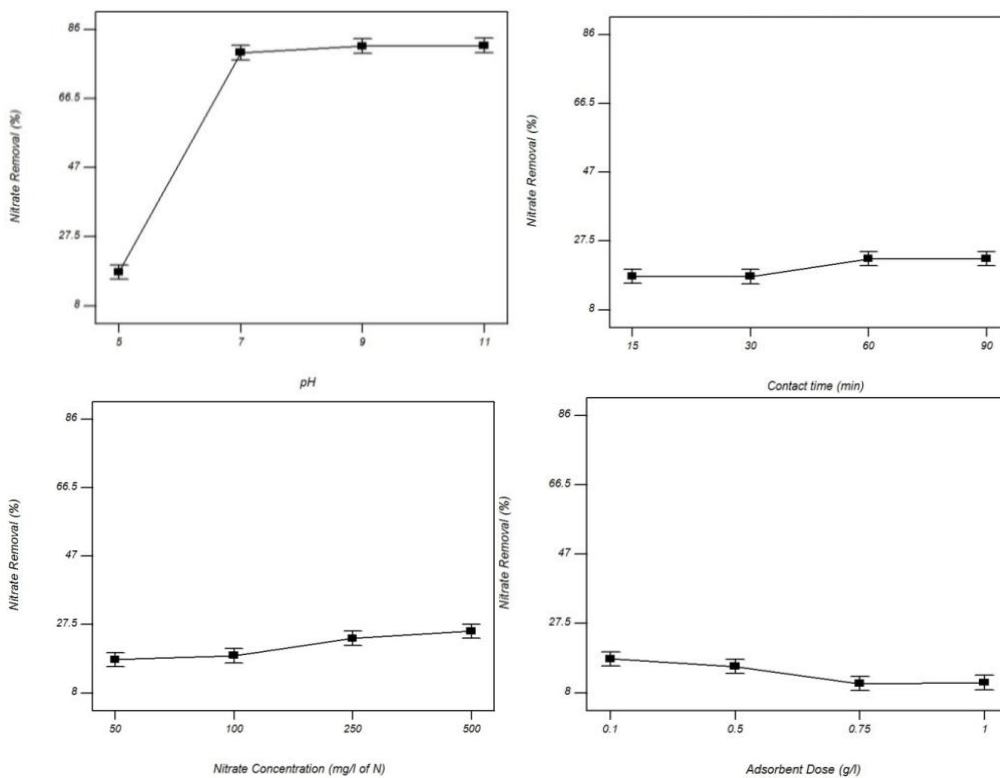


Figure 3: The influence of various factors on nitrate removal by Fe₃O₄ magnetic nanoparticles

Table 2: Isotherm and kinetic parameters for adsorption of nitrate by Fe₃O₄

	Freundlich			Langmuir		
	n	K	R ²	b	q _{max}	R ²
Isotherm	0.93	1.4	0.98	0.001	434.78	0.93
Kinetic	Pseudo-first order			Pseudo-second order		
	K ₁	q _e	R ²	K ₂	q _e	R ²
	0.005	139.42	0.97	0.0007	172.41	0.96

Table 3: The efficiency of different adsorbents' in nitrate removal¹¹

Absorbent	pH	Absorbent dose (g/l)	Initial concentration	Removal percentage
Active carbon	2-10	0.25-1	100	54.3- 71
Sepiolite	2-10	0.25-1	100	29.3-35.4
Activated Sepiolite with HCl	2-10	0.25-1	100	76.4- 99.6
Active carbon resulted from bagas	3	0.1	100	41.2
Active carbon residual	6	0.25	25-125	12.8-29.9
Commercial active carbon	4	0.25	25-125	31.1-81.3
Magnetic nanoparticles	9	0.75	500	85

Discussion

Optimal conditions of nitrate adsorption were studied based on removal output of this compound by experimental design. Results of test design (Table 1) show that the highest rate of nitrate removal in initial concentration can happen in 500 mg/l, adsorbent dosage of 750 mg/l, contact time of 90 minutes, and pH = 9, that in this case 86% of nitrate was eliminated by magnetic nanoparticles. These results were corresponded with the study of Hadeie et al. on removal of benzene and ethylene by magnetic nanoparticles¹².

