

Nitrate removal from water using alum and ferric chloride: A comparative study of alum and ferric chloride efficiency

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Abstract

Background: Nitrate is an acute and well-known hazardous contaminant, and its contamination of water sources has been a growing concern worldwide in recent years. This study evaluated the feasibility of nitrate removal from water using the traditional coagulants alum and ferric chloride with lower concentrations than those used in the conventional coagulation process.

Methods: In this research, two coagulants, alum and ferric chloride, were compared for their efficiency in removing nitrate in a conventional water treatment system. The removal process was done in a batch system (jar test) to examine the effects of coagulant dosages and determine the conditions required to achieve optimum results.

Results: The results revealed that ferric chloride at an initial dose rate of 4 mg/L reduced nitrate concentration from 70 mg/L to less than the World Health Organization (WHO) guideline value (50 mg/L N-NO₃). However, the removal efficiency of alum was not salient to significant nitrate reduction.

Conclusion: In conclusion, ferric chloride was more effective than alum in removing NO₃⁻, even in common dosage range, and can be considered a cost-effective and worthy treatment option to remediate nitrate-polluted water. Furthermore, the removal of nitrate by coagulation can be simple and more economical than other treatment alternatives.

Keywords: Nitrate, Water treatment, Coagulation, Alum, Ferric chloride

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Introduction

Nitrate (NO₃⁻) is found naturally in the environment and is an important plant nutrient (1). However, the contamination of water sources by nitrate has been a growing concern worldwide in recent years (2). Nitrate in water sources is related to nitrogen fertilizer and domestic wastewater (3). This problem is found in both developed and developing countries. In European Union (EU) countries, nitrate concentrations in 20% of groundwater resources were more than 50 mg NO₃⁻/L between the years 1996 and 1998 (4,5). In several Middle Eastern countries, including some places in Iran (6), Iraq (7), Saudi Arabia (8), and the United Arabic Emirates (9), high nitrate concentrations have been detected in ground water. Nitrate causes disease and negatively affects health with such issues as methemoglobinemia, goiter, thyroid disorder, stomach cancer, cytogenetic defects, and birth defects (10,11). The maximum

concentration level (MCL) of nitrate is 50 mg NO₃⁻/l as set by the World Health Organization (WHO) standards for drinking water, and the Environmental Protection Agency (EPA) and EU have determined the MCL of nitrate to be 10 and 11.3 mg N/L, respectively (12-14). Thus, the removal of nitrate from contaminated water for drinking purposes is important.

There are numerous physical and chemical methods to remove nitrate from water, including ion exchange, reverse osmosis, and electrodialysis. These methods are useful but produce concentrated brine as a waste by-product which should be treated or disposed of, and this requires expensive processes (6,12).

Nitrogen and phosphorus compounds are typically removed from wastewater with biological processes. Biological denitrification is an extensively used procedure for the reduction of nitrate from water and wastewater (15).



The most significant problem with the denitrification process is that it requires disinfection in order to remove bacteria. Furthermore, this process is very sensitive to some parameters, such as temperature, pH, conductivity, and toxic compounds (10,12,16). Other biological treatment options include treatment using fluidized beds or a fixed bed and membrane biofilm reactor. Chemical reduction methods using media such as zero valent iron (ZVI) and sulfur modified iron (SMI) have also been used recently (17,18).

Coagulation and flocculation may be broadly described as chemical and physical processes that mix coagulating chemicals and flocculation aids with water. Coagulation destabilizes particles and enables them to become attached to other particles so that they may be removed in subsequent processes (19). Three main mechanisms, electrostatic coagulation (reduction of electrostatic forces and separation of particles), sweep coagulation (entrapment of particles by coagulant metal-hydroxides), and adsorptive coagulation (destabilization by adsorption of polymers or long hydroxide chains to the particle surface), are considered for the coagulation/flocculation process (20).

In summary, these processes are low-cost, simple methods for the destabilization of suspended particles and the removal of turbidity, natural organic matter (NOM), disinfection by product precursors or color in raw water. Al(III) and Fe(III) coagulants are two main inorganic compounds used in water treatment plants. Ferric sulphate, aluminum sulphate, and ferric chloride are the most common coagulants (21,22).

