Preliminary study of the process of nitrate removal optimization from aqueous solutions using Taguchi method.

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Abstract.- One of the most common pollutants in the water is nitrate. High nitrate concentration in water can cause methemoglobinemia in children, and also the formation of carcinogenic nitrosamines. The aim of this study was to optimize the process of nitrate removal from aqueous solutions using the Taguchi method. In this study, the effect of five parameters including adsorbent type, adsorbent amount, contact time, pH and initial concentration of nitrate on nitrate removal efficiency were investigated. The adsorbents used include crushed leaves of palm trees, crushed wheat straw and beech tree wood chips. The range of adsorbents amount used was 1 to 50 g, pH was 5 to 12, the contact time was 1 to 8 hours, and the initial nitrate concentration was 1 to 50 mg/L. The results showed that maximum removal of nitrate was happened with 20 mg/L of initial nitrate concentration at pH = 7, adsorbent mass 30 g and contact time 6 hours. Also, the results showed that nitrate removal efficiency increased with increasing adsorbent mass, initial concentration of nitrate, acidity and contact time to the optimum level, and then decreasing. Also, from the studied adsorbents, crushed leaves of the palm tree have a higher nitrate removal efficiency than other adsorbents.

Keywords: nitrate removal; Taguchi method; palm tree leaves; wheat straw; beech tree wood chips.

Estudio preliminar de la optimización del proceso de remoción de nitrato de soluciones acuosas utilizando el método de Taguchi.

Resumen.- Uno de los contaminantes más comunes en el agua es el nitrato. La alta concentración de éste puede causar metahemoglobinemia en los niños y también la formación de nitrosaminas cancerígenas. El objetivo de este estudio fue optimizar el proceso de eliminación de nitratos de soluciones acuosas utilizando el método de Taguchi. En tal sentido, se investigó el efecto que sobre la eliminación o remoción de nitrato tienen cinco parámetros que incluyen: el tipo de adsorbente, la cantidad del mismo, el tiempo de contacto, el pH y la concentración inicial de nitrato. Los adsorbentes utilizados fueron hojas trituradas de palmas, espigas de trigo triturada y astillas de madera de haya. El rango de cantidad de adsorbentes utilizados fue de 1 a 50 g, el pH fue de 5 a 12, el tiempo de contacto fue de 1 a 8 horas y la concentración inicial de nitrato fue de 1 a 50 mg/l. Los resultados mostraron que la eliminación máxima de nitrato se consiguió con 20 mg/l de concentración inicial a pH = 7, una masa adsorbente de 30 g y un tiempo de contacto de 6 horas. Además, los resultados mostraron que la eficiencia de eliminación de nitrato aumentó con el incremento de la masa adsorbente, la concentración inicial de nitrato, la acidez y el tiempo de contacto hasta el nivel óptimo, y luego disminuyó. Además, a partir de los adsorbentes estudiados, las hojas trituradas de la palmera tienen una mayor eficiencia de remoción de nitratos que otros adsorbentes.

Palabras clave: Remoción de nitrato; método de Taguchi; hojas trituradas de palmas; espigas de trigo trituradas; astillas de madera de haya.

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1. Introduction

One of the most common environmental pollutants in groundwater and surface water is nitrate [1]. High nitrate concentration in water caused methemoglobinemia in children, and also the formation of carcinogenic nitrosamines

[2]. Rupert [3] studies in the United States, showing that in more than 20 % of rural wells, nitrate nitrogen concentrations are higher than the drinking standard. Jackson *et al*. [4] reported rapid movement of nitrate in the soil and rapid leaching of soil profile and contamination of groundwater, followed by surface waters. Increasing the concentration of nitrate in water resources due to excessive use of chemical fertilizers and pesticides and irrigation with sewage has now become a serious problem around the world [5]. Nitrate pollution of groundwater in developing countries has been reported as a consequence of increasing levels of fertilization [6].

