



## Nitrate Removal of the Agricultural Lands Drainage Water by Columns of the Organic and Inorganic Materials

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**ABSTRACT:** This study have investigated the performance of the Sandstone- Sand filters with organic and inorganic materials to reduce the nitrate concentration and electrical conductivity (EC) of agricultural land drainage water, such as poultry manure drainage water, with 10 treatments in three replications. The treatments were in the polyethylene tubes with 62 cm diameter and 100 cm height. The height of absorbent material was considered 20 cm in each column; this height was divided in equal parts based on the number of materials of each column. A solution with EC of 20 ds/m and nitrate concentration of 80 mg /L was added to treatments in 5-step. The outputs during the first two hours, third two hours and fifth two hours were collected and transferred to the laboratory to determine the qualitative and quantitative characteristics. The treatments showed high ability to reduce nitrate concentrations and salinity. The nitrate concentration decreased from 80 mg/l to 20-50 mg/l in drainage water of different treatments during this period, this is equivalent to 43% to 78% nitrate removal. The optimum treatment was related to the Sandstone- Sand- Sawdust- Barely straw filter that its average nitrate concentration reduced from 80 mg /L to 20 mg /L. The highest nitrate reduction was 78.39% that obtained by the treatment in the second stage of sampling. All the treatments reduced the salinity of 20 ds/m to 7 -10 ds/m that were equivalent to 50 % to 72% reduction. The filter of Sandstone- Sand- Sawdust- zeolite was the optimal treatment to reduce salinity. The high efficiency of the treatments obtained in the second stage of sampling.

**Keywords:** Barley straw, Filter; Nitrate remove, Salinity, Sandstone - Sand, Sawdust, Zeolite

### INTRODUCTION

Nitrogen (N) is an essential input for the sustainability of agriculture (Shrestha and Ladha, 2002; Schröder *et al.*, 2004). The nitrate, largely derived from agricultural activity, is considered the most ubiquitous ground water contaminant worldwide (Spalding and Exner 1993). The nitrate is soluble and negatively charged and thus has a high mobility and potential for loss from the unsaturated zone by leaching (DeSimone and Howes, 1998; Chowdary *et al.*, 2005). Many studies showed high correlation and association between agriculture and nitrate concentration in groundwater (Ling and El-Kadi, 1998; Shrestha and Ladha, 2002; Jordan and Smith, 2005).

nitrate-contamination of groundwater used for drinking is a health hazard due to harmful effects of nitrate (e.g. asphyxia and methemoglobinemia of infants) including the increased risk of cancer development (Shuval and Gruener 1977; Weisenburger *et al.* 1991; Crespi *et al.* 1991). The World Health Organization recommends that drinking water should not contain more than 50 mg

$l^{-1}$  of  $NO_3$  (or  $10\text{ mg } l^{-1} NO_3^{-N}$ ), based on its potential to cause methaemoglobinaemia (WHO, 2003).

Poultry and livestock manures have been widely applied as important organic fertilizers sources in agriculture (Houang., 2001). Poultry manure has a higher proportion of biodegradable organic matter than the excrements of any other livestock (Bujoczek *et al.* 2000). Furthermore, as this substrate is rich in organic nitrogen (Yokoyama *et al.* 2007) surface fertilization with poultry manure, which can contain up to 89% of its N in the  $NH_4^+$  form (Beauchamp 1986), can result in losses due to volatilization of  $NH_3$  or leaching of nitrates (Warman and Cooper., 2000). This is so all over the world where human activities, particularly agriculture, are continuously increasing contamination with nitrates. Ion exchange, biological denitrification, and membrane desalting by reverse osmosis, as well as hyper filtration or electro dialysis are common methods for removal of nitrates from water supplies (Shrimali and Singh 2001; Wisniewski *et al.* 2001).

Numerous studies have investigated the denitrification of drinking water, residential wastewater, and agricultural runoff testing agricultural and wood by-products as structured biofilter media. Results from studies by Aslan and Turkman (2003) indicate that wheat straw can be used as biofilter media and as a carbon source for the denitrification of drinking water. Kim *et al.* (2003) investigated the use of both wood chips and wheat straw for nitrate removal in a bioretention study. Volokita *et al.* (1996) studied shredded newspaper as a biofilter media in denitrification columns.

Zeolite is a collective term for a group of naturally occurring aluminosilicate minerals. The most abundant zeolitic mineral is clinoptilolite (Erdem *et al.*, 2004). Clinoptilolite-rich zeolite has been widely used to improve water and air quality due to its large specific surface area and cation exchange capacity (CEC), low cost, and mechanical strength (Erdem *et al.*, 2004; Ackley *et al.*, 1992; Chung and Son, 2000). When placed in water raw, zeolite particles have a net negative surface charge (Rozic *et al.*