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Effects of loading rate, resin height, and bed volume on nitrate removal from drinking water by non-selective strong anion exchange resin (A400E)

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ABSTRACT

The aim of this study was to compare the performance of down- and up-flow non-selective strong anion exchange resin (A400E) in the removal of nitrate from drinking water due to loading rate, height and volume of resin, as well as passing water volume. In this study, totally, 270 samples were taken and analyzed for evaluating the amount of outcome nitrate. The results showed that the trend of removing nitrate decreased in terms of increasing the passing water volume and loading rate in both systems. While the altitude of ion-exchange column increased due to the up-flow, the removal efficiency of nitrate increased continuously. In the down-flow resin, the efficiency of the system was gradually reduced while increasing the height of resin up to 60 cm; whereas the system efficiency increased at the resin height of 60–90 cm. The efficiency of both ion-exchange systems were affected as a result of the some factors including volume of passing water, resin height, and loading rate at high, medium, and low levels, respectively. Overall, to achieve the sufficient water quality, it is required to consider the height of resin and amount of passing water volume to reach the cost and effectiveness of the system.

Keywords: Ion-exchange system; Up-flow; Down-flow; Groundwater contamination; Nitrate removal

1. Introduction

Nitrate is one of the most significant water pollutant factors, particularly in groundwater, which have been considered by a lot of ecologists [1]. The main sources of nitrate pollutant in water resources might be due to the use of nitrogen fertilizers in the farm land, sewage irrigating, discharging the municipal and industrial wastewater to water resources, and decaying the plants [2,3]. Nitrate could cause various environmental problems. It can be stated that the natural water resources could be premature death (supply oriented) due to accumulated nitrate and phosphate amount in those water resources. Moreover, excessive nitrate concentration (more than 50 mg/L) in drinking water as a result consumed by people could cause some diseases such as methemoglobinemia in infants (less than 6-month old), abdominal pain, diarrhea, vomiting, blood pressure, increased infants mortality, diabetes, spontaneous fetus abortion, increased potential of carcinogenic and mutagenic nitrosamine compounds, as well as infection of the respiratory system [4–7]. Nitrate is highly soluble in water and could easily transmit to underground water supplies through the soil texture [4]. To protect the consumers' health due to the nitrate effects in drinking water, the World Health Organization (WHO), the US Environmental Protection Agency (EPA), and the Standard of European Union recommended the standard of nitrate in drinking water less than the 50, 45, and 25 mg/L mg-NO_3^-, respectively [8].

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It can be said that the nitrate removal in the conventional water treatment plants is very hard [4,5]. However, various methods have been used to remove nitrate from water resources, which include chemical renewal, ion exchange, reverse osmosis, electrodialysis, as well as hydrogen catalytic and biological denitrification. The biological reactor is used for treated water with high nitrate concentration, but it is difficult to keep the biological processes in optimal conditions [3,5,9,10]. Moreover, it is a useful process for treating ground and surface waters due to its easy application; but according to chemical absorbent and its performance, it should be modified for the removal of nitrate anion. Ion-exchange process is a simple, effective, and reliable method with relatively low costs, so it is very useful for treated water resources in small communities with nitrate contamination [4,11,12].

In recent years, a number of selective and non-selective resins are used to remove nitrate, which include Duolite A-101D, A-104, Dowex SAR A-550, Amberlite IRA-900, IRA-910, A 520E, and A400E [13–17]. A400E resin made by Purolite company is a very strong non-selective alkalinity resin for removing nitrate from drinking water, which contains high-capacity and low residual silica content [10]. So far, few studies have been carried out on the effectiveness of the A400E resin to remove nitrate. Many factors could impact the performance of resin to remove nitrate that have not been considered in previous studies, those could be noted as follows: water taking point from different heights of resin, loading rate (Bv/h 1), and volume of passing water (Bv 2). This study aims to evaluate the effect of loading rate, passing high water volume, and height of the A400E resin function with up- and down-flows to remove nitrate from groundwater against the application of response surface methodology (RSM).

2. Materials and methods

In this study, the strong A400E anion resin involve non-selective property of nitrate removal was investigated. The resin properties, which made by Purolite Company, UK, are presented in Table 1. Owing to the high concentration of nitrate in drinking well water in Kermanshah, pilot of ion-exchange columns was installed in chamber number 2, which supplied drinking water to a part of Kermanshah. Ion-exchange column properties with the up-flow and down-flow are presented in Table 2. Three taps water were installed along the length of the resin column with equal distance (30, 60, and 90 cm) to monitor the resin function in terms of absorbing nitrate (Fig. 1).