There are different physical, chemical and biological methods to remove nitrate from urban, industrial and agricultural wastewater, and even water resources, which may include physical method processes, membrane processes such as reverse osmosis and nanofiltration. These methods, usually are costly and require high pretreatment wastewater. Due to the high cost of activated carbon as a physical method, researchers are constantly looking for an alternative to this issue, so the use of natural carbon resources that can adsorb nitrates has been considered in recent decades. So far, many studies have been conducted on the adsorbent of harmful ions from water using cheap agricultural waste such as cedar tree wood chips [7], coconut skin powder [8], lentil husk [9], rice husk [10], pine tree wood chips [11] and oak charcoal [12]. Demiral [13] investigated the removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. In this research, activated carbons were prepared from sugar beet bagasse by chemical activation and were used to remove nitrate from aqueous solutions. In chemical activation, $ZnCl_2$ was used as chemical agent. The effects of impregnation ratio and activation temperature were investigated. The produced activated carbons were characterized by measuring their porosities and pore size distributions. The microstructure of the activated carbons was examined by scanning electron microscopy (SEM). The maximum specific surface area of the activated carbon was about 1826 m^2/g at 700 °C and impregnation ratio of 3:1. The effects of pH, temperature and contact time were investigated. Farasati *et al*. [14] investigated the effect of sugarcane straw and Phragmites australis anion exchanger nano adsorbents for removal of nitrate from aqueous solutions. Also, the effects of operating conditions such as pH, contact time, adsorbent loading, initial anion concentration, and the presence of competitive ions on the adsorption performances were examined. The results showed that the equilibrium time was 2 hours and the pH was 6. With pH of the solution varying from 2 to 10, the nitrate removal efficiency for sugarcane straw and Phragmites australis nano adsorbent increased up to maximum of 45 % to 76 % and 60 % to 86 % reached at pH 6. With an increase in the nitrate concentration from 5 to 120 mg/L, the removal efficiency decreased from 86 % to 66 % and 90 % to 67 % for sugarcane straw and Phragmites australis nano adsorbent, respectively. For Phragmites australis nano adsorbent, with an increase in the adsorbent dosage from 0,1 to 0,3 grams, the removal efficiency increased from 60 % to 85 %, but remained almost unchanged when adsorbent dosage ranged from 0,3 to 1 grams. For sugarcane straw nano adsorbent as the adsorbent dosage increased from 0,1 to 0,5 grams, the removal efficiency of nitrate increased from 45 % to 75 %, but remained almost unchanged for the increase of 0,5 to 1 grams. Adsorption kinetics of nitrate ions could most successfully be described by Freundlich isotherm. This study indicated that sugarcane straw and Phragmites australis nano adsorbents could be used for the removal of nitrate ions in water treatment and Phragmites australis nano adsorbent has higher adsorption than sugarcane straw nano adsorbent for nitrate removal.

Divband Hafshejani *et al*. [15] compared of biochar and vermicompost sugarcane bagasse performance on nitrate removal from contaminated water and determine the optimum conditions for adsorption process. In this research, after providing of sugarcane bagasse biochar and vermicompost and determining their characteristics, the effect of different parameter such as initial pH (2-11), dosage of adsorbent (1-10 g/L), solution temperature (10, 22 and 30 °C), the presence of competing ions (phosphate, sulphate, carbonate and chloride) and contact time (0-180 min), were investigated on the efficiency of adsorbent. The results of this study showed that the optimum pH of nitrate adsorption by sugarcane bagasse biochar and vermicompost was 4,64 and 3,78, respectively. Also, optimum adsorbent dosage was obtained (2 g/L). Among the competing anions, carbonate and chloride had the highest and the lowest impact on the reduction of nitrate removal and nitrate removal efficiency was increased as the temperature increases. According to kinetic of experiment, equilibrium time for nitrate adsorption by biochar and vermicompost was obtained (60 and 120 min, respectively). The higher removal of nitrate by biochar (73,7 %) in compare to vermicompost (48 %) was due to specific surface area, the amount of carbon and anion-exchange capacity of sugarcane bagasse biochar is higher than vermicompost.

