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Design a Treatment Unit to Remove Nitrates from Groundwater Using Waste of Zero Iron

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Abstract - In this study, a treatment unit was designed to remove nitrate ions from groundwater using zero iron taken from waste of industrial workshops. The various conditions for the nitrate return reaction with zero iron were studied and the best conditions of batch system were determined to obtain a high removal yield, which was to conduct the treatment in an acidic medium pH =2 and add. Zero iron, with a granular size of 75µm, at a concentration of 8g/L for 120 min at normal temperature, where the removal rate reached more than 93% when using synthetic water with an initial nitrate concentration of 150ppm.

The continuous treatment unit for removing nitrates in the research gave high effectiveness, as the unit includes a tank for removing nitrates with zero iron within the conditions that were deduced, followed by a tank for removing ammonium ions resulting from the first stage, then a filtration stage using a sand filter, and finally a tank for mixing the treated water with quantities determined from untreated raw water to obtain an appropriate residual level of nitrate ions.

The proposed treatment unit was used in this research to treat a sample of well water containing 64 parts ppm of nitrates. The proposed treatment unit confirmed its effectiveness in treatment, as the nitrate concentration decreased to 38 ppm and was almost free of ammonium. The by-products of the treatment did not affect the Water specifications were greatly compared to the standard drinking water specifications issued by the World Health Organization.

Key Words:
Groundwater,
Nitrates,
Reduction**,**
Water treatment,
Zero iron**.**

تصميم وحدة معالجة لإزالة النترات من المياه الجوفية باستخدام مخلفات الحديد الصفري

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المستخلص - في هذه الدراسة تم تصميم وحدة معالجة لإزالة أيونات النترات من المياه الجوفية باستخدام الحديد الصفري المأخوذ من الورش الصناعية. تمت دراسة الظروف المختلفة لتفاعل عودة النترات مع صفر حديد وتم تحديد أفضل الظروف لنظام الدفعة للحصول على ناتج إزالة عالي والذي يتمثل في إجراء المعاملة في وسط حمضي 3 = pH وإضافة الحديد الصفري، بحجم حبيبي 75 ميكرومتر، بتركيز8 غم/لتر لمدة 120 دقيقة عند درجة الحرارة العادية، حيث وصلت نسبة الإزالة إلى أكثر من 93 %عند استخدام المياه التركيبية بتركيز نترات أولي ppm 150. أعطت وحدة المعالجة المستمرة لإزالة النترات في البحث فعالية عالية، حيث تشتمل الوحدة على خزان لإزالة النترات بصفر حديد ضمن الشروط التي تم استخلاصها، يليه خزان لإزالة أيونات الأمونيوم الناتجة من المرحلة الأولى، ثم تصفية مرحلة استخدام مرشح رملي، وأخيراً خزان لخلط المياه المعالجة بكميات محددة من المياه الخام غير المعالجة للحصول على مستوى متبقي مناسب من أيونات النترات. تم استخدام وحدة المعالجة المقترحة في هذا البحث لمعالجة عينة

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من مياه الآبار تحتوي على 64 ppm من النترات. أكدت وحدة المعالجة المقترحة فعاليتها في العلاج، حيث انخفض تركيز النترات إلى38 ppm وكانت خالية تقريباً من الأمونيوم. لم تؤثر نواتج المعالجة الثانوية على مواصفات المياه بشكل كبير مقارنة بالمواصفات القياسية لمياه الشرب الصادرة عن منظمة الصحة العالمية

الكلمات المفتاحية: النترات، الحديد الصفري، معالجة المياه، المياه الجوفية، الارجاع.

Introduction

Long-term exposure to high levels of nitrates poses varying degrees of risk to human health. Nitrates may cause the conversion of hemoglobin in the blood into methemoglobin in infants, which is also known as “blue baby syndrome,” because methemoglobin is unable to bind oxygen and causes lack of cerebral oxygen, and nitrates cause the formation of N-nitrosamines, which are considered cancer-causing compounds. For this reason, The International Agency for Research on Cancer (IARC) has classified ingested nitrates and nitrites as potentially carcinogenic to humans (Elisante *et al*., 2017; Xin *et al*.,2021; Muhib *et al*., 2023; van den *et al*., 2020). Nitrate is removed from water by biological denitrification, ion exchange, nanofiltration (NF), and reverse osmosis (Fernández *et al*. 2023) and (Sultan *et al*., 2022).