Nitrate removal efficiency was examined at three different loading rates (10, 25, and 40 Bv/h) and five water flow volumes (40, 100, 160, 220, and 280 Bv). The number of trial phases of these experiments was obtained as 45 phases (3 × 3 × 5) according to the variables, and based on 3 times of sampling at each phase. Therefore, totally 135 samples were analyzed in terms of water nitrate removal efficiency via the resin. To evaluate the nitrate concentration of raw inlet water to the resin, in present research, five raw well water samples were taken at various times and the nitrate concentration, electrical conductivity, sulfate, chloride, alkalinity, and pH were measured according to standard methods for water and wastewater [18]. Design of Expert software (version 7) was used for data analysis and modeling of effluent nitrate regarding the required variables. In this study, all the possible situations were considered in order to analyze the response of surface historical data design.

Table 1
Physical and chemical properties and A400E resin

Characteristics	Description
Structure of polymer	Porous polystyrene with divinylbenzene vertical attached
Ionic form	Cl^-
Feature shape	Golden and transparent balls
Functional groups	Quaternary ammonium type 1
Real density	0.695
Relative humidity	48%–52%
Particles size	0.3–1.2 mm
The total capacity of ion exchange	1.3 meq/mL
Maximum operating temperature	100°C
pH range (operational)	4.5–8.5

Table 2
Characteristics of ion-exchange column of up-flow and down-flow A400E resin

Characteristics	Description
Column material	Plexiglass
Column height	1.5 m
Column outer diameter	15 cm
Existence resin height in column	90 cm
Free height	60 cm
Column inner diameter	14 cm
Column shape	Cylindrical
Volume of resin	14 l = 9.6 kg

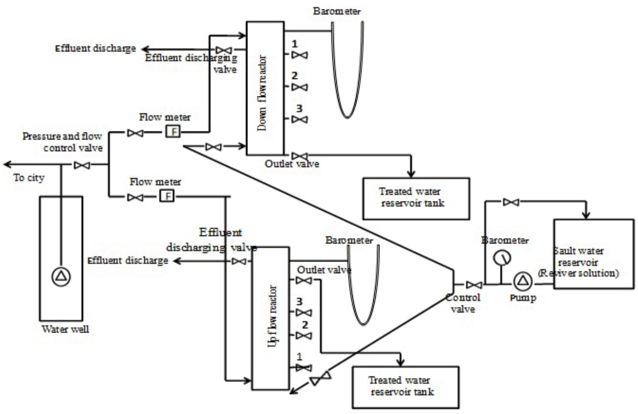

Fig. 1. Scheme of ion-exchange column with up- and down-flow (resin A400E).

3. Results and discussion

Figs. 2–7 represent the average amount of output nitrate due to investigating the variables of both ion-exchange systems with up- and down-flows. The optimization point based on two factors, that is, volume of passing water and height of resin, to achieve the output nitrate less than 25 and 50 mg/L was shown in Figs. 8 and 9 (up-flow) as well as Figs. 11 and 12 (down-flow). Investigation of the effective parameters on the resin efficiency in nitrate removal is presented in Fig. 13.

According to obtained results, factor A (water flow) impacted on the amount of effluent nitrate compared with two other factors among all investigated factors, significantly, and the next factor with maximum effectiveness particularly in the reverse form was the resin height. Afterward, the effect of factor C (loading rate) is represented in Table 3 and Figs. 2–7, 10, and 13. Results showed that the most appropriate model proposed for the ion-exchange column with up-flow using the software was the linear model with R^2 = 0.8987, while in the column with down-flow, the quadratic model with R^2 = 0.8995 was more suitable than linear model (Table 3). Regarding the results that presented in Table 4, the amount of nitrate in influent water to the ion-exchange column was higher than the standard level (50 mg-NO_3^-). The average concentration of effluent nitrate at various loading rates, volume of passing water, and samples taken from different column heights are given in Table 5.

3.1. *Investigating effect of the volume of passing water through the resin with up- and down-flows*

According to the obtained results, with the increased volume of passing water, the concentration of output nitrate was increased in both of the investigated ion-exchange systems (with the up- and down-flows). A possible reason could be increased the volume of passing water through the special and fixed areas of resin and increased the amount of transported absorbed nitrate (mass transfer) in the resin beads, which could return resin to the equilibrium form and quickly saturate nitrate ions. On the other hand, the resin reached the equilibrium situation in shorter time due to the volume of passing water, while the product nitrate concentration increased; at that time, the resin should be revived [19]. Other related restorable reasons could be that each column of the resin had known capacity, upon achieving to which (at high volume of passing water, this capacity could be rapidly reached), the significant ion in electrolyte was not exchanged with its similar ion and the ion-exchange process was essentially discontinued [20]. Therefore, the most important factors that affect the ion-exchange process includes the volume of water flow and mass transfer. Observing that the total mass of exchangeable ions is almost fixed shows mass ion transfers