The main source of drinking water in most of Iran's cities is ground water, which generally contains higher concentrations of nitrate. The current study aimed to evaluate the feasibility of nitrate removal from drinking waters with conventional coagulation treatments by applying alum and ferric chloride in a batch system. Furthermore, the efficiency rates of nitrate removal by alum and ferric chloride were compared, and the effects of factors such as initial nitrate concentration and coagulant dosage were studied.

Methods

Containers and synthetic water preparation

All containers were glass. They were washed with diluted acid (H_2SO_4 , 10%) and then rinsed with tap water and de-ionized water. Synthetic water samples in concentrations of 10, 30, 50, 70, and 100 mg/L NO_3^- -N were prepared from nitrate stock solution (dissolving KNO_3 [Merck Co., 99.0%] in tap water). All samples were stored at temperatures below 4°C, and experiments were carried out within 24 hours of sample preparation. The main source of tap water was groundwater with no special treatment except chlorination. The physico-chemical characteristics of the tap water are shown in Table 1.

Experimental procedure

In this study, the most common coagulants, i.e. alum (aluminum sulfate, $Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$),

Table 1. Physico-chemical characteristics of tap water

Parameter	Values
pH	7 ± 0.2
EC (µS/cm)	690
Temperature (°C)	20 ± 2
Turbidity (NTU)	0.5
Alkalinity (mg/L)	317
TDS (mg/L)	448
SO_4^{2-} (mg/L)	58
Cl^- (mg/L)	21
Total Hardness (mg/L)	285
Mg (mg/L)	25
Ca (mg/L)	72
Na (mg/L)	33
K (mg/L)	4

were applied to determine the nitrate removal efficiency of a conventional water treatment system.

The coagulation-flocculation process was performed in a batch system (jar test) with a six-paddle stirrer (Hach), and the chemicals, dosages, and conditions required to achieve optimum results were evaluated (ASTM, 1995). The alum and ferric chloride solutions at desired concentrations were prepared by diluting the stock solution [10 g/L] immediately before use. Coagulant dosages for the removal of nitrate were 2.5, 3, 3.5, 4, and 4.5 mg/L. Conventional coagulation by alum depends on pH and temperature (23); in this study, the pH values of solutions were around 7 ± 0.2, and tests were conducted at room temperature which is recommended for $FeCl_3$ and alum usage. Acidic pH may lead to the formation of weak HNO_3 ions or the complexation of NO_3^- ions with dissolved aluminum (24). Therefore, in this study, acidic pH was not applied. Furthermore, as reported in the literature, a pH above 9 is not efficient in the coagulation process for nitrate removal (25).

Rapid mixing was simulated for 1 minute at 120 rpm and flocculation was done by slow mixing at 20 rpm for 15 minutes. The flocs were then allowed to settle for 20 minutes without mixing.

Sample analyses

The samples were analyzed for residual nitrate concentration using a UV spectrophotometer apparatus (HACH DR/5000) at a wavelength of 220 nm according to the 1998 standard methods for the examination of water and wastewater (4500- NO_3^- B) (5).

The pH values of samples were measured with a pH meter WTW 3110 at the end of the settling period.

Statistical analysis

The data acquired from the comparative surveys was analyzed by SPSS 16.0 for Windows (Chicago, IL, USA). Due to the lack of normal data distribution, the non-parametric statistics analysis Mann-Whitney U Test was used to further analyze the data. All data was analyzed with Microsoft Excel 2007.

Results

The effect of initial nitrate concentration on the efficiency of the conventional coagulation-flocculation process was investigated at different nitrate concentrations (10, 30, 50, 70, and 100 mg/L N-NO₃). The removal percentages of different concentrations of nitrate using ferric chloride and alum as a function of coagulant dosages are separately presented in Figure 1. Results of the Mann-Whitney U tests showed significant differences in the abilities of ferric chloride and alum to remove nitrate ($P < 0.01$).

Clearly, ferric chloride exhibited a greater removal efficiency than aluminum sulfate. As can be seen, the nitrate uptake by both ferric chloride and alum decreased when the initial nitrate concentrations were increased from 10 to 100 mg/L N-NO₃.

Figure 2 shows the typical operating ranges for the coagulants. Taking into account the primary pH values and optimum dosages of coagulants, the predominant removal mechanisms for nitrate could be attributed to adsorption and sweep precipitation.