Norisepehr *et al*. [16] compared the chitosan function as adsorbent for nitrate removal using synthetic aqueous solution and drinking water. Also, effects of parameters such as pH, contact time, initial concentration and adsorbent concentration of nitrate on nitrate removal from aqueous solution was studied. Function of chitosan in synthetic aqueous solution and drinking water according to the slurry system results, the optimum condition was obtained at pH = 4, 20 min contact time and increasing the initial concentration of nitrate enhance the adsorption capacity of chitosan. Also optimum dosage of adsorbent was obtained at 0,5 g/l. Although efficiency of nitrate removal in synthetic aqueous solution was better than drinking water, adsorption process using chitosan as an option for the design and selection nitrate removal should be considered in order to achieve environmental standards. Bafkar and Baboli [17] investigated the efficiency of nitrate removal from aqueous solution using oak leaf nanostructure adsorbent. In this research, oak leaf adsorbent was first crushed against a relatively dry sunshine by household grinder and then passed through the sieve 200 to prepare adsorbent nanomaterials. After being washed with distilled water in an oven at 70 °C for 24 hours. In this study, the effects of factors such as pH, adsorbent mass, contact time and initial concentration of nitrate were tested. The results showed that for the adsorbent, the equilibrium time after 120 min and the maximum nitrate adsorbent at pH = 5 were obtained. By increasing the adsorbent mass from 0,3 to 0,7 grams, the removal efficiency ranged from 88,93 to 93,82 percent, however, with increasing adsorbent content from 0,7 to 1,6 g, the adsorbent efficiency almost reduced. By increasing the concentration of dissolved nitrate (5-120 mg/L), the removal efficiency decreased from 94,41 to 89,35 %. Therefore, it can be stated that oak leaf can be used as a suitable and cost effective adsorbent with the least technology in nitrate removal.

Safdari *et al*. [18] investigated the efficacy of date kernel ash on removal of nitrate from aqueous solutions. In this research, the effect of initial nitrate concentration (50, 100, and 150 mg/L), initial pH (3, 5, 7, and 9), time (15, 30, 60, 120, and 180 minutes), and adsorbent weight (0,4, 0,6, and 0,8 g) were investigated. The increase of adsorbent dose from 0,4 g to 0,8 g in 100 mL nitrate solution with concentrations of 50 and 100 mg/L caused increase in adsorbent efficiency respectively from 75 % to 91 % and from 53 % to 65 %. Increase in solution's initial pH from 3 to 9 caused decrease in the adsorbent efficiency from 52 % to 8 %. The palm kernel ash is a natural and inexpensive adsorbent that can be used to remove environmental pollutants. Marezi *et al* [19] investigated the use of date palm fiber in the production of adsorbent material for nitrate sorption from aqueous solution. In this research, palm fibers were burned at temperatures of 450, 600 and 750 °C in a limited supply of oxygen condition. The produced biochar at temperature of 600 °C was chosen due to its high ability in removal of the nitrate from aqueous solution. Biochar made from these fibers washed with hydrochloric acid 0,5 N and then with distilled water to increase performance. The FTIR (Fourier transform infrared spectroscopy) method was used to investigate groups of the adsorbent. Additional studies were performed to measure the effects of pH, adsorbent dose, time and temperature on nitrate sorption. The optimal conditions for removal of nitrate were found (0,5 g of adsorbent in 20 ml solution, temperature of 10 °C, 30 min and neutral pH). Under these conditions, the nitrate removal efficiency was over 96 %. The general objective of this research was to study the ability of wheat straw, Beech wood chips and palm date leaf as an adsorbent to remove nitrate from aqueous solutions and determine the effect of different parameters (type and amount of adsorbent, initial concentration of nitrate, pH and contact time) on the process of remove nitrate and determination of optimum points for the adsorption process.

2. Materials and methods

Palm tree leaves were collected from palm trees on the Aburaihan college, University of Tehran. Then, the leaves were washed four times with water and twice with distilled water to remove the dust and dried in an oven at 80°C for 24 hours. After drying, the leaves were separated from the middle stem and divided by hands into very small pieces. Beech wood chips after being prepared from carpenters in Tehran province, was first washed with plenty of water and then washed well with the use of grease cleaners. It was then washed four times with water and twice with distilled water and dried in an oven at 80°C for 24 hours. Wheat straw was obtained from farms of Tehran province and in order to increase the accuracy of the experiment, weed straw was removed from the straw. After clearing the wheat straw, the grass was washed four times with water and twice with distilled water and dried in an oven at 80°C for 24 hours. Storage solutions (1000 mg/L) were prepared using potassium nitrate salt (1,645 g). Then solutions were made at concentrations of 1, 5, 20 and 50 mg/L of the storage solution. In all experiments, the volume of the solution used was 500 ml. The pH of the solutions was adjusted to 5, 7, 9 and 12 by NaOH and HCl 0,1 M. The pH adjustment of the nitrate solution was performed using a pH-meter device. After preparing the adsorbent and preparing a solution of nitrate, 1, 5, 30 and 50 g of all adsorbents were poured into beakers and the nitrate solution was added to them, and after completion of the specified contact time, the solutions were pased through the whatman filter paper 42 and were flattened. The final concentration of nitrate of the samples was measured by micro Kjeldahl device.