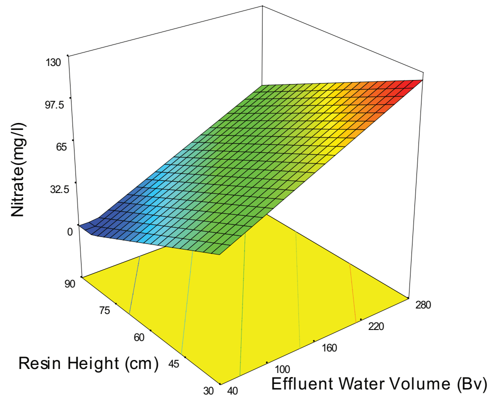

Fig. 2. Effect of resin height, and volume of passing water on the concentration level of output nitrate in the up-flow resin.

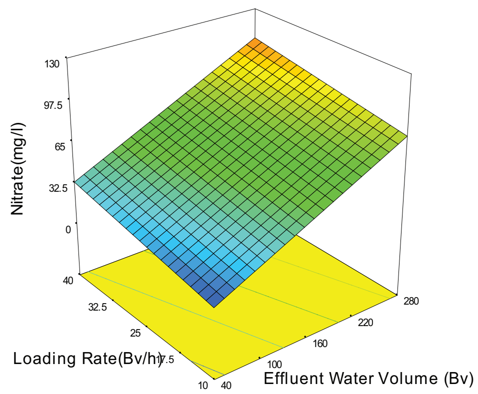

Fig. 3. Effect of loading rate, and volume of passing water on the concentration level of output nitrate in the up-flow resin.

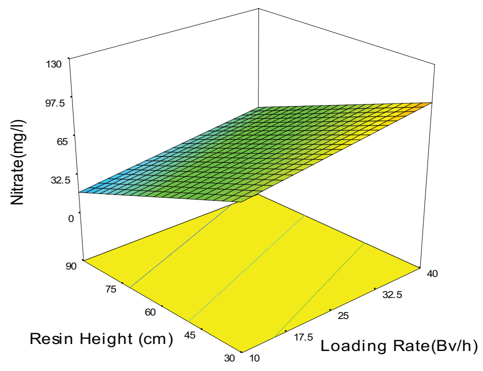

Fig. 4. Effect of loading rate, and resin height on the concentration level of output nitrate in the up-flow resin.

Table 3
Output nitrate model considering the investigated factors

Up-flow	Nitrate of effluent (mg/L) = 59.18 + 36.06A – 29.38B + 11.19C		
Down-flow	Nitrate of effluent (mg/L) = 77.80 + 50.13A – 16.23B + 1.23C – 20.53AB + 0.5AC + 11BC + 20.94A^2 – 48.11B^2 – 1.25C^2		
Parameters	A	B	C
	Volume of passing water (Bv)	Resin height (cm)	Resin load (Bv/h)

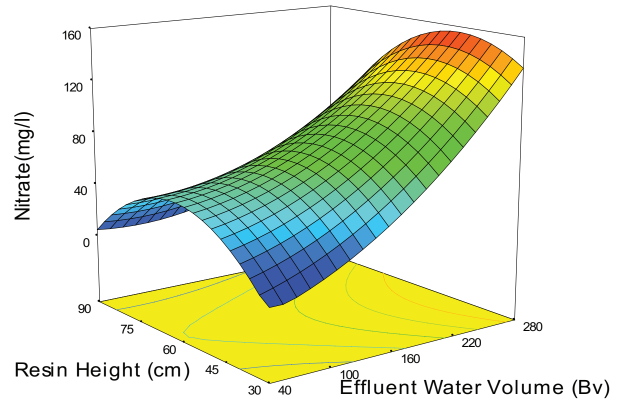

Fig. 5. Effect of resin height, and volume of passing water on the concentration level of output nitrate in the down-flow resin.

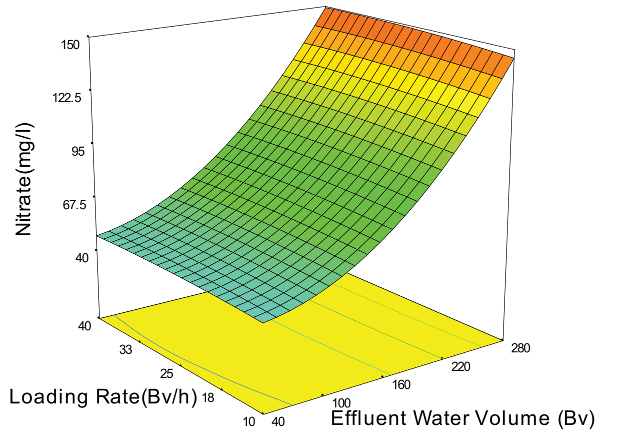

Fig. 6. Effect of loading rate, and volume of passing water on the concentration level of output nitrate in the down-flow resin.

