

Influence of Adding Clay in Removing Nitrate from Groundwater by Zerovalent Iron

Maan Bitar *¹, *Muhammad Haitham Haboub* ¹, *Nawzat Nebghali* ²

¹Department of Environmental Engineering, Faculty of Civil Engineering, University of Aleppo, Aleppo, Syria.

²Department of Basic Sciences, Faculty of Civil Engineering, University of Aleppo, Aleppo, Syria.

*Corresponding Author.

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Abstract

The method of removing nitrates from water using zero-valent metals is one of the methods that proves to be highly effective day after day, especially zero-valent iron. However, the most prominent obstacles that cause an obstacle to continuing its use are the exposure of its surface to passivation during the reaction and the production of ammonium ions as a main product for the reduction of nitrates under conditions of treatment.

In this research, the effect of clay during the removal of nitrate by Fe⁰ was studied. Raw clay, acid-activated clay, and clay modified with iron nanoparticles at a ratio of (1:1) were used. The results showed that 80% of nitrate ions in water can be removed by using Fe⁰ at a concentration of 40 g/L with 4 ≥ pH for 120 min at room temperature, adding raw clay reduced the efficiency due to its alkaline properties, which led to the inhibition reaction of Fe⁰ with nitrates. while Acid-activated clay led to an increase in nitrate removal by increasing dosage.

Modified clay has given greater effectiveness than raw clay and acid-activated clay, removal rate increased to 95.33% under conditions of treatment, while ammonium was decreased with increasing the added clay in all its forms (raw, activated and modified). Finally, it is noted that adding 5 gr/L of clay (raw, activated, modified) was sufficient to reduce the percentage of nitrate and ammonium within the permissible limits according to Syrian Specification No. 45/2007 for drinking water.

Keywords: Activated clay, Natural clay, Water pollution, Water treatment, Zero iron.

Introduction

Long-term exposure to high levels of nitrates poses varying degrees of risks to human health. Nitrates can convert hemoglobin in the blood to methemoglobin in infants, a condition known as "blue baby syndrome" because methemoglobin is unable to bind oxygen and causes cerebral oxygen deficiency^{1,2}. Nitrates also lead to the formation of N-nitrosamines, which are considered carcinogenic compounds. For this reason, the International Agency for Research on Cancer (IARC) classified ingested nitrates or nitrites as potentially carcinogenic to humans^{3,4}.

Several techniques have been developed to remove nitrate residues from water, sewage, and waste streams. These include biological denitrification, ion exchange, nano filtration (NF), and reverse osmosis^{5,6}.

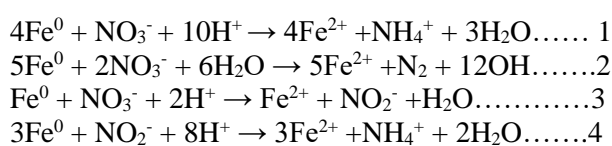
While biological denitrification is widely used for relatively low-cost removal of nitrogen from sewage water, the presence of residual organic matter and bacterial contamination poses significant limitations for its application in drinking water treatment⁷, ion exchange treatment generates saline waste that

requires additional processing and incurs extra costs⁸.

Membrane fouling in nano filtration processes represents a challenging issue, as in any membrane separation process, and may be further complicated by nano-level reactions. Nanofiltration partially removes nitrates due to their monovalent negative charge^{9, 10}.

Reverse osmosis allows for concentrating pollutants in a saline solution without altering their molecular structure, making it suitable for drinking water. However, disposing of this concentrated saline solution poses challenges related to contamination, high pressure, and degradation of reverse osmosis membranes¹¹⁻¹³.

Chemical denitrification using zero-valent minerals has garnered significant interest due to its simplicity, relatively low cost, high efficiency, and the ability to convert pollutants into less harmful forms^{14, 15}. Besides zero-valent iron (ZVI), other zero-valent metals such as aluminum (Al⁰), copper (Cu⁰), zinc (Zn⁰), and magnesium (Mg⁰) have been tested for nitrate reduction. Zero-valent iron (ZVI) has been the most researched and applied due to its affordability and widespread availability. Acidic conditions are often used to enhance the efficiency of ZVI in nitrate reduction; however, adding acids may increase operational costs and anion content in liquid waste, posing health risks. The following Eqs. 1, 2, 3 and 4. illustrate the reaction between zero-valent iron and nitrate residues^{16, 17}.