Although biological denitrification is widely applied to remove nitrogen from wastewater and is relatively inexpensive, the long treatment time required and the sludge production that requires safe disposal represent important limitations to its application to drinking water (Amaia *et al*., 2022). Ion exchange processes also produce waste in the form of brine that requires subsequent treatment, with additional costs (Alguacil *et al*., 2022). One of the most problematic features of NF nanofiltration ،as in any membrane separation process, is the phenomenon of waste, clogging of membranes and the difficulty of cleaning them. Nitrate is partially removed by nanofiltration because it a monovalent anion (Abayie and Leiviskä, 2022).

Reverse osmosis allows the concentration of a pollutant in a brine solution without modifying its molecular structure, and is suitable for drinking water **(** Li *et al*., 2017). Ion exchange processes also produce waste in the form of brine that requires subsequent treatment, with additional costs (Alguacil *et al*., 2022). One of the most problematic features of NF nanofiltration ،as in any membrane separation process, is the phenomenon of waste, clogging of membranes and the difficulty of cleaning them. Nitrate is partially removed by nanofiltration because it a monovalent anion]8[. Reverse osmosis allows the concentration of a pollutant in a brine solution without modifying its molecular structure, and is suitable for drinking water (Li *et al*. , 2017) and (Ibrahim, 2022).

However, disposal of the concentrated brine poses an important problem and obstacle to the application of this technology. Moreover, reverse osmosis membranes are exposed to problems of contaminant accumulation, pressure and damage (Nam, 2000).

Chemical removal Nitrogenation through zero-valent metals has received great interest due to its many advantages, such as simplicity of application and control, relatively low costs, high efficiency, and the possibility of converting pollutants to less hazardous forms. Therefore, many zero-valent substances have been tested such as iron zero-valent iron ZVI, aluminum ZVA magnesium ZVM, copper ZVC ،and inc ZVZ(Nam 2000).

Zero-valent iron ZVI is of most interest to researchers among other zero- valent metals , it is cheap, easily available, and highly abundant ZVI has been applied to remove a variety of pollutants, such as heavy metals, dyes, chlorinated organic compounds, and nitrates Al-Naemi *et al*., (2021). In general, to enhance the reactivity of iron, nitrate is recovered under acidic conditions Huang *et al*., (1998). However, the addition of acids may result in higher operating costs and increased anion content in the effluent, which may pose a health risk. The following equations show the reaction between zero iron and nitrate ions (Siciliano *et al*., 2019):

$4Fe + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$ (1)
$5Fe + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + N_2 + 12OH^-$ (2)
$Fe + NO_3^- + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$ (3)
$3Fe + NO_2^- + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O$ (4)

The aim of this study is to determine the best conditions for designing a treatment unit to remove groundwater pollution with nitrates using zero iron resulting from waste and widespread iron workshops.

Materials and Methods

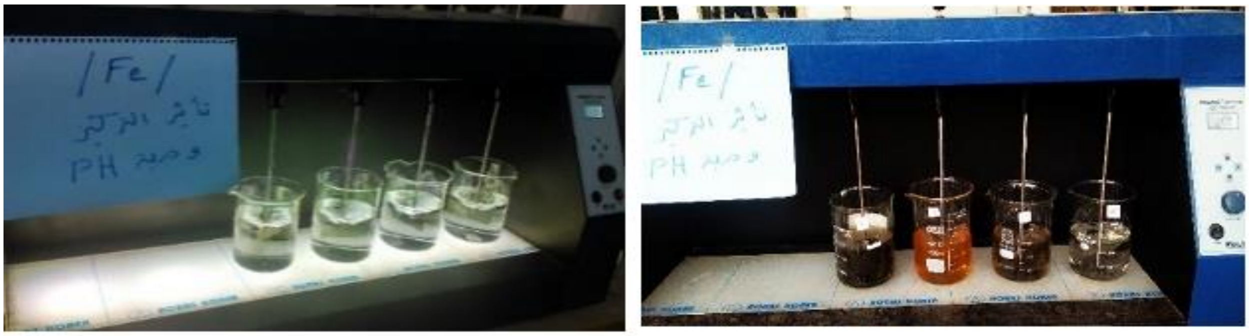
Collecting Samples of Iron Waste and Purifying them

Samples of iron filings resulting from industrial workshops in the city of Aleppo were collected, then a process of purifying and revitalizing the surface of the granules was carried out with the aim of getting rid of the oxide and rust layers on the surface of the iron granules by treating them with diluted hydrochloric acid with a concentration of 5% for 10 minutes with gentle stirring and heating less than 50°C, then washing with distilled water, followed by washing with acetone to remove water to avoid subsequent oxidation, and finally drying at 50˚C Then, granular sorting of the pure powder was carried out, and the samples were kept in tightly sealed containers, away from moisture. To perform the necessary chemical analysis.

