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Research Article

APPLICATION OF RESPONSE SURFACE METHODOLOGY FOR EFFICIENCY ANALYSIS OF STRONG NON-SELECTIVE ION EXCHANGE RESIN COLUMN (A 400 E) IN NITRATE REMOVAL FROM GROUNDWATER

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Abstract

Ion exchange process is the common and effective method in removing of nitrate from groundwater that different types of resins used for this purpose. This study was to evaluate the loading rate, resin height and volume of water passing effects on performance of down – flow strong non-selective ion exchange resin column (A 400 E) in terms of nitrate removal from groundwater. In present study was used the strong anionic resin A400E with non-selective properties for nitrate removal (Manufacture purolite UK). To effect study of height resin factor, three collection valves were mounted in the same spacing (30, 60 and 90 cm) on the column. Nitrate removal was studied in the three different load rate (10, 25 and 40 Bv/h), and five volume of water passing (40, 100, 160, 220 and 280). Totally 135 samples were taken. Nitrate measurement conducted based on standard test method for water and wastewater. Design of Expert (Ver.7) software was used for data analysis and charts draw. Results showed that with increasing of volume of water passing and loading rate, the efficiency removing of nitrate decreased, while the efficiency gradually decreased by increasing the height of resin up to 60 cm and system efficiency increased in height of 60 to 90 cm. Based on the influencing factors of studied parameters in the obtained model, the impact rate of operational parameters were evaluated on the performance of resin, " The volume of water passing ", "resin height" and " loading rate " respectively. It is necessary to consider that the

height resin and flow rate given the cost effectiveness of system, to achieve the water quality with nitrate standard (less than 50 mg/L).

Keywords: Ion exchange column, Down flow reactor, Groundwater contamination, Nitrate removal.

Introduction

Some nitrogen compounds including ammonia, nitrite, and nitrate are found widely in water. Nitrate is one of the most water pollution especially groundwater, which is interest to ecologists (1). The nitrogen fertilizers utilize and irrigation with municipal sewer, and industrial wastewater discharged into water sources and decaying plants are the most important sources of water pollution by nitrates (2, 3). Nitrate can cause many environmental problems. This compound and phosphate, causes premature death of water natural resources (eutrophication) (4). moreover, entry excessive nitrate obtained by human, causes some diseases including methemoglobinema in infants less than 6 months (at concentrations of 50 mg/L), and also creates complications including abdominal pain, diarrhea, vomiting, blood pressure, increased infant mortality, diabetes, spontaneous abortion of the fetus, increasing the potential for product of nitrosamine compounds, carcinogens, mutagens and respiratory infection(5-7). Nitrate has high solubility in water and can easily transfer through soil into groundwater sources (5). The World Health Organization (WHO), America Environmental Protection Agency (EPA) and the Europe Union standard, has recommended the nitrate level in limit of 50, 45 and 25 mg/L (as mg-NO_3^-) to protect the consumers against complications from nitrates(8). Nitrate removal is very difficult by conventional drinking water treatment plants (5, 6). Different methods are used to remove nitrate from water, such as chemical reduction, ion exchange, reverse osmosis, electro dialysis, hydrogen catalytic and biological denitrification. The biological reactor used for water treatment with high nitrate, but the keep of biological processes in optimum conditions is difficult (3, 6, 9, 10). Adsorption is a useful process for groundwater and surface treatment, due to its easy application (11). However, using of adsorption method to removing of nitrate ion, need to chemical surface modification of absorbent, therefore, its performance is not reliable (12). Therefore, ion exchange process is a simple method, effective, be revived, cost effectiveness and is very useful for water sources of small communities contaminated with nitrates (5, 13, 14). In recent years, several selective and non-selective resin were proposed for removing of nitrate, that can be cited to Duolite A-101D, A-104, Dowex SAR, A-550, Amberlite IRA-900, IRA-910, A 520E and A 400E (15-18). Resin A 400 E manufacturing purolite company is one of the strong alkaline resins, non-selective for the nitrate removal from drinking water that has high-capacity and low residual silica content(18). The few studies conducted related to the A400E resins performance for nitrate removal. Many factors can be affecting the performance of resin including water intake points from different heights of resin, loading rate (Bv.h)[1] volume of water passing (Bv)[2] which has not addressed in previous studies. in present study the natural well water was used for nitrate evaluation, unlike other studies that have used synthetic solution, that it is possible exist interferences (such as organic matter) and Competitors (such as ammonium versus nitrates), while it is ignored in synthetic solutions and may be not represent the actual performance of resins. According to mentioned reasons, present study was to evaluate the effect of loading rate, height of resin and volume of water passing through the resin (A 400E) with down-flow method for nitrate removal from groundwater (wells resources of drinking water of Kermanshah) using response surface methodology (RSM).