Discussion

Effect of initial nitrate concentration and coagulant dose
As seen in Figure 1, ferric chloride removed nitrate with a higher efficiency than that of alum. Results of the Mann-Whitney U test also showed significant differences in ferric chloride and alum abilities for nitrate removal ($P < 0.01$).

The highest removal efficiency rate using each one of the applied coagulants was obtained for an initial nitrate concentration of 10 mg/LN-NO₃, and minimum removal was found for a 100 mg/LN-NO₃ concentration (see Figure 1). When initial nitrate concentration was 10 and 30 mg/LN-NO₃, the removal fraction using FeCl₃ was more than 90%; however, for 70 mg/LN-NO₃, it was reduced to less than 35% even when applying the highest coagulant dose (4

mg/L). Thus, it can be concluded that when the concentration of the contaminant is increased, removal efficiency is decreased. This is true for alum as well.

Koparal and Öğütveren achieved similar results in the removal of nitrate from water by an electrochemical process and reported that removal efficiency was inversely related to initial nitrate concentration (26). It seems that increasing nitrate concentration is an important factor effecting the removal of nitrate from water.

The experimental results also showed removal restrictions in concentrations above 50 mg/L of pollutant, and ferric chloride was more effective in the removal of low ranges of N-NO₃ (<30 mg/L). Similarly, another study which investigated nitrate removal from water by a coagulation process reported removal efficiency as 85% when 0.3 g of hydrotalcite-like compounds were used in the NO₃⁻ solution with an initial concentration of 10 mg/L (27). Nonetheless, the optimum dosage of ferric chloride in the current study was 4 mg/L, which is less than the typically used coagulation dosage in the water treatment industry. In the case of alum, applied dosages ranged from 2.5 to 4 mg/L, which is also less than the typically used dosages for the coagulation process. The maximum removal efficiency was attained in higher ranges of alum (3.5-4 mg/L), but in nitrate concentrations of more than 30 mg/L, it had a negligible efficiency. Ayyasamy et al studied the removal of remained nitrate from groundwater samples using chemical coagulation after a one-stage biological treatment. They reported that the optimum dosage of alum for the removal of nitrate at a concentration of 50 mg/L was 150 mg/L and removal efficiency of the process was 74.3% (10). In this dosage of alum, the residual aluminum concentration in water treated by the coagulation process may be above the guidelines of the WHO and the admissible limit set by the Institute of Standard and Industrial Research of Iran, and

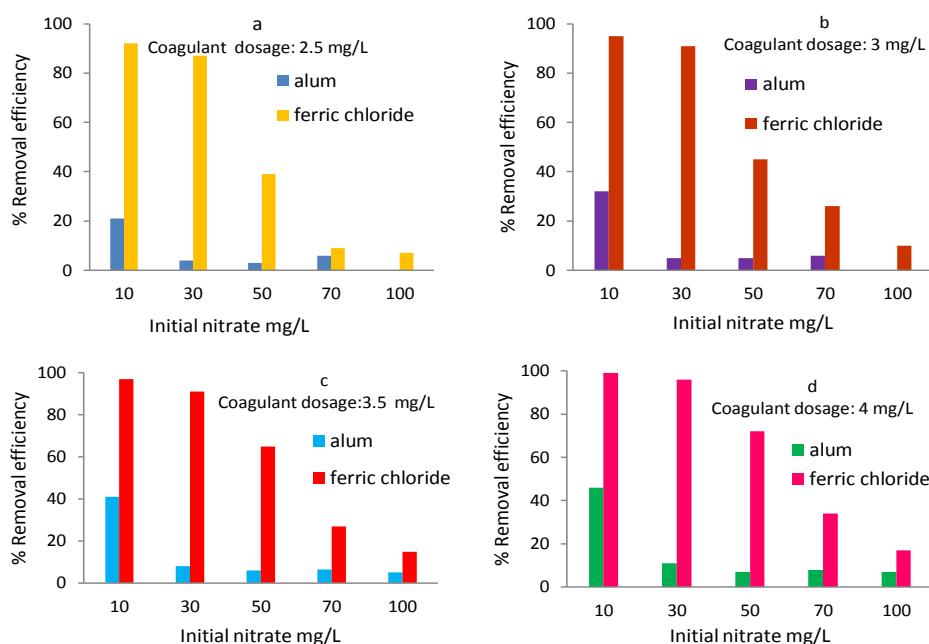


Figure 1. Efficiency of alum and ferric chloride in nitrate removal.