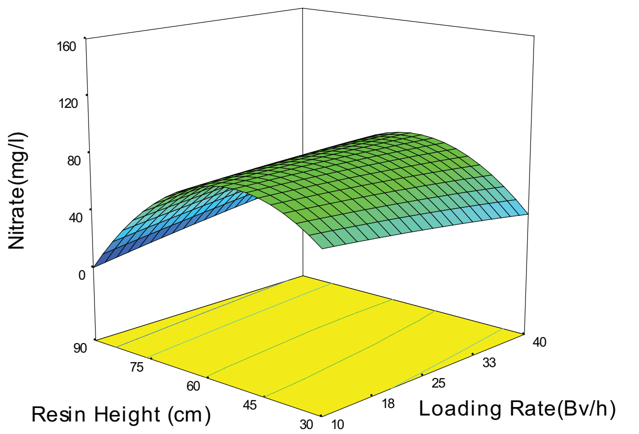

Fig. 7. Effect of loading rate, and resin height on the concentration level of output nitrate in the down-flow resin.

in a short time (by increased water volume) or long time (by reduced water volume) [19,20].

According to the obtained results of the optimization conditions, to achieve water quality standards in terms of nitrate, water flow should be increased to about 250 Bv to acquire low levels of nitrate concentration (50 mg/L) in the system with

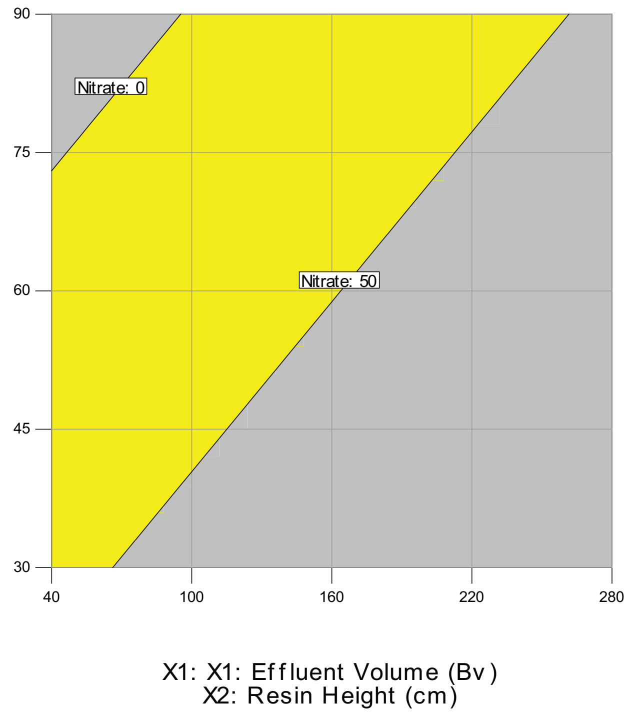

Fig. 8. Optimal area (for the obtained nitrate concentration of less than 25 mg/L) in terms of the most important parameters affecting on the effluent nitrate of up-flow water (volume of water passing through the height of resin).

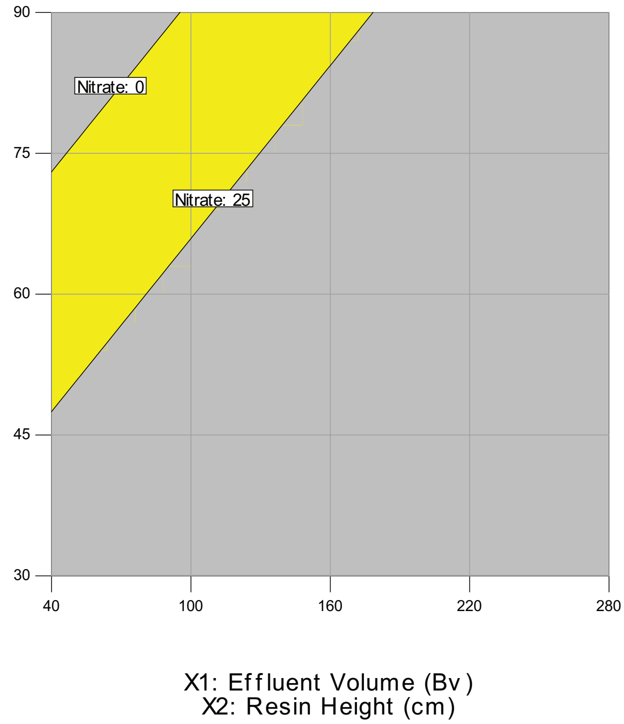

Fig. 9. Optimal area (for the obtained nitrate concentration of less than 50 mg/L) in terms of the most important parameters affecting on the effluent nitrate of up-flow water (volume of water passing through the height of resin).