A chemical analysis of pure iron filings was carried out by taking 1gr of the iron sample and dissolving it in concentrated hydrochloric acid with heating and stirring until complete dissolution. Then the solution was diluted to 100ml using a standard flask and a sample was taken from it and its concentration was determined spectrophotometrically using a Lovibond spectrophotometer using standard reagents. The final analysis result indicated that the purity of the iron grains was 99%.

Effect of pH on Removal of Nitrates by Fe^0

The study was carried out by preparing a standard solution of nitrate ions, based on the pure sodium nitrate $NaNO_3$, where a solution with a concentration of 150ppm of nitrate ions was prepared (optional value for the study, taking 500ml of nitrate solution 150ppm and the pH value of the solution was adjusted at different values using diluted hydrochloric acid and sodium hydroxide solution according to the following values pH= 2, 3, 4, 5, 6, 7, 8, 9, 10. Then 0.5gr of zero iron was added to each solution. The concentration became 1g/L with granular size of less than 100µmThe solution was stirred for 60 min, as in Figure 1. The sample was filtered, then the percentage of remaining nitrate ions and the percentage of removal were determined by the color spectrophotometric method using a Lovibond device and standard detectors of nitrate ions for the high range 4-130 ppm.



(Figure 1) W aterTreatment by Fe^0

Effect of Fe^0 Concentration on Nitrate Removal

To study the effect of zero iron concentration on the effectiveness of treatment, increasing amounts of zero iron less than 100µm were added. For the prepared nitrate solution prepared to obtain concentrations 1, 2, 4, 6, 8, 10 g/L, the pH was set at pH=2, and the treatment was carried out for 60 min.

Effect of Treatment Time on Removal Nitrate by Fe^0

To study the effect of the added treatment time on the effectiveness of treatment using zero iron, treatment was carried out for increasing periods of time 60, 120, 180, 240 min. With the pH fixed at pH=2, the zero iron concentration is 8g/L and the particle size is less than 100µm .

Effect of the Grain Size of Fe^0 on Nitrate Removal

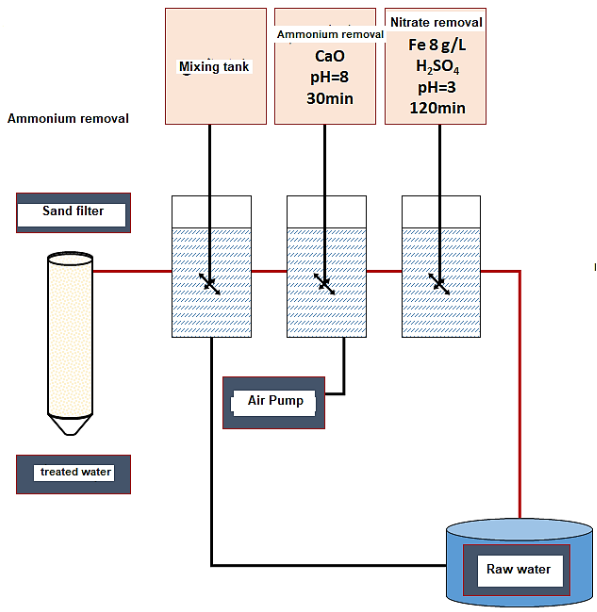
To study the extent to which the particle size of zero iron affects the effectiveness of treatment, zero iron was treated with different granular sizes (300, 200, 100, 75, 25) µm with stabilization and the pH was fixed at pH=2, zero iron concentration 8g/L, treatment time 120min.