Materials and methods

Characteristics of resin:

In present study, the non-selective strong anion resin A400E was used to removing of nitrate. The resin manufacturing by Purolite Company of England that its characteristics are presented in Table 1.

Table-1: **Physical, chemical, and operational characteristics of A400E resin.**

characteristics	Description
Polymer buildings	polystyrene porous with Vertical connection in vinyl benzene
Ionic form	Cl^-
facial features	Golden balls and transparent color
Functional groups	Quaternary ammonium type I
Actual density	0.695
relative humidity	48-52%
Particle size	0.3-1.2 mm
The total capacity of ion exchange	1.3 meq/mL
Maximum temperature operation	100 °C
The range of pH (operation)	4.5- 8.5

- **Characteristics of ion exchange column (A400E) with down- flow.**

Due to the high concentration of nitrate in some drinking water wells in Kermanshah, pilot ion exchange columns was installed in the water wells Module (2) that suppliers part of the drinking water of Kermanshah city. The ion exchange column was made in form of down flow (Table 2).The three collection taps were installed as same distance on the length of column (30, 60 and 90 cm) to investigate the resins ability for nitrate adsorption (figure 1).

Table - 2: Characteristics of ion exchange column (A400E) with down-flow.

Property	Description
material of column	Plexiglas
High of column	1.5 m
Outside diameter of column	15 cm
Height of resin column	90 cm
Free board	60 cm
Internal diameter of column	14 cm
Column form	Cylindrical
Resin volume	14 liters equal with 6.9 kg

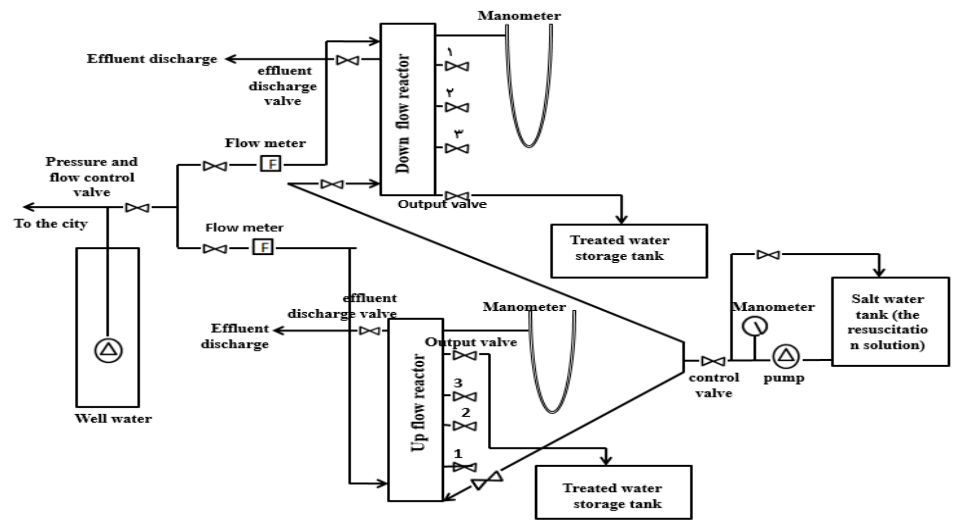


Figure-1: Schematic ion exchange column with flow downward.

- **sampling method , doing experiments and considered variables:**

The nitrate removal rate was examined in three different loads (10, 25 and 40 Bv/h), three-height resin (30, 60 and 90cm) and five volume of water passing (100,160,220 and 280 Bv). Due to the variables range, the experiment's Run obtained 45 Run (3×3×5) and so that triplicate in totally 135 samples was examined. For information of the entering water nitrate concentration to the resin, five sample were taken from raw water of well at different intervals times. Thus, the amount of nitrates, conductivity, sulfate, chloride, alkalinity, and pH were measured. Nitrate was measured using spectrophotometer (Hatch,DR2000) at A wavelength of 500 nm according standard methods number 4-85, other parameters, were measured according to standard methods of water and wastewater tests (18).