In experimental design, the relative importance of Taguchi's capabilities is ease of use, decreasing the number of tests, determining interactions and optimization [20]. In the Taguchi method, the inputs variable of the process are deliberately changed, so that the effect of that in the process response is detected and identified. In other words, the Taguchi method is a useful way to identify the key variables that affect the parameter of the process [21][22]. By using this method, controllable input factors can be systematically changed and their effects evaluated on output parameters [23][24]. In Taguchi design, the results are presented in terms of average standards or the signal-to-noise ratio (S/N) [25]. However, in order to provide noise-to-noise results, at least trials must be repeated two or three times. The higher the ratio (S/N) for a larger factor, the more effective the response to the response [23]. Today, there are softwares devoloped to test the design by Taguchi method and after taking the results of the experiments, analyze the data and determine the optimal conditions and the importance of each of the variables. One of these software is Qualitek-4, which is used in this research. To optimize nitrate removal test by Taguchi method, five factors were considered: adsorbent type , contact time, adsorbent mass, pH and initial concentration of nitrate. Table 1 shows each of the factors tested and their levels.

If we want to do all possible combinations without having to repeat the test, then there should be 768 tests for crushed adsorbents. This is not economically feasible and time-consuming. As a result, was used the Qualitek-4 software, with Taguchi's test design. After giving the variables to software, according to Table 2, a 16-array is provided for performing the tests. It should be noted that all experiments are repeated three times.

Finally, after performing these tests, the results were submitted to Qualitek-4 software to analyze the data and to obtain optimal conditions and importance of each variable.

Table 1: Variables and selective levels for designing tests

adsorbent	Retention Time (h)	Adsorbent mass(g)	pH	Initial concentration of nitrate (mg/L)
A	1	1	5	1
B	4	5	7	5
C	6	30	9	20
-	8	50	12	50

A:Palm leaves
B:Beech wood chips
C:Wheat straw

3. Results and discussion

After performing the tests predicted by Qualitek-4 software, the percentage of removal efficiency was entered as the test response in the result section of the software and results were analyzed in the analysis section. In the ANOVA analysis, the total observed changes in cells were called ANOVA, and the share of changes in each factor in the total dispersion of responses was observed. Finally, the following results were deduced from this method:

1. Effect of different factors (adsorbent mass, initial nitrate concentration, acidity, contact time and type of adsorbent) on nitrate removal efficiency.
2. Optimal conditions for maximum removal efficiency.
3. Percentage of the contribution of various factors (adsorbent mass, initial concentration of nitrate, acidity, contact time and type of adsorbent) on nitrate removal efficiency (sensitivity analysis).

It should be noted, that output charts and analyzes are based on the signal-to-noise ratio (S/N), which indicates that the higher the signal-to-noise ratio at each level than the parameters, the disturbance of other factors to achieve the desired target (The highest nitrate removal efficiency) is less in the test, and that level of the parameter is the optimum level. Figure 1 shows the changes in the efficiency of the removal of nitrate relative to the type of adsorbent. Crushed leaves of palm tree, crushed wheat straw and beech wood chips have the highest S/N rates, respectively. So, investigating changes in the efficiency of nitrate removal compared to adsorbent type showed that crushed leaves of palm tree, crushed wheat straw and beech woodchips, respectively, were the optimum adsorbent for nitrate removal from aqueous solutions.

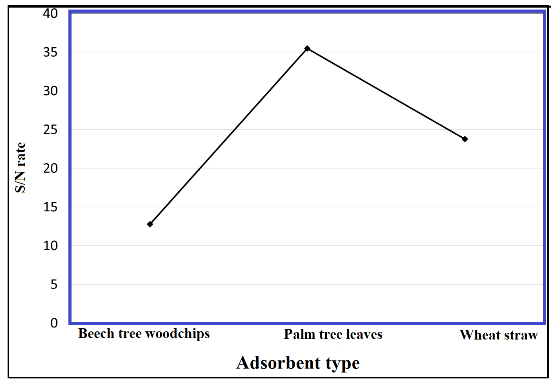

Figure 1: Changes in the efficiency of nitrate removal relative to adsorbent type