In the study of nitrate adsorption, influence of pH on the chemical properties of aqueous solution and sites of adsorption in the absorbent is an important factor. The results of experiments indicate that the maximum efficiency of nitrate removal by magnetic nanoparticles is in pH = 9 (Figure 3). This increase of removal in pH_s of above 7 is due to the increase of electrostatic force between the absorbent and nitrate. Also, the nitrate removal efficiency has reduced in pH of 7 and higher. This removal reduction in high pH_s is due to OH⁻ ion and negative charge that have made the surface of magnetic nanoparticles negatively charged. Hence a repulsive force is created between the adsorbent and nitrate that ultimately causes reduction of the removal efficiency in this environment²⁰. Liu et al. in their study reported

that arsenate removal efficiency at pH 8 by the loaded Fe₃O₄ was high on activated carbon, but by reduction of pH, the efficiency decreases rapidly²¹. Xu et al. indicated that the neutral condition to remove nitrate by Fe²⁺ and Fe₃O₄ is very appropriate²².

The contact time efficiency diagram (Figure 3) shows that nitrate adsorption rate increases from 15 to 90 minutes with increase of contact time. This rate of nitrate adsorption can be attributed to functional groups of magnetic nanoparticles. Suzuki et al. studied the nitrate adsorption on zero-valent iron and reported that high levels of nitrate adsorption occur at the time of more than a hour²³. Bekhradinassab and Sabbaghi, also represented in their study that the maximum nitrate absorption occurs at contact time of more than 16 hours²⁴.

Results of the initial concentration impact stage on the removal of nitrate (Figure 3) indicated that removal rate increases by increase of the initial concentration. Results of the study carried out by Qaderi et al. showed that Fe₃O₄ nanoparticles' removal efficiency increases by increase of acridine initial concentration so that when the initial concentration of the acridine increases from 3.7 mg/l to 184 mg/l the removal efficiency also increases¹⁹.

The effect of adsorbent dosage on the adsorption of nitrate was assessed and the results (Figure 3)

indicate that nitrate removal reduces by increasing the amount of adsorbent. This is because of the increase in the surface area and the number of places available to absorb ions in the early stages. These results are in consistency with results achieved by Sepehri et al. on nitrate adsorption through modified zeolite by the studied zero-valent iron²⁵.

Freundlich and Langmuir adsorption isotherms were investigated to determine the relationship between the adsorbent and nitrate and in order to evaluate the nitrate ion adsorption capacity on magnetic nanoparticles. It is assumed that the adsorption is monolayer and there is an interaction between adsorbed species in Langmuir model. When the test data follow the Langmuir isotherm model, it represents the uniform distribution of active sites on the surface of adsorbent and the fact that absorption is monolayer.

Adsorption is done onto heterogeneous and multilayer surfaces in the Freundlich model, it is reversible and not limited to absorption layer. According to the results of Table 2, Freundlich isotherm model has a stronger correspondence with experimental data compared with the Langmuir isotherm model in this study ($R^2 = 0.93$). Also, the constant of Freundlich model (0.98) was near 1 which represents proper conditions of nitrate absorption by Fe_3O_4 ²⁰.

In addition, investigation of nitrate adsorption kinetic (Table 2) showed that the adsorption data follows both first-order ($R^2 = 0.97$) and second-order kinetics ($R^2 = 0.96$). Kamaraj et al. studied nitrate removal with nano zinc oxide and reported that adsorption data follow more the Freundlich isotherm and kinetics of the second order²⁶. Wang et al. represented that adsorption data by the remnants of modified wheat follow the Freundlich isotherm and kinetic of the second order²⁷. Sepheri et al. investigated nitrate adsorption by modified zeolite with zero-valent iron nanoparticles and concluded that removal of nitrate follows from the second order kinetic model²⁵.

One of the significant factors in the adsorbents used to remove nitrate of aqueous solutions is the

comparison of their removal efficiency with other adsorbents to estimate their costs and environmental compatibility. The results tabulated in Table 3 indicate that magnetic nanoparticles have better removal efficiency compared to other adsorbents. However, this difference in nitrate removal by the adsorbent can be attributed to any adsorbent's characteristics such as structure, functional groups, and the surface area.

Conclusion

Optimal condition to identify high performance of magnetic nanoparticles for nitrate adsorption was studied in this study. The results showed that the magnetic nanoparticles have a high absorption capacity for nitrate of aqueous solution in batch condition. Also, it was found that pH of solution has a significant impact on efficiency of removal.

Freundlich isotherm model had more consistency with data in comparison with Langmuir model indicating adsorption on the heterogeneous and multi-layered surfaces. Comparison between the magnetic nanoparticles and other adsorbents showed that the performance and efficiency of magnetic nanoparticles were very high. Therefore, this adsorbent can be considered as an effective option for the removal of nitrate from aqueous solutions due to the high specific surface area, high adsorption capacity of magnetic nanoparticles, as well as its easy isolation from the environment.

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Conflict of interest

The authors have declared no conflict of interest.

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