- **Analysis of results:**

Results were analyzed and modeling using Design of Expert software program (ver.7), in present study was used Response Surface Method (Historical Data Design), due to need to evaluate the all considered possible modes.

Results

The results revealed that the factor A (volume of water passing) has more effect on nitrate output than the other factors. After of factor A, the most effective related to factor B but in reverse (Height resin), and thereafter is related to factor C (loading rate), all factors have a significant effect on the nitrate removal ($P<0.05$),(fig 2and 3). The results showed that the most appropriate model suggested by software is quadratic model ($R^2=0.8995$). The model is as follows:

$$Nitrate\ of\ \ Effluent\,(mg/L)=$$
$$77.80+50.13A-16.23B+1.23C-20.53AB+0.5AC+11BC+20.94A^2-48.11B^2-1.25C^2$$

Based on results, the amount of nitrate input to ion exchange column is more than the standard level (50 mg/L-NO_3) (Table 3). The average nitrate output in different modes including loading rate, volume of water passing and sampling from different column heights presented in Table 4. Figure 2 showed the fluctuation of average nitrate output. Figure 3 showed the optimal area according to two-factor of the volume of water passing and height of the resin to achieve the nitrate output in less than 50 and 25 mg/L.

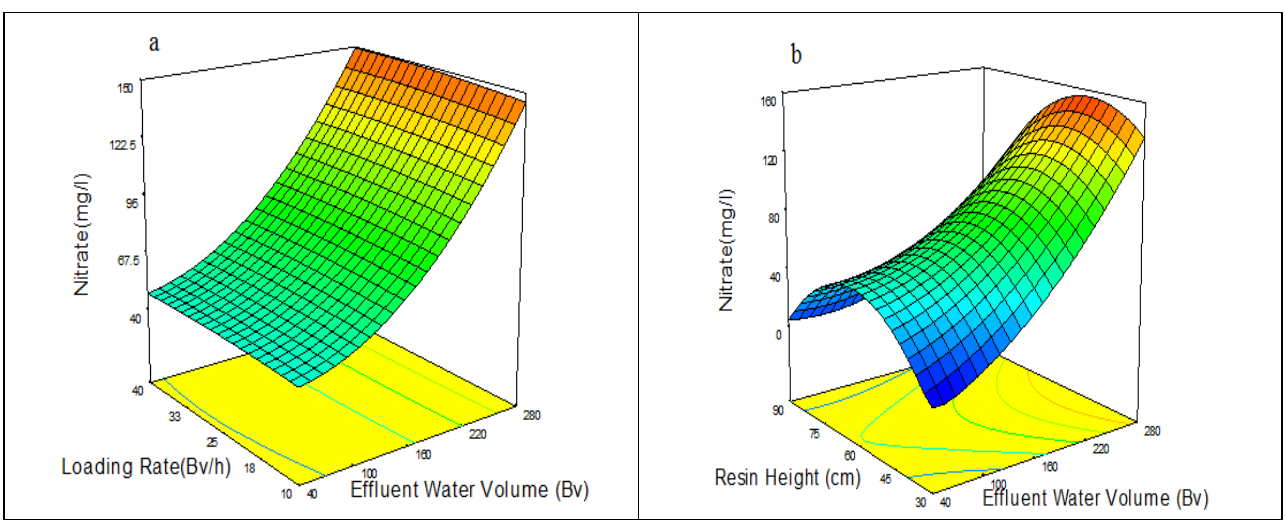
Table -3: The characteristics of water input to the ion exchange column at different volumes of water passing.

volumes of water passing (Bv)	pH	Conductivity (µS/cm)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Alkalinity (mg/L)
50	7.08	1275	105	91	92	372
150	7.04	1271	105	89	96	380
250	7.18	1257	105	78	90	378
350	6.99	1257	105	78	92	378
450	7.03	1315	105	85	90	366

Table -4: **The average of output nitrate concentration from ion exchange column in the loading rate and volumes of water passing.**

Run	Considered factors			The average of nitrate concentration in treated water (mg/L)
	volumes of water passing (Bv)	height of resin(cm)	Loading rate (Bv)	
1	280	30	25	158.3±11.5
2	40	30	10	0
3	160	90	25	4.5±0.3
4	220	60	10	110.65±6.8
5	100	90	25	4±0.1
6	160	90	40	5.15±0.7
7	280	60	25	115.8±6
8	220	60	40	107.5±7.5
9	100	30	25	2.6±0.1