Figure 2 shows the changes in nitrate removal efficiency relative to the initial nitrate concentration. Changes in the efficiency of nitrate removal compared with the initial concentration of nitrate showed that by increasing the initial concentration of nitrate from 1 to 20, the rate of S/N increased, indicating that the removal rate had a rising concentration of 1 to 20 mg/L. After concentrations of 20 mg/L, the S/N rate is declining, indicating a reduction in removal efficiency. With increasing initial concentration of nitrate, the thrust force increases, which increases the nitrate removal efficiency [26]. The efficiency of nitrate removal is greater in the first moments. This phenomenon is due to the presence of large vacant places in the early moments on the adsorbent. Over time, these sites are occupied by nitrate molecules. As a result, nitrate removal will be reduced over time [27]. Therefore, it can be said that in concentrations of 1 to 20 mg/L nitrate, the number of active sites for adsorption on the surface of crushed leaves of palm tree, crushed wheat straw and beech woodchips more than when the concentration of nitrate in the range of 20 to 50 mg/L. This conclusion is consistent with

Table 2: Experiments determined by Qualitek-4 software

Test number	adsorbent type	Retention time (h)	Adsorbent mass (g)	pH	Initial concentration of nitrate (mg/L)
1	B	1	1	5	1
2	C	1	5	7	5
3	A	1	30	9	20
4	B	1	50	12	50
5	B	4	1	7	20
6	A	4	5	5	50
7	C	4	30	12	1
8	B	4	50	9	5
9	C	6	1	9	50
10	B	6	5	12	20
11	B	6	30	5	5
12	A	6	50	7	1
13	A	8	1	12	5
14	B	8	5	9	1
15	B	8	30	7	50
16	C	8	50	5	20

A:Palm leaves
B:Beech wood chips
C:Wheat straw

the results of Akhtar *et al* [28] and Malakootian *et al* [29]. Malakootian *et al*[29] reported the lack of active sites the cause of decreased nitrate adsorption in high concentrations. The researchers reported that with increasing initial concentration of nitrate, the number of anions increases to be in adsorption sites, and adsorbent active sites are saturated, thereby reducing the nitrate uptake. Akhtar *et al* [28] also showed that in high concentrations, adsorption through surface binding due to saturation of adsorbent sites is negligible. Therefore, it can be said that at high concentrations, it is difficult to occupy adsorbent empty surfaces. Because there is a repulsion between the adsorbed molecules on the solid surface and the molecules that are in the solution phase.

Figure 3 shows the changes in the efficiency of nitrate removal relative to pH. Changes in efficiency of nitrate removal compared to pH showed that with increasing acidity, the rate of S/N increased, indicating that the rate of removal of nitrate also increased in pH 5 to 7, and after pH 7, the rate of S/N takes downward trend, which indicates a reduction in the removal efficiency after pH 7. This result can be explained by the fact that, the nitrate ion has a negative charge, in acidic pHs (5<pH< 7), the nitrate adsorbent rate increases due to the electrostatic interaction

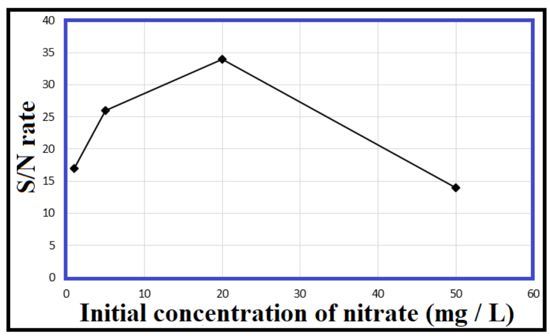

Figure 2: Changes in the efficiency of nitrate removal relative to initial concentration of nitrate

between positive surface charge and anions occur (Olgun *et al*, 2013). However, increasing the amount of hydroxide ions in high pH causes competition between hydroxide ion and nitrate in the adsorbed process and prevents more nitrate adsorbent.

Figure 4 shows the changes in nitrate removal efficiency relative to the retention time (duration of the contact). The changes in the efficiency of nitrate removal compared to the duration of the contact showed that by increasing the duration of contact from 1 to 6 hours, the S/N rate increased, indicating that the rate of removal of nitrate also increased in the duration of contact from 1 to 6 hours. After contact time of 6 hours, the S/N rate goes down