It has been demonstrated that using zero-valent iron nanoparticles (nZVI) enhances the performance of the process because Nano-sized particles have a large surface area due to their small size, leading to higher efficiency compared to micron-sized iron particles, several studies have explored the possibility of supporting nano-sized particles with carrier materials such as activated carbon, graphene, and biochar^{18, 19}.

Materials and Methods

Zero iron Fe⁰ with a grain size of 100-125µm and purity of 98% from Kanto Chemical Co., Japan, each of sodium nitrate NaNO₃ with a purity of 99%, hydrochloric acid HCl with a purity of 38%, sodium hydroxide NaOH with a purity of 99%, ferric

These carriers help reduce oxidation and aggregation of zero-valent metals, especially nano-sized ones, by interacting with other substances in water, thus maintaining their activity and effectiveness in nitrate removal. Noble metals like gold, platinum, palladium, and copper have also been used to form bimetallic catalysts that promote nitrate reduction with zero-valent iron and make it more selective in producing nitrogen gas instead of harmful ammonium by products^{20, 21}.

The major concern associated with -mediated nitrate reduction by Fe⁰ is the generation of ammonium as an end product. Besides, the iron corrosion products (lepidocrocite, goethite, akaganeite, maghemite, and siderite) have been deemed to cause passivation of Fe⁰ ²². The successful treatment of nitrate by Fe⁰-based systems depends on how long the surface reactivity of Fe⁰ can be retained and how well ammonium production can be minimized²³.

The utility of silica minerals for reducing surface passivation of Fe⁰ has been demonstrated in a previous study in which the rate-enhancing effect of the minerals was attributed to the scavenging of the reaction precipitates. So the use of clay minerals in combination with Fe⁰, especially those with high adsorption capacity for cations, can be beneficial for reducing iron passivation²⁴.

Recently, it was reported that the use of pillared bentonite in combination with Fe⁰ substantially enhanced nitrate removal and suggested ferrous iron scavenging by bentonite as one of the reasons for the enhanced removal. Besides, another anticipated role of clay minerals in Fe⁰-based nitrate treatment is that they could serve as an adsorbent for ammonium because of the negative charge on the surface in near-neutral and alkaline conditions^{25, 26}.

Because of there is no previous study on the use of Syrian clay as an enhancer for removing nitrates with zero iron, this study was conducted to remove nitrate by Fe⁰ then demonstrate the importance of raw clay, activated clay by the acid method and activated clay loaded with Fe⁰ particles in removing nitrate to avoid the release of ammonium ions and maintaining the effectiveness of Fe⁰ particles by eliminating the problem of surface passivation.

chloride hexahydrate FeCl₃.6H₂O, and sodium borohydride NaBH₄ were brought from National Medicines Corporation Ltd.

-Raw Clay

Raw clay was obtained from the Wadi Al-Zakara region in Syria. The raw clay sample was ground using a porcelain mill with balls of different sizes, and particles smaller than 63µm were isolated using a standard sieve, chemical composition of the raw clay was determined using X-ray fluorescence (XRF) analysis (McScience Co.), crystal phases were identified using X-ray diffraction (XRD) with a nickel filter and Cu K_{α1} radiation (λ=1.5405Å) from a (BRUKER AXS Diffractometer D8).

-Activated Clay

Activated clay was prepared by adding 3N hydrochloric acid to the clay at a ratio of acid to clay (1:10) with heating at 60°C and stirring for 3 hours using a magnetic stirrer. After treatment, the clay was filtrated, washed with distilled water then dried at 105°C.

-Modified Clay with Iron Nanoparticles

Activated clay loaded with iron nanoparticles was prepared according to the following stages:

- 10g of activated clay was dispersed in 200ml of deionized water using ultrasonic waves to obtain a stable suspension.
- 48.214g of ferric chloride hexa hydrate FeCl₃·6H₂O (equivalent to 10g of Fe) was dissolved in 100ml of deionized water, then added gradually to the suspended activated clay with rapid stirring using a mechanical stirrer.
- 20g of sodium borohydride NaBH₄ was dissolved in 25ml of deionized water.
- Sodium borohydride solution was gradually added dropwise to the activated clay suspension with ferric chloride, with continuous and rapid stirring until the complete addition of the sodium borohydride solution (20min).
- Stirring was continued for an additional 30min to ensure complete reduction of ferric ions. During the addition, the reduction reaction illustrated in Eq. 5. occurred, resulting in nano iron particles loaded on the surface and pores of the activated clay, turning the color into dark black:
$$4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^0 + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2 \dots \dots \dots 5$$
- The modified clay was separated by filtration, washed several times with absolute alcohol, and dried at a temperature of 105°C.
- Crystal phases were identified using X-ray diffraction (XRD), Scanning electron microscopy (SEM) photographs of modified clay, were obtained using a Philips-FEI XL30

ESEM-TMP (Philips Electronics Co., Eindhoven, Netherlands). Photographs of samples were recorded at various magnifications at an operating voltage of 5 kV.

Effect of pH in Nitrate Removal by Zero-valent Iron

The study was conducted by preparing a solution of nitrate with a concentration of 150ppm (an optional value for the study), by dissolving 0.20g sodium nitrate NaNO₃ in 1liter. 100 ml of the nitrate solution (150 ppm) was taken, and the pH value of the solution was adjusted to different values using hydrochloric acid 1N and sodium hydroxide 1N solutions according to the following values: pH = 2, 3, 4, 5, 6, 7, 8, 9, 10, pH of solution was measured using a pH meter (Horiba, Ltd. Kyoto, Japan).

0.5 g of zero-valent iron was added to each nitrate solution, and the solution was stirred for 120 minutes using a mechanical stirrer at a rotation speed of 150 rpm within the laboratory temperature (25°C). The sample was filtered, the remaining nitrate concentrations and removal percent were determined by spectrophotometer method (DR4000/HACH, USA).

Effect of Zerovalent Iron Amount in Nitrate Removal

To investigate the impact of the added amount of zero-valent iron on treatment effectiveness, the dose of zero-valent iron added was increased. Quantities of 0.5, 1, 2, 3, 4, 5 g were added to 100ml nitrate solution, while maintaining the initial acidity at the best level according previous step.

Effect of Treatment Time in Nitrate Removal

To study the impact of treatment time on the effectiveness of treatment using zerovalent iron, treatment time was increased to 180, 240, 300, 360 minutes while keeping the initial pH and amount of zerovalent iron at the best level according previous step.

Effect of Clay (Raw, Activated, Modified) in Nitrate Removal

100ml of prepared nitrate solution was taken and amount of zerovalent iron (the best according previous step) was added to it. Different doses of clay (1, 2, 3, 4, 5, 6) gr were added to solution, stirred using a mechanical stirrer at a rotation speed of 150 rpm at room temperature (25°C). Samples were taken from the treated solution after 120 minutes, filtered using a 0.45µm filter, then nitrate was determined,

ammonia content in the solution was determined using Nessler's method with UV/Vis spectrophotometer (DR4000/HACH, USA).

Results and Discussion

Characterization of Clay (Raw, Activation, Modified with Nano Fe)

Chemical analysis of the raw clay revealed a high Percent of silicon dioxide SiO_2 at 47.44%, which is the main component in accordance with the siliceous structure of clays. Aluminum oxide Al_2O_3 accounted for 19.25% of the studied clay components. Chemical analysis was performed to determine the effectiveness of treatment and specifications of the resulting activated clay, showing improved characteristics and reduced impurity levels Table 1. XRD patterns of raw clay in Fig. 1 showed that it contains kaolinite as the major mineral, illite, quartz, the peaks for kaolinite, illite and quartz still occur in the XRD pattern of activated clay and modified clay Fig. 2, additionally were two peaks in modified clay at 44.7° , and 65.2° , These were characteristic peaks of Fe^0 and are consistent with the results of previous studies²⁴. This indicates that Fe^0 nanoparticles were successfully synthesized and supported on the activated clay.

Scanning electron microscopy (SEM) photographs of activated clay, modified clay in Fig. 3 showed that activated clay is a kind of schistose, mineral sheet, and there are small plentiful, irregular and acicular crystals. There were many black granules among the schistose, sheet interlamination, which were synthesized Fe^0 nanoparticles, the diameter of Fe^0 nanoparticles ranged from 50 to 120 nm, the objective was to prepare iron nanoparticles on the surface and pores of the clay to preserve the nanoparticles from agglomeration, this was the scanning electron microscope images showed.

Table 1. Chemical composition of clay (raw, activated).

compound	raw clay%	activated clay%
SiO_2	47.44	55.01
Al_2O_3	19.25	23.47
Fe_2O_3	8.5	3.81
MgO	1.79	0.77
CaO	6.18	0.89
Na_2O	0.19	0.01
K_2O	2.35	0.11
L.O.I	13.05	7.47

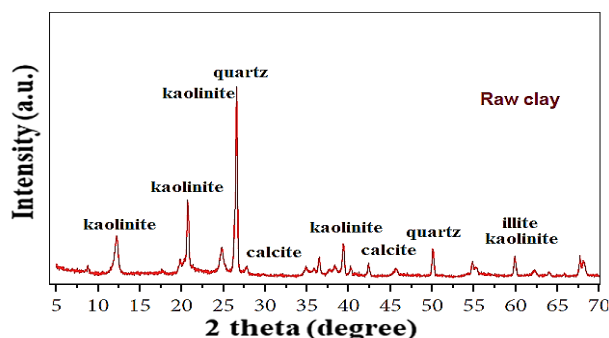


Figure 1. XRD spectrum of raw clay.

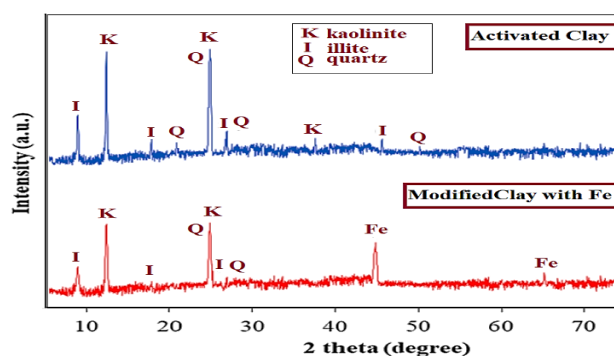
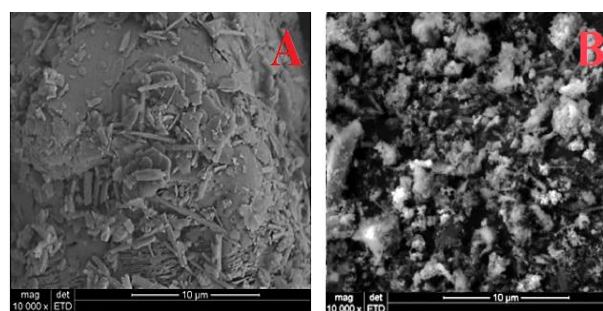


Figure 2. XRD spectrum activated clay and modified clay.



A- activated clay

B- activated clay with Fe^0 nanoparticles

Figure 3. Scanning electron microscopy (SEM) of activated clay, activated clay with Fe^0 nanoparticles.

Effect of pH on Nitrate Removal by Zero-valent Iron

The analysis results in Table 2. and Fig. 4 indicated that nitrate removal by zero-valent iron is significantly affected by the pH level, and nitrate removal decreased with increasing initial pH, as the percentage decreased from 72.67% at $\text{pH} = 1$ to

13.33% at pH =8, therefore treatment requires an acidic medium with a pH of 4 or less, because in neutral or alkaline conditions, iron hydroxides and iron corrosion products are formed on the surface of the particles (it were appeared as yellowish-brown sediments and suspensions) which limits the continuation of the reaction and reduces the quality of treatment, that was consistent with the previous study^{14,15}.

Table 2. Effect of pH on treatment efficiency using zero iron.

Sample	pH	Initial NO ₃ ⁻ ppm	Final NO ₃ ⁻ ppm	removal rate % 100*{(C ₀ -C)/C ₀ }
1	2	150	41	72.67
2	3	150	49	67.33
3	4	150	62	58.67
4	5	150	85	43.33
5	6	150	97	35.33
6	7	150	101	32.67
7	8	150	121	19.33
8	9	150	130	13.33

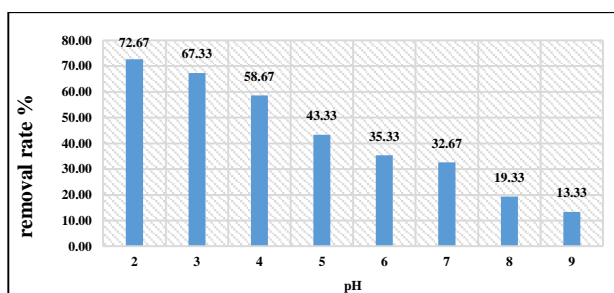


Figure 4. Effect of pH on treatment efficiency using zero iron.

Effect of Zerovalent Iron Amount in Nitrate Removal

After analysis, the results are shown in Table 3. and Fig. 5. It was found that the treatment effectiveness was related to the amount of zero-valent iron added, and the removal rate was 67.33% when treated with 0.5g Fe⁰, this percentage increased gradually as the amount of added Fe⁰ increased until it reached to 80% when treated with 4g where it remained almost constant when a larger amount was added. this was because the large quantities of iron corrosion products that passivated surface of Fe⁰. Therefore, it can be considered that an amount of 4g per 100 ml, equivalent to a concentration of 40g/L, was sufficient to obtain good results under the applied conditions.

Table 3. Effect of the amount of zerovalent iron on the treatment efficiency.

Zero iron gr	Initial NO ₃ ⁻ ppm	Final NO ₃ ⁻ ppm	Removal rate % 100*{(C ₀ -C)/C ₀ }
0.5	150	49	67.33
1	150	44	70.67
2	150	40	73.33
3	150	32	78.67
4	150	30	80.00
5	150	29	80.67

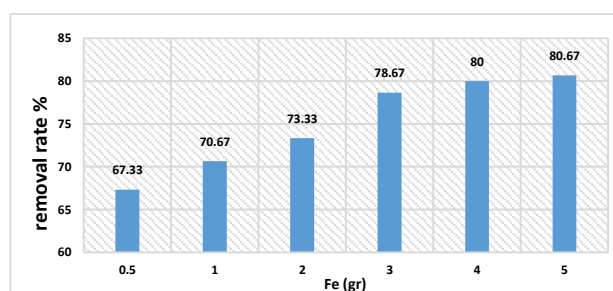


Figure 5. Effect of the amount of zerovalent iron on the treatment efficiency.

Effect of Treatment Time on Nitrate Removal

Treatment efficiency increased with increasing time, as it increased from 80% when treating for 120min to 91.33% at 240 min. The increase weakened after this time, despite the formation of iron corrosion products that caused passivation of the surface Fe⁰, increasing the treatment time contributed to greater contact between the surfaces Fe⁰, which was still active and nitrate ions in the solution, which led to the reduction of an additional portion of them. So, the most of the nitrate removal occurs within the first 120 min of treatment under the experimental conditions applied in this study Table 4. and Fig.6.

Table 4. Effect of treatment time on nitrate removal by zerovalent iron.

Treatment time min	Initial NO ₃ ⁻ ppm	final NO ₃ ⁻ ppm	removal rate % 100*{(C ₀ -C)/C ₀ }
120	150	30	80.00
180	150	22	85.33
240	150	18	88.00
300	150	13	91.33
360	150	9	94.00

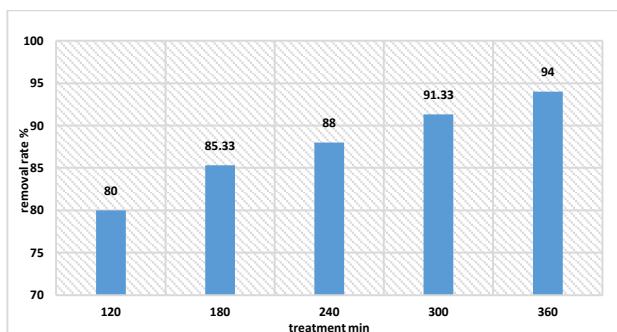


Figure 6. Effect of treatment time on nitrate removal by zerovalent iron.

Effect of Adding Clay (Raw, Activated, Modified) in Nitrate Removal

The results in Table 5. and Fig. 7 showed that when raw clay is added, the treatment efficiency decreases, as the removal percentage decreases from 65.33% to 47.33% when the added clay increases from 1 gr to 6gr, respectively. The apparent alkalinity of the raw clay caused an increase in pH to 8, which inhibited reaction of Fe⁰ with nitrate, as was discussed in this research.

When adding activated clay or modified clay, the removal efficiency increases with increasing dosage, because the alkaline nature of the raw clay was removed through activated with acid. Therefore, it will not cause an increase in the pH during treatment, which allowed the continuous reaction, the iron corrosion products were adsorbed on the surface of clay, and these made the surface Fe⁰ more active,

removal percentage increased from 74.00% to 84.66% when activated clay was increased from 1gr to 6gr, respectively.

When using modified clay, it increased from 82.66% to 95.33% by increasing the dose from 1gr to 6gr, respectively. It was noticed that modified clay has given a much better result because the FeO nanoparticles have a higher effectiveness and a larger specific surface area, due to their small size, which limits the effect of iron corrosion products on surface passivation.

As for ammonium ions, their concentration decreases with the increase in the dose of added clay in all its raw, activated and modified forms, as they become adsorbed on the surface of the clay or leave the solution in the form of ammonia.

Adding 5 grams of clay (raw, activated, and modified) was sufficient to reduce the percentage of nitrate and ammonium within the permissible limits according to Syrian Standard No. 45/2007 for drinking water.

The most important positive aspect of using clay modified with nano-iron is reducing the amounts needed for treatment with a higher degree of effectiveness. For example, when it was treated with activated clay and zero iron, 5 grams of activated clay with 4 grams of zero iron (4 + 5 = 9 grams) were used to obtain a percentage Removal of 84.00%, but when using modified clay by adding only 5 grams, the removal rate was 94.66%.

Table 5. Removal of nitrate by Fe⁰ in the presence of clay (raw, activated, modified).

Clay type	Clay weight gr	Initial NO ₃ ⁻ ppm	Final NO ₃ ⁻ ppm	removal rate % 100*{(C ₀ -C)/C ₀ }	Final NH ₄ ⁺ ppm
Natural clay	1	150	52	65.33	19
	2	150	57	62.00	6
	3	150	66	56.00	2
	4	150	69	54.00	1.6
	5	150	75	50.00	0.7
	6	150	79	47.33	0.6
Activated clay	1	150	39	74.00	12
	2	150	35	76.66	4
	3	150	30	80.00	1.3
	4	150	28	81.33	0.9
	5	150	24	84.00	0.6
	6	150	23	84.66	0.6
Modified clay	1	150	26	82.66	10
	2	150	20	86.66	4
	3	150	14	90.66	0.9

4	150	11	92.66	0.3
5	150	8	94.66	0.2
6	150	7	95.33	0.2

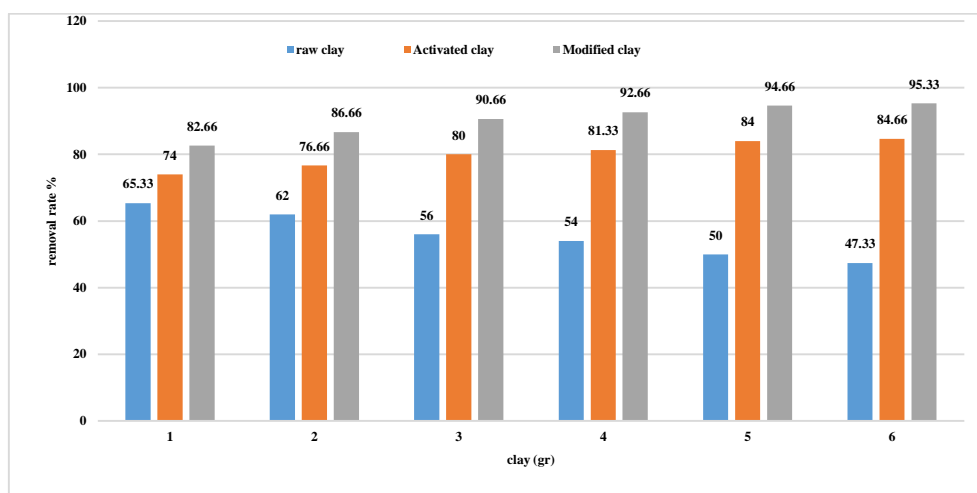


Figure 7. Nitrate removal by Fe^0 in the presence of natural and activated clay (raw, activated, and modified).

Conclusion

- 80% of nitrate ions in water can be removed by using zero iron at a concentration of 40 g/L with $4 \geq \text{pH}$ for 120 min at room temperature, these conditions are suitable for treating water containing nitrate up to 150 ppm.
- Adding raw clay reduces the efficiency of removing nitrates by Fe^0 , due to its alkaline properties, which caused a rise in pH, which led to the inhibition reaction of Fe^0 with nitrates.
- Acid-activated clay led to an increase in nitrate removal by increasing dosage, which it increased from 74.00% to 84.66% when the activated clay was increased from 1 gram to 6 grams per liter of water, respectively
- Adding clay modified by iron nanoparticles at a ratio of (1:1) to remove nitrates has given greater effectiveness than raw clay and acid-activated clay. The removal rate increased from 82.66% to 95.33% by increasing the dose from 1 gram to 6 grams, respectively.
- Ammonium was decreased with increase the dose of the added clay in all its forms (raw, activated and modified), which adsorbed on the surface of the clay or leave the solution in the form of ammonia.
- Adding 5 gr of clay (raw, activated, and modified) was sufficient to reduce the percentage of nitrate and ammonium within the permissible limits according to Syrian Specification No. 45/2007 for drinking water.

Acknowledgment

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Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been

- included with the necessary permission for republication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.

- No potentially identified images or data are present in the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee at University of Aleppo, Aleppo, Syria.

Authors' Contributions Statement

M. B. conducted laboratory experiments and interpreting the results. M H. H. and N. N. made revising and correcting.

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تأثير إضافة الغضار على إزالة النترات من المياه الجوفية بواسطة الحديد صفري التكافؤ

معن بيطار¹، محمد هيثم حبوب¹، نوزت النبغلي²

¹قسم الهندسة البيئية، كلية الهندسة المدنية، جامعة حلب، حلب، سوريا
²قسم العلوم الأساسية، كلية الهندسة المدنية، جامعة حلب، حلب، سوريا.

الخلاصة

تعتبر طريقة إزالة النترات من الماء باستخدام المعادن صفيرية التكافؤ من الطرائق التي تثبت فعاليتها العالية يوماً بعد يوم، وخاصةً الحديد صفيري التكافؤ. إلا أن أبرز العوائق التي تشكل عقبةً أمام الاستمرار باستخدامه هي تعرض سطحه للتخميل أثناء التفاعل، وتشكل أيونات الأمونيوم كمنتج رئيسي لاختزال النترات تحت ظروف المعالجة. تم في هذا البحث دراسة تأثير الغضار أثناء إزالة النترات بواسطة الحديد الصفيري، تم استخدام الغضار الخام والغضار المنشط بالطريقة الحمضية والغضار المعدل بجسيمات الحديد النانوية بنسبة (1:1). أظهرت النتائج أنه يمكن إزالة 80% من أيونات النترات الموجودة في الماء باستخدام Fe⁰ بتركيز 40g/L مع pH ≤ 4 لمدة 120 دقيقة عند درجة حرارة الغرفة، كما أن إضافة الغضار الخام يقلل من الكفاءة بسبب خواصه القلوية مما أدى إلى لتفاعل تثبيط تفاعل Fe⁰ مع النترات. بينما أدى الغضار المنشط بالحمض إلى زيادة إزالة النترات بزيادة الجرعة المضافة. كما أعطى الغضار المعدل فعالية أكبر من الغضار الخام والغضار المنشط بالحمض، وزادت نسبة الإزالة إلى 95.33% تحت ظروف المعالجة المطبقة. بينما تم تخفيض الأمونيوم مع زيادة الغضار المضاف بجميع أشكاله (الخام والمنشط والمعدل). وأخيراً لوحظ أن إضافة 5 غرام/لتر من الغضار (الخام، المنشط، المعدل) كانت كافية لتخفيض نسبة النترات والأمونيوم للحدود المسموح بها حسب المواصفة السورية رقم 2007/45 لمياه الشرب.

الكلمات المفتاحية: الغضار المنشط، الغضار الطبيعي، تلوث الماء، معالجة الماء، الحديد الصفيري.