10	220	30	40	87.7±5
11	100	90	40	0
12	280	30	40	106.7±4.5
13	220	90	25	5±0.1
14	100	30	40	0
15	100	90	10	0
16	160	30	25	17±1.4
17	280	90	10	75±3
18	160	60	40	96.45±5.9
19	280	90	40	133.3±7.4
20	220	60	25	105±2
21	160	60	25	117.1±2.6
22	40	30	40	0
23	280	30	10	153.3±8
24	40	90	25	0
25	40	90	10	0
26	40	60	40	55±2.5
27	220	90	40	68±4
28	220	30	10	146.7±3
29	220	90	10	0
30	100	60	10	60.3±3.5
31	280	60	10	110±4
32	40	90	40	0
33	40	60	25	52.3±4.1
34	160	30	40	20.8±2.1
35	280	60	40	102.5±5.2
36	160	90	10	0
37	40	30	25	0
38	40	60	10	55±3
39	100	30	10	0
40	160	30	10	3.7±0.3
41	100	60	25	73.3±5
42	280	90	25	51.7±3.4
43	100	60	40	59.5±4
44	160	60	10	91.15±5.1
45	220	30	25	136.6±9.2



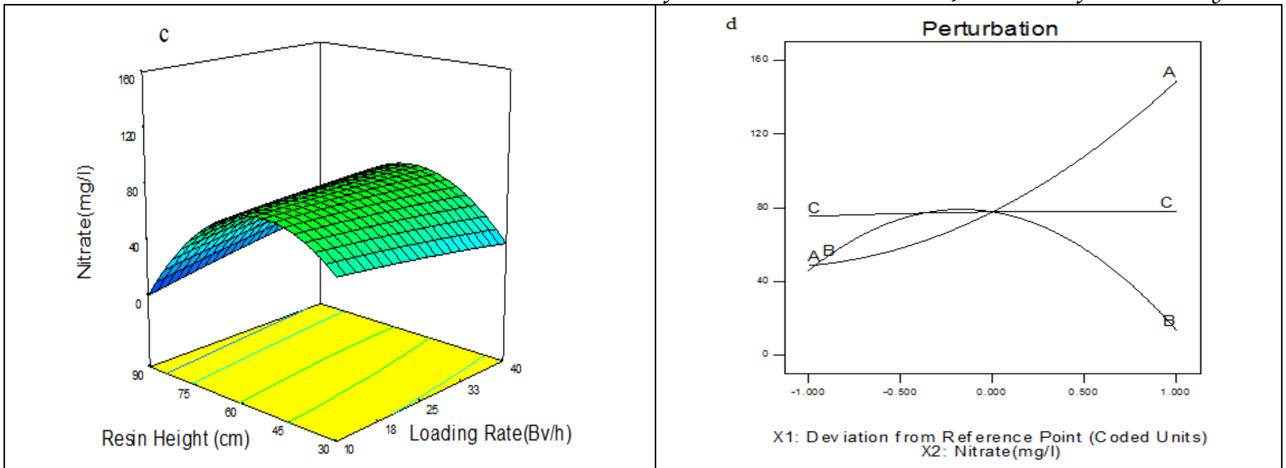


Figure – 2: The effects of load rate, height of resin and volume of water passing on nitrate level in treated water