up-flow; but in the system with down-flow, volume of water flow was increased to about 160 Bv in the 30 cm height of resin column before need to restore the resin column. However, with increasing the height of resin column to 90 cm, water flow could be increased to about 240 Bv. Anyway, the purpose was to produce more treated water by increasing the volume of passing water and also meet the standard of nitrate level of less than 50 mg/L; thus, it is necessary to pay special attention to height of ion-exchange column due to increasing the water volume, because the height of resin column has a significant effect on the output nitrate. The optimum condition for the standard amount of nitrate (25 mg/L) in treated water was similar to the optimum condition for obtaining the standard level of nitrate of less than 50 mg/L, except that with regard to the amount and kind of influencing the passing water volume and height of resin, a more limited and stringent situation was required in terms of both the mentioned variables.

In the column with up-flow, with increased the volume of passing water, effluent nitrate concentration was continuously increased; therefore, it was expected that the removal of nitrate by the strong non-selective ion-exchange resin (A400E) with up-flow would obey a linear model in terms of volume of passing water, whereas in the column with down-flow, through increased the volume of passing water, effluent nitrate at height levels of 30, 60, and 90 cm of resin column did not increase linearly due to increased column loading rate; so it was expected that the removal of nitrate by ion-exchange resin (A400E) with down-flow would obey the non-linear model, which was demonstrated according to the results obtained from the investigating and drawing the related diagram.

According to the obtained model and investigation of the examined factors (impact factor) in both systems with up- and down-flows, the volume of passing water significantly affected the nitrate removal efficiency by the ion-exchange system. This issue will be important when two factors of resin, height and loading rate, have certain limitations for

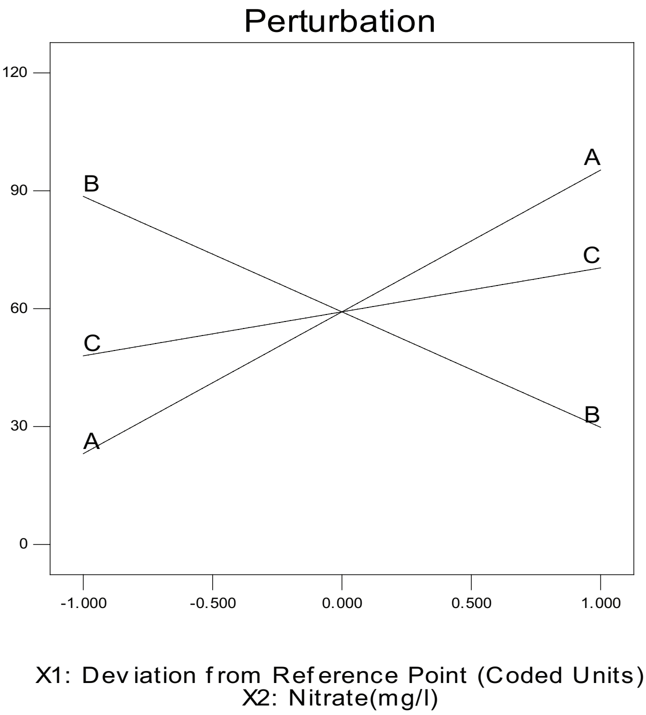

Fig. 10. Effect of loading rate, height, and volume of passing water on the concentration level of effluent nitrate of up-flow resin.

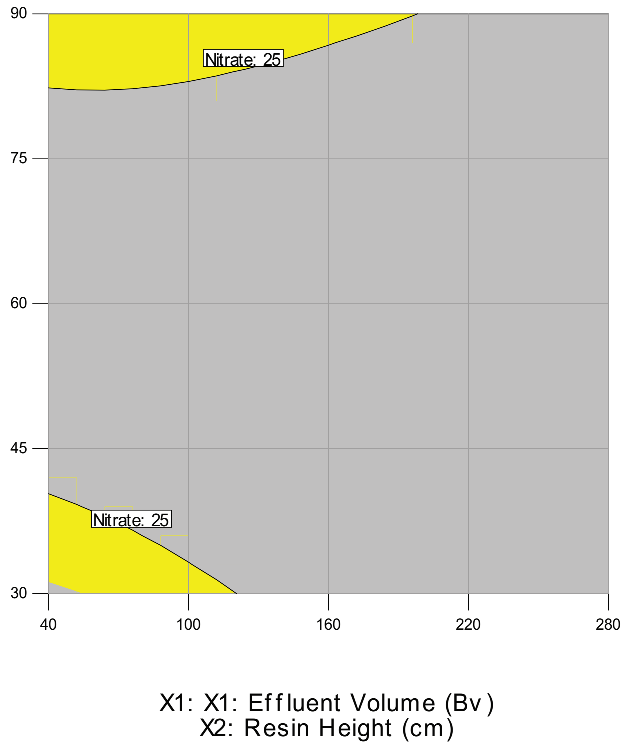

Fig. 11. Optimal area (for the obtained nitrate concentration of less than 25 mg/L) in terms of the most important parameters affecting on the effluent nitrate of down-flow water (volume of water passing through the height of resin).