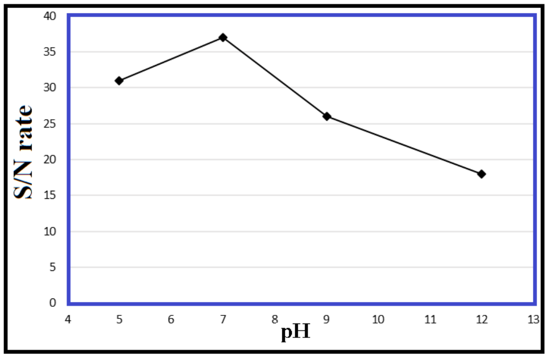

Figure 3: Changes in the efficiency of nitrate removal relative to pH

that indicate a reduction in the removal efficiency after that value. This result can be explained by the fact that, the high nitrate removal efficiency in the first 6 hours for crushed leaves of palm tree, crushed wheat straw and beech woodchips is due to the available space for adsorbent. By filling these spaces after 6 hours, the nitrate removal efficiency also decreases. This result is consistent with the results of Naseri [30]. The researchers showed that nitrate adsorbent was carried out at high speed in the early minutes and, as time went on, the adsorption decreased.

Figure 4: Changes in the efficiency of nitrate removal relative to retention time

Figure 5 shows the changes in the efficiency of nitrate removal relative to the adsorbent mass. Changes in the efficiency of nitrate removal, compared to the adsorbent mass, showed that with increase the mass adsorbent, the S/N rate increase and it indicates that the rate of removal of nitrate increased with increase of adsorbent mass to 30 g, and after the adsorbing mass of 30 g, the S/N rate has a downward trend, that indicate a decrease in the removal efficiency after the adsorbent mass takes that value. This result can be explained by the fact that, as the adsorbent mass increases, the adsorption surface also increases, and the continuation of this process causes the adsorbent particles to join together and find the agglomeration state, thereby reducing the adsorbent surface, which produces decreasing on nitrate removal efficiency. Other research results also confirm the theory that by increasing the amount of adsorbent, adsorption capacity increases (Jaafarzadeh [31]; Tehrani-Bagha [32]) and by increasing the amount of adsorbent over the optimal amount, efficiency of nitrate removal, is reduced (due to the reduction of the effective surface of adsorbent)(Janos [33]).

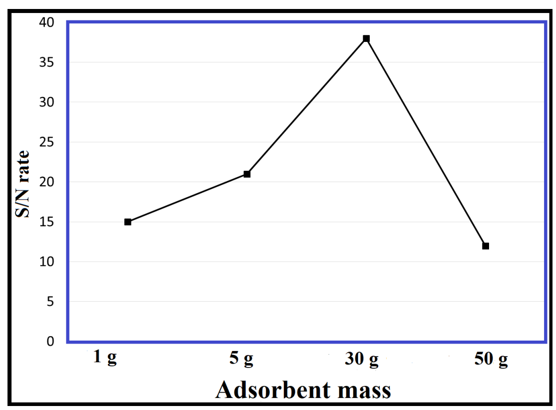

Figure 5: Changes in the efficiency of nitrate removal relative to adsorbent mass

According to Table **??**, the optimum conditions for nitrate removal using Taguchi analysis shows that all the factors studied in this research play an important role in the process and optimal values to achieve maximum efficiency Nitrate removal.

Table 3: Optimal levels of parameters examined

Factor	Best answer
adsorbent type	Palm leaves
Retention time (h)	6
Adsorbent mass (g)	30
pH	7
Initial concentration of nitrate (mg/L)	20

Qualitek-4 software uses the sensitivity analysis technique to determine the effect of parameters studied on the process of nitrate removal from treated water. Table 4 shows the percent contribution of each agent to the nitrate removal efficiency. According to Table 4, the type of adsorbent used has the most effect on the process of nitrate removal from aqueous solutions and acidity in this process has the least effect.

Table 4: Determination of the percentage of each agent's contribution to the nitrate removal efficiency

Factor	Factor's impact (%)
adsorbent type	28,3
Retention time(h)	24,6
Adsorbent mass (g)	21,6
pH	12,3
Initial concentration of nitrate (mg/L)	13,2

4. Conclusion

The results of this study showed that the process of nitrate removal from aqueous solutions is affected by adsorbent mass, initial concentration of nitrate, acidity, contact time and type of adsorbent. By increasing the adsorbent mass, initial concentration of nitrate, acidity, contact time to optimum, the nitrate removal efficiency also increases. After crossing the optimum point, with increase of adsorbent mass, the initial concentration of nitrate, acidity, the contact time, the decreasing in nitrate removal efficiency. Also, from the studied adsorbents, broken leaves of palm trees have a higher nitrate removal efficiency than other adsorbents. Therefore, the leaves of palm tree can be used as an economic adsorbent and with the lowest technology in the removal of nitrate from aqueous solutions.

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