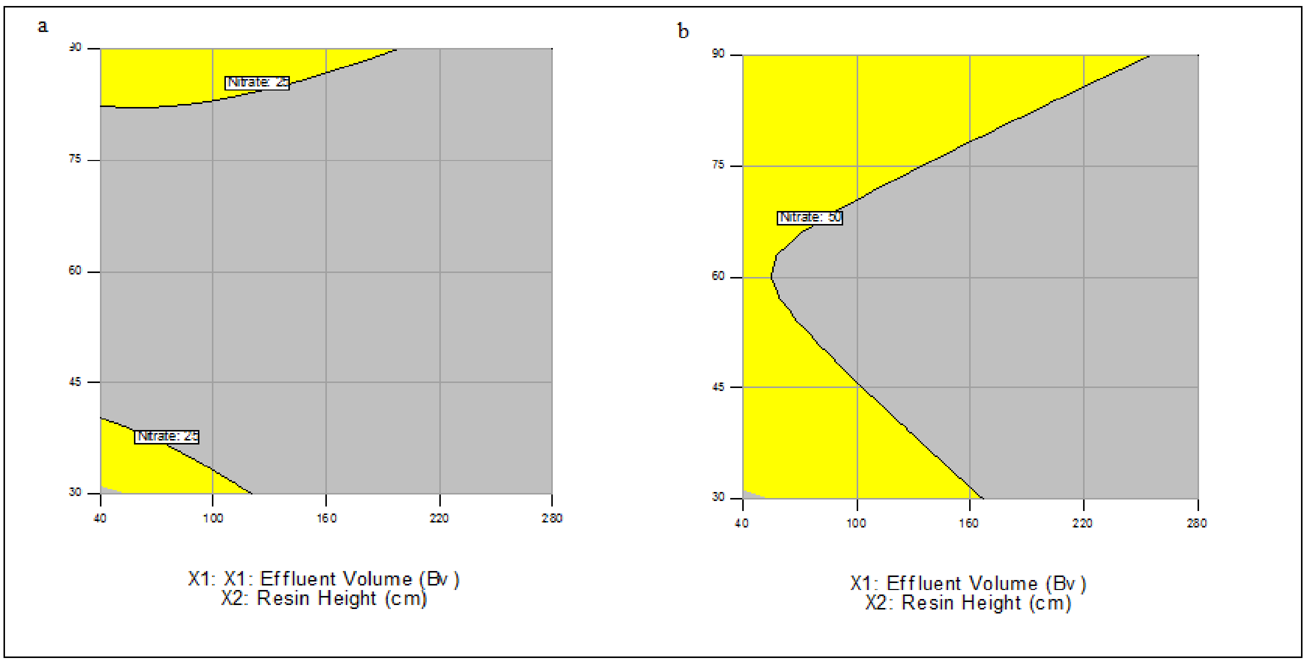


Figure – 3: The optimum area to achieve nitrate [less than 25 mg/L] (a) and [less than 50 mg /L] (b) Based on the most important parameters affecting the nitrate output of the ion exchange columns (the volume of water passing and height of resin).

Discussion

1. The survey effect of the volume of water passing through the resin

Results indicated that with increasing of the volume of water passing the amount of nitrate output increased. This can be due to with the increasing volume of water passing in certain and stable resin height, the transfer of nitrate (mass transfer) and its adsorption on resin beads increased and cause the resin faster to reach equilibrium (saturation of nitrate ions). In other words, by increasing the volume of water passing, the need time for reach to equilibrium of resin dropped and increased the level of nitrate output, resulting should be done operations of the resin revive (19). Other reasons in this regard it can be said that each column of resin has certain practical capacity that this capacity when reached to equilibrium (in upflow water passing, quickly reaches to this capacity) causes exchangeable ions in the electrolyte with similar ion in resin is not exchange and ion exchange process essentially stops(20). Therefore, one of the most important factors affecting ion exchange is the volume of water passing and mass transfer. Given that the total mass of exchangeable ions are almost constant, therefore, it can be done mass transfer in a short time (with increasing of the volume of water passing) or long time (by decreasing of the volume of water passing)(20, 21). considering the results of the optimization conditions, to achieve water quality standards of nitrate (less than 50 mg/L), the volume of water passing can be increase to about 160Bv, for 30 cm height of resin column before the need to revive the resin column. Whereas by increasing the height of resin column to about 90 cm, the volume of water passing can be raised approximately 240 Bv. accordingly, it is necessary to simultaneous increase of resin column height with increasing of volume of water passing, because height of resin column has essential role at level of nitrate output. The conditions reaching to the nitrate standard in treated water (25 mg / L) based on the result of optimized conditions is similar to same conditions reaching to nitrate standard less than 50 mg/L, with this deference that due to effect of level and type of water passing and resin height, there are more restrictive conditions and more stringent terms this two variables. Considering the nitrate output does not increase linearly at levels of resin column height (30, 60 and 90 cm) and increasing the load conditions by increasing the volume of water passing, therefore, it is expected that nitrate removal by strong non-selective ion-exchange resin (a400e) with down flow, in terms of simultaneously effect of these variables obeyed the non-linear model approximately that the study showed such results. According to the obtained model and estimate coefficients (impact factor) relating to the considering factors, the volume of water passing is a more effective for nitrate removal by ion exchange system. This topic is important when the two-factors include resin height and loading rate has certain limitations for a particular purpose. By little change in volume of water passing can be reach to the desired goal (nitrate output). Small and limited change in volume of water passing is high and effective influence on the efficiency of the system.

- **Evaluate the effect of height resin**

The results of nitrate level in different heights of resin column showed that nitrate output of minimum height of resin column (30 cm) is low but by increasing the height of resin column (up to 60 cm), the nitrate output was increased.