Table 4
Characteristics of influent water to ion-exchange columns at different volumes of water passing through the column

The volume of passing water (Bv)	pH	Electrical conductivity (µS/cm)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alkalinity (mg/L)
50	7.08	1,275	105	91	92	372
150	7.04	1,271	105	89	96	380
250	7.18	1,275	105	78	90	378
350	6.99	1,275	105	78	92	378
450	7.03	1,315	105	85	90	366

Table 5
Average concentration of output nitrate from ion-exchange column with up-flow and down-flow resins based on different loading rates, height, and volume of effluent water of column

Run	Investigation factors			Output nitrate rate (mg/L)	
	Volume of passing water (Bv)	Resin height (cm)	Resin load (Bv/h)	Ion-exchange column with up-flow	Ion-exchange column with down-flow
1	280	30	25	108.3 ± 5.2	158.3 ± 11.5
2	40	30	10	30 ± 2	0
3	160	90	25	4.85 ± 0.2	4.5 ± 0.3
4	220	60	10	66.65 ± 3.5	110.65 ± 6.8
5	100	90	25	0	4 ± 0.1
6	160	90	40	15 ± 1.4	5.15 ± 0.7
7	280	60	25	115.8 ± 7	115.8 ± 6
9	100	30	25	93 ± 4.3	2.6 ± 0.1
10	220	30	40	120 ± 4	87.7 ± 5
11	100	90	40	0	0
12	280	30	40	98.3 ± 5.5	106.7 ± 4.5
13	220	90	25	5.3 ± 0.1	5 ± 0.1
14	100	30	40	101.7 ± 7.4	0
15	100	90	10	10 ± 0.2	0
16	160	30	25	113.35 ± 5.1	17 ± 1.4
17	280	90	10	66.7 ± 2.5	75 ± 3
18	160	60	40	69.2 ± 3.4	96.45 ± 5.9
19	280	90	40	105 ± 0	133.3 ± 7.4
20	220	60	25	115 ± 5	105 ± 2
21	160	60	25	84.25 ± 4.6	117.1 ± 2.6
22	40	30	40	75 ± 4	0
23	280	30	10	96.7 ± 3.9	153.3 ± 8
24	40	90	25	0	0
25	40	90	10	0	0
26	40	60	40	11.65 ± 1.4	55 ± 2.5
27	220	90	40	88 ± 3.5	68 ± 4
28	220	30	10	80 ± 5	146.7 ± 3
29	220	90	10	41.7 ± 2.9	0
30	100	60	10	27.5 ± 1.5	60.3 ± 3.5
31	280	60	10	90.8 ± 3.1	110 ± 4
32	40	90	40	0	0
33	40	60	25	15.35 ± 1.1	52.3 ± 4.1
34	160	30	40	106.7 ± 5.2	20.8 ± 2.1
35	280	60	40	105.85 ± 8.5	102.5 ± 5.2
36	160	90	10	24.7 ± 1.8	0
37	40	30	25	66.7 ± 5.5	0
38	40	60	10	17 ± 1	55 ± 3
39	100	30	10	36.7 ± 2.5	0
40	160	30	10	61.7 ± 3.6	3.7 ± 0.3
41	100	60	25	45.65 ± 2.8	73.3 ± 5
42	280	90	25	52.3 ± 4.4	51.7 ± 3.4
43	100	60	40	36.35 ± 1.2	59.5 ± 4
44	160	60	10	50.35 ± 4.9	91.15 ± 5.1
45	220	30	25	106.7 ± 8.1	136.6 ± 9.2

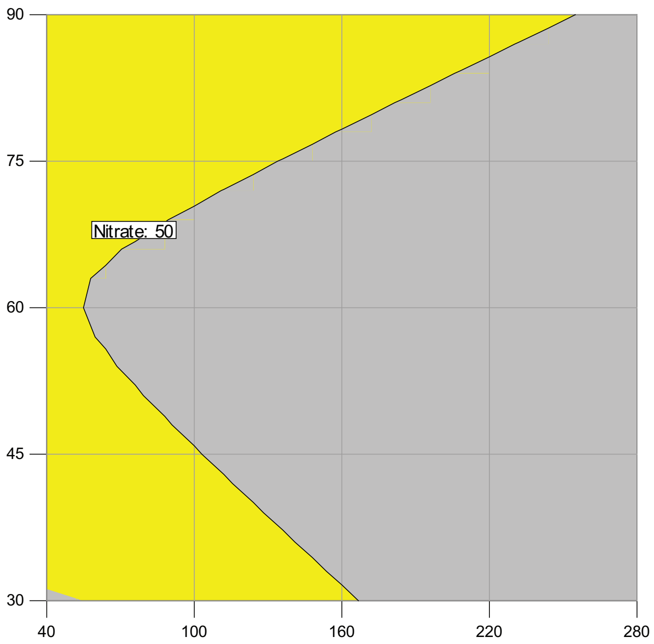

Fig. 12. Optimal area (for the obtained nitrate concentration of less than 50 mg/L) in terms of the most important parameters affecting on the effluent nitrate of down-flow water (volume of water passing through the height of resin).