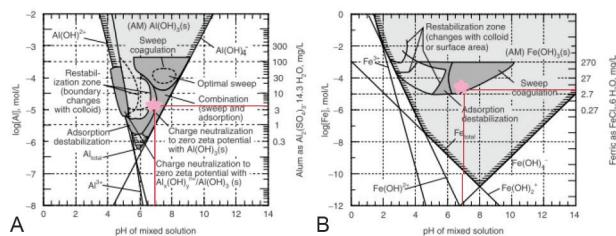


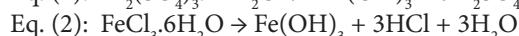
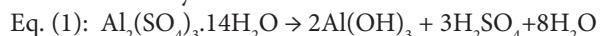
Figure 2. Typical operating ranges for coagulants: (A) alum and (B) ferric chloride (24).

it is suspected in Alzheimer disease (21).

Nitrate removal mechanism

To determine the nitrate removal mechanism using alum and ferric chloride coagulants, direct chemical reactions and adsorption mechanisms were appraised. As reported in the literature, for a chemical reaction between aluminum and nitrate or iron and nitrate, pH values should be raised above 9 (24,25,28). However, due to the high stability and solubility of the chemical products of this reaction in water, nitrate removal was not expected in pH values above 9 (24,25).

In pH values less than 9, anions of Cl^- and SO_4^{2-} could compete with nitrate for reduction by coagulants ($\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$) (27). According to equations 1 and 2, adding alum and ferric chloride in the range of 3 to 4 mg/L could lead to the production of HCl and H_2SO_4 ; therefore, the range of the operating region diminished for iron and especially for aluminum hydroxide.



Since the initial pH was 7, nitrate removal could not be achieved by a chemical reaction. Hence, bulk reactions for nitrate removal by ferric chloride and alum were adsorption and sweep precipitation (see Figure 2) (24).

Comparison of alum and ferric chloride abilities in removing nitrate

Based on the results, an initial ferric chloride dose of 4 mg/L induced a reduction in nitrate concentration from 70 mg/L to less than the WHO guideline value (50 mg/L as NO_3^-) (13). Alum efficiency, however, was not sufficient. As previously stated, ferric ions are better than aluminum ions for adsorption and sweep coagulation because a lower dosage is needed.

Comparing the solubility of alum and ferric chloride showed that ferric chloride is more insoluble than aluminum in a wide range of pH values. Moreover, adding alum in ranges of 3.5 to 4 mg/L could lead to the production of H_2SO_4 and decreased pH. Therefore, the optimum range of pH for alum is less than that for ferric chloride, and decreases in pH values are greater with alum than with ferric chloride. Therefore, the application of ferric chloride could be more effective than alum for the removal of nitrate in a water treatment plant.

The high stability and solubility of nitrate in water makes the removal of this anion from water sources with high

nitrate concentrations difficult (11,29). As such, various chemical and biological methods have been examined for their ability to remove this soluble anion. Some types of treatment methods should be considered highly experimental since there are currently no full-scale applications, such as biological treatment, subsurface biological treatment, phytoremediation, and nanotechnology (e.g., using nanoscale ZVI, SiO_2 –FeOOH, polyvinyl alcohol/polymer composites, etc.) (30–33).

Although conventional treatment methods such as ion exchange, reverse osmosis, electrodialysis, and biological denitrification are feasible, effective options for nitrate removal from potable water, their applications have some limitations.

Conclusion

The main objective of the current study was to evaluate the ability of conventional water treatment processes to reduce nitrate contamination. Although the studied method is not a specialized or ideal technology for the treatment of nitrate, it may be used in some circumstances to reduce the health risks associated with nitrate contamination of drinking water. As the results of this study showed, the conventional coagulation process using alum and ferric chloride could be effective in removing nitrate at concentrations less than 50 mg- NO_3^- /L; ferric chloride exhibited a greater removal efficiency than alum. Therefore, the use of ferric chloride for water treatment, even in common dose ranges, can play a basic role in the removal of nitrate from water.

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Ethical issues

The authors hereby certify that all data collected during the study is as stated in this manuscript, and no data from the study has been or will be published separately elsewhere.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

All authors contributed equally and were involved in the study design, data collection, and article approval.

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