More adsorption and exchange nitrate in upper height can be due to that in the strong base or acid resins with down flow, the process of ion exchange initially occur in the level of resin that had the first encounter with water or electrolyte-containing ion exchange (For example, in 5 cm of resin height from the surface of the substrate). This means that most exchange occurs at high level of resin bed and lower levels (next layers) are less exposed and at the result amount of exchange is decreased at the lower levels(20, 21). After saturation of the initial surface levels of exposure, other levels in order to establish the resin column, ion exchange process to achieve to equilibrium of ion at resin and electrolytes to be continued (up to a maximum height of about 60 cm). Possible reasons for reducing of the resin capacity at the height of 30-60 cm could be considering the high nitrate concentration of water in first encounter water with resin, the initial levels of exposure has not ability to adsorb of nitrate in water, therefore, a lot of nitrate ion will transfer to lower level (after 30cm height). This means that the part of nitrate was transfer from the height of the first contact surface (30 cm) and adsorbed by the next surface levels (30 -60cm) and on the basis of the exchange capacity of the second height level after saturation level the initial height has severely reduced. So that the 30 -60 cm height of resin column, the nitrate output of resin has increased, insofar as that at this height level, the less volume of water will passes resin until the saturated. After the resin saturation to a height of about 60 cm, new cycle nitrate adsorption will start on resin beads in the next altitude levels. Considering at this the height range of resin column (60-90cm), the problem leakage of extra nitrate (as was observed in the height range of 0-60 cm), with the gradual increase in height (from 60 to 90 cm), the adsorption rate of nitrate was increased resulting nitrate rate of output is reduced and almost has reached to zero. On this basis, height of resin has an important role in the process of ion exchange and can be prevent unwanted exhaust of nitrate ions in the electrolyte.

Resulting the height of ion exchange column must be chosen so in addition to the gradual process of ion exchange to reaching to equilibrium, in terms of implementation, operation and maintenance should be answerable. since the mid-level of resin (30-60 cm), the second layer is the exposure of anion with resin that any anion which leakaged from first level of resin adsorbed in this layer, therefore, after the equilibrium of first layer, the second layer lost part of its exchange capacity and causes the earlier reached to equilibrium and basically, plays the role of transition layer from the first layer to the third layer (60-90 cm). Thus for avoid leakage of nitrate anion from the first level while be considered achieving to nitrate output less than 50 mg/L (21, 22), it is recommended that the height of the ion exchange columns to be at least 60 cm to removing of nitrate. but if the purpose of water treatment is achieving to the amount of nitrate output less than 25 mg/L, due to rapid saturation transition layer (height of 30-60 cm), it is recommended minimum height of the resin bed be selected 90 cm.

- **Evaluate effects of loading rate**

According to the obtained model and evaluating estimate coefficients (impact factor) relating to the considered factors, the loading rate has less effect (compared to two other factors) in efficiency removal of nitrate by ion-exchange system. This subject shows that the manipulation and fluctuations in loading factor cannot have a great impact on performance of ion exchange system.

In an ion exchange system, operating the concentration of unwanted ion is the most important factor. So that the ion exchange process will continue in an ion exchange process until reaching to equilibrium. Therefore increasing of load rate in the system, just afford the reducing time of equilibrium.

Conclusion

According to the results it can be concluded that about performance of strong non-selective anion exchange system of nitrate (A400E) with down flow, Three factors including volume of water passing, height of resin and loading rate have high, medium and low effect respectively, and their effect in the removing of nitrate was obeyed the non-linear model. By increasing the volume of water passing (with high coefficient effect) and the load rate (with low coefficient of effect), the levels of nitrate output increased, while levels of nitrate output reduced by increasing the height of resin column. Based on results, although the volume of water passing of the resin have more effective role in the control and operation system. While, to meet the standard water of nitrate (25 or 50 mg/L), it is necessary the considering of both factor (water volume passing and height resins). So that the least of 30 cm height resin column is need to meet the nitrate output lower than 50 mg/L at the treated water to obtain the Bv160 volume of water passing, while to achieve the volume of water passing (Bv240), the 90 cm height is required. However, to achieve the treated water with lower nitrate levels of 25 mg/L in the strong non-selective anion exchange system of nitrate (A400E) with down flow reactor, the volume of water passing at two-mentioned height reduced to 120 and 190 Bv respectively.

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