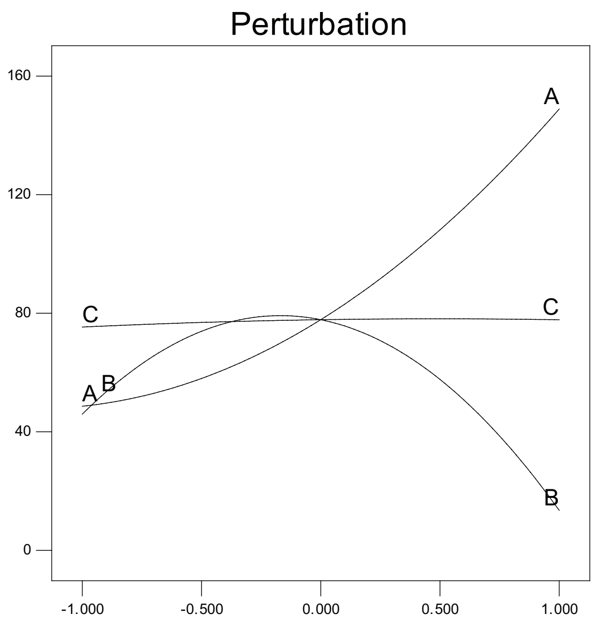

Fig. 13. Effect of loading rate, height, and volume of passing water on the concentration level of effluent nitrate of down-flow resin.

achieving a specific goal. In this situation, the acceptable level of effluent nitrate rate could be achieved with few changes in water flow. Owing to the effectiveness of this factor, little and limited manipulation of this factor could significantly influence the efficiency of the system.

3.2. Effect of resin height on the up-flow system

According to the results, by increasing the height of the resin system with up-flow, nitrate concentration of water was linearly decreased, because in strong acid or strong base resin with up-flow, leakage of nitrate ions from the lower layers to the upper layers was minimal, which could be explained by the lack of direction of water flow and gravity line. In fact, gravity prevented quick moving of nitrate ions along the resin and also its leakage from one layer to another (unlike the down-flow). It can be stated that, in the resin with up-flow, the maximum contact of electrolyte with the resin surface occurred due to the expansion of the resin beads and limited adhesion of the resin beads. After equalizing each part of the resin with electrolyte, the higher layer of the resin completed the exchanging process [9]. So, in the exchange resin with up-flow, after complete saturation of each level, higher levels were exposed to nitrate, respectively, until the whole part of resin became saturated. Therefore, according to the results and findings of DOE software, the linear trend of absorbed nitrate and nitrate ion exchange of electrolyte was observed based on the height of the resin and the linear model confirmed this issue.

The volume of passing water considered variables due to the height of the ion-exchange column to achieve lower levels of output nitrate, that is, less than 50 mg/L; meaning that, with increasing volume of passing water, the ion-exchange column height was raised. However, useful minimum height of ion-exchange column was 30 cm. If the purpose was to achieve effluent nitrate of less than 25 mg/L, the useful minimum height would be 50 cm considering the coefficient factors of resin column height, volume of water flow, and loading rate, the obtained model showed that the height of resin column relatively affected the removal of nitrate from the ion-exchange system.

3.3. Effect of resin height on the down-flow system

Results obtained from the measurement of nitrate amount in the water samples at different heights of the resin column with down-flow showed that the concentration of effluent nitrate was low at low height levels (30 cm), while with increasing the height of the resin column (up to 60 cm), the nitrate concentration of the output nitrate increased. It can be stated that the cause of absorbing and exchanging more nitrate at a high level of the ion-exchange resin could be the occurrence of the ion-exchange process at the height of the resin, which had the first exposure to water or an electrolyte containing exchangeable ions (e.g., 5 cm height of the resin from the resin bed), particularly in the strong acid or base resin with the down-flow. This issue could be related to the point that the highest ion exchange occurred at a higher level of the resin bed and the lower level was less exposed; therefore, the rate of ion exchange at lower levels would be low [19,20]. After the saturation of the initial exposure levels, other levels would follow the exchange process until reaching ion balance in the resin and electrolyte (i.e., up to the maximum height of about 60 cm). The reason of decreased capacity of the resin at the column height of 30–60 cm could be that, in the ion-exchange resin with down-flow, due to the high concentration of nitrate in water at the initial contact with the resin, the initial exposure level of resin was not able to absorb the whole amount of the existing nitrate in water; therefore, a large amount of nitrate was transferred to lower levels (below the resin height of 30 cm), which means that a part of nitrate leaked from the first level of the resin height (30 cm) and was subsequently absorbed by higher levels (30–60 cm). However, the ion-exchange capacity of the second height level after the saturation of the first height level decreased intensively. Therefore, the output nitrate increased from 30 to 60 cm height of the resin column so that, at this height, the low volume of water was passed until the resin reached the saturation mode. After the saturation of resin up to the height of about 60 cm, the new cycle of nitrate absorption on the resin beads was started at the next weight level.