Effect of Temperature on Nitrate Removal by Fe^0

The extent of the effect of temperature on the effectiveness of the treatment was studied by adjusting the temperature by placing the reaction vessel in a water bath and heating with an electronic electric heater until the desired temperature was reached and maintained. The following temperatures were studied (25, 40, 60, 80)˚C with fixation. Optimal conditions according to previous experiences.

Design a Treatment Unit to Remove Nitrates

After conducting experiments and determining the best conditions for removing nitrates with zero iron, work was done to design an integrated treatment unit consisting of the stages shown in Figure 2. The raw water is taken to a denitrification tank where the appropriate amount of zero iron is added and the pH was adjusted by adding sulfuric acid 5N pH =3 with stirring for 120 min, then the water moves to the ammonium removal tank, where it represents the main product of nitrate recovery under the applicable conditions. The pH value in this tank is adjusted to pH =8 by calcium oxide, where the ammonium ions are converted to NH_4^+ To ammonia NH_3 Which is expelled by pumping air and stirring for 30 min. Then, the water moves to a sand filter to get rid of the products of the treatment process and then finally to the mixing tank where it is mixed with an equivalent percentage of untreated raw water which is added according to the percentage of nitrates in the raw water and the degree of removal to be achieved.



(Figure 2) The proposed groundwater nitrate removal unit

A one-liter sample of well water from Aleppo contained nitrate ions at a concentration of 64 ppm. To this sample, 5N sulfuric acid was added until the pH reached 3, followed by 8 grams of zero-valent iron with a granular size of 75 µm. The sample was stirred with a mechanical mixer for 120 min, then the sample was left for layering, then transfer it to another beaker and add calcium oxide to it until pH=8, with stirring and pumping air bubbles with an air pump. The process continued for 30 min. The sample was filtered using a column containing fine sand so that the height of the liquid column was 4 times the height of the sand, which is an experimental value that was adopted. After several experiments that achieved good filtration speed and efficiency, 1 liter of untreated raw well water was added to the filtered water and mixed. A chemical analysis was then conducted to assess the characteristics of the water sample before and after treatment.

Results

Table 1 shows the results of measuring the concentration of nitrate ions and the treatment efficiency using different pH levels.

It is noted from the results of the analysis that the removal of nitrates with zero iron is greatly affected by the degree of acidity of the medium, so the degree of removal of nitrate ions decreases with the increase in the initial pH value. Using zero iron for treatment requires an acidic medium pH=4 or less, while the moderate or alkaline medium is not suitable for treatment due to its low The removal rate and these results are consistent with the reference studies (Alguacil *et al*., 2022), (Siciliano *et al*., 2019).

(Table 1) Effect of pH removal nitrate by Fe^0

pH	NO_3^- Final ppm	% Removal rate 100*{(C_0-C)/C_0}
2	41	72.67
3	49	67.33
4	62	58.67
5	85	43.33
6	97	35.33
7	101	32.67
8	121	19.33
9	130	13.33

The results in Table 2 demonstrate that the effectiveness of the treatment is linked to the concentration of zero-valent iron. As the concentration increases, the contact surface area between the iron and nitrate ions also increases, enhancing the reaction intensity and resulting in a higher removal rate. The final nitrate concentration dropped below 50 ppm, aligning with WHO standards for drinking water. However, concentrations above 8 g/L did not significantly improve efficiency under the studied conditions, making 8 g/L the most suitable concentration for this treatment.

(Table 2) Effect of Fe0 removal nitrate

Fe^0concentration gr/L	NO_3^- Final ppm	% Removal rate 100*{(C_0-C)/C_0}
1	49	67.33
2	44	70.67
4	40	73.33
6	32	78.67
8	30	80.00
10	29	80.67

Results in Table 3 showed that the effectiveness of the treatment increases significantly with increasing treatment time, but the treatment lasted for 120 minutes. Sufficient, after which the removal rate increases to a small degree, so 120 minutes is sufficient for treatment.

Table 3. Effect of treatment time on nitrate removal by Fe^0

Treatment Time min	NO_3^- Final ppm	% Removal rate 100*{(C_0-C)/C_0}
60	32	78.67
120	16	89.33
180	15	90.00
240	11	92.66

Effect of particle size of Fe0 on nitrate removal in Table 4, showed the effectiveness of the treatment is related to the granular size of the zero iron used in the treatment as a result of the change in the contact surface between the iron and the nitrate ions. It can be considered that the best size is 75 µm because the work has a granular size. A smaller dose is associated with a slight increase in treatment effectiveness.

(Table 4) Effect of particle size of Fe^0 on nitrate removal

Granular size of Fe^0 µm	NO_3^- Final ppm	% Removal rate $100*\{(C_0-C)/C_0\}$
300	89	40.67
200	67	55.33
100	32	78.67
75	10	93.33
25	8	94.66

It has been observed from Table 5 that the rate of nitrate removal increases with an increase in temperature as a result of activating the reaction, but this increase is accompanied by several negative aspects, the most prominent of which is the economic cost of heating and the increase in water evaporation as a result of the increase in temperature. Therefore, considering the effect of temperature in general, we conclude that there is no need to raise the temperature of the water sample, but it is sufficient to treat it at the normal temperature, as the increase in treatment effectiveness is rather low and is not compatible with the economic cost.

(Table 5) Effect of temperature on nitrate removal

Temperature °C	NO_3^- Final ppm	% Removal rate $100*\{(C_0-C)/C_0\}$
25	10	93.33
40	7	95.33
60	4	97.33
80	2	98.66

The results were according to Table 6, where the results showed the effectiveness of the applied method, so the nitrate concentration decreased to 8ppm, with a small percentage of ammonia amounting to 0.4ppm, in addition to identical values of electrical conductivity (EC), dissolved solids (TDS) and sulfates. With the WHO standard specification for drinking water, the focus was on these indicators because the additives that were used during treatment mainly affect these indicators.

(Table 6) Specifications of raw and treated water samples

Amount	symple	WHO standars	Raw water	Aftertreatment
pH	pH	6.5 – 9	7.3	7.7
Nitrates	NO_3^-	50 mg/l	64	38
Ammonia	NH3	0.5 mg/l	1	0.4
Sulfates	SO_4^{2-}	500 mg/l	122	160
Turbidity	NTU	5	11.3	2
Iron	Fe	1 mg/l	0	0.2
Suspended Solid	SS	10 mg/l	22	7
Total dissolved salts	TDS	1200 mg/l	355	477
Electrical conductivity	EC	1500 µS/cm	585	781
Chemical need for oxygen	COD	3mg/l	28	1
Biological need for oxygen	BOD_5	2mg/l	17	0.5

Discussion

Some points must be noted:

Sulfuric acid and calcium oxide were chosen to adjust the pH of the medium because they cause the formation of calcium sulphate as a by-product of treatment, which is a salt with low solubility that precipitates and is removed by filtration using a sand filter in the last stage. It does not significantly affect the value of conductivity and dissolved solids as stated in the analysis of the treated water. While choosing hydrochloric acid and sodium hydroxide leads to the formation of highly dissolved sodium chloride and thus causes an increase in the value of electrical conductivity and dissolved solids to high values that negatively affect the properties of the treated water.

In the ammonium removal stage, when the pH is set to 8 these conditions lead to the precipitation of iron ions in the form of poorly soluble hydroxides that appear in orange color within the treatment medium. These materials play a positive role as they are among the coagulants that reduce water pollution and are disposed of in the sand filtration stage.
Thus, the concentration of residual iron ions in the aqueous sample after treatment was very small.

Working according to the treatment unit proposed in this research ensures obtaining treated water equivalent to twice the amount of raw water to be treated. When treating a liter of water and adding a liter of raw material to the mixing tank, we ultimately obtain two liters of treated water.

When what is required is to provide 2 liters of treated water, working according to the proposed treatment unit requires using only one liter and then mixing with a liter of untreated water to obtain what is required. This process reduces the proportions of chemicals used in treatment and thus reduces their negative secondary effects.

Conclusions

Conducting the necessary experiments and tests, it became clear that the best conditions for removing nitrates from groundwater using zero iron are to carry out the treatment in an acidic medium pH = 2 and add zero iron with a granular size of 75µm at a concentration of L / 8g for 120min at normal temperature, where the removal rate was more than 93% when using synthetic water with an initial nitrate concentration of 150 ppm.

The treatment unit for removing nitrates proposed in the research gave high effectiveness, through which it is possible to obtain drinking water that contains acceptable levels of nitrates according to the standard specifications and is almost free of ammonium, without the secondary treatment products affecting the water specifications significantly. Drinking water was obtained according to the WHO standars.

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