Given that in the range of resin column height of 60–90 cm and also height of 0–60 cm, the problem of additional nitrate leakage was not observed, with gradual increases of the resin height (from 60 to 90 cm), the amount of nitrate was absorbed more and more; thus, the output nitrate was decreased gradually to reach zero. Accordingly, the height of resin plays a significant role in the ion-exchange process and prevents leaving unwanted nitrate ions in the electrolyte. Consequently, the height of the ion-exchange column should be selected in addition to gradual ion-exchange process to balance the model in terms of application, operation, and maintenance. Since the mid-level (30–60 cm) of the resin was the second layer of resin exposure to water containing anions, any leakage of these anions occurred at the first layer would be absorbed by it. Therefore, after the first layer of resin reached the equilibrium, the second layer lost its exchanging capacity cause, reached balance mode earlier, and played the transition layer between the first and third layers (60–90 cm). Therefore, to avoid leakage of nitrate anions from the first level to achieve the output nitrate of less than 50 mg/L [19,20], the height of the ion-exchange column of at least 60 cm is recommended to remove nitrate. If the purpose of water treatment is to obtain the nitrate amount of less than 25 mg/L, because of the rapid saturation of the transition layer (height of 30–60 cm), the minimum resin height of 90 cm is recommended.

Due to the different roles of the resin surface layers, as the second layer (30–60 cm) reached saturation state more quickly than the other two layers, it should be expected that the model of nitrate removal by the ion-exchange column resin does not obey a linear model in terms of the resin height. Therefore, according to the results, the model of potent non-selective ion-exchange resin (A400E) with down-flow for nitrate removal is a non-linear model in terms of resin height.

3.4. Effect of loading rate on the system with up- and down-flows

According to the obtained model and investigation of the estimate factors (impact factors) of the examined issue in both ion-exchange systems with up- and down-flows, loading rate had the minimum effect compared with the two other factors in terms of removing nitrate by the ion-exchange system. It indicates that the manipulation and volatility of loading factor had a light effect on the ion-exchange of the system performance. The most important factor in an ion-exchange process is non-selective ion concentration. Therefore, in an ion-exchange system, the ion-exchange process continues until the whole exchangeable sites of nitrate ion reach the equilibrium situation [19,20]. As a result, increased loading rate in the system just led to gradually decreased time of reaching the equilibrium condition.

4. Conclusion

According to the results, it can be concluded that, in high performance the non-selective ion-exchange resin (A400E) in both the up- and down-flow systems, three factors including the volume of passing water, the height of resin, and loading rate had high, medium, and low effects, respectively, and their kinds of effectiveness in removing nitrate in up- and down-flows obeyed linear and non-linear models, respectively. By increased the volume of passing water through the system (high impact) and loading rate (low influencing factor), the amount of output nitrate was increased, while the height of the resin column increased and concentration of nitrate in the treated water decreased. According to the results of this study, it can be said that, although the volume of passing water through the resin had a more effective role in the control and operation of systems, to achieve water with standard quality in terms of nitrate (25 or 50 mg/L), it is necessary to pay attention to both heights of resin and volume of passing water through it. In the resin with up-flow, to achieve the output nitrate of less than 50 mg/L, the volume of water through the height of the ion-exchange column could be observed as a variable. This means that, with increased the volume of passing water, the height of the ion-exchange column could be increased. Nevertheless, the minimum useful height of the ion-exchange column should be considered 30 cm. However, if the purpose of output nitrate is less than 25 mg/L, the minimum useful height of the ion-exchange column must be 50 cm. In the ion-exchange system with a down-flow, to achieve the output nitrate of less than 50 mg/L in treated effluent water until the volume of water (160 Bv) from the resin column, the minimum resin height should be 30 cm. However, to achieve the volume of 240 Bv, the minimum height should be 90 cm. And, to achieve the output nitrate of less than 25 mg/L, the volume of passing water in both height ranges should be decreased to 120 and 190 Bv, respectively.

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Conflict of interest

The authors have declared no conflict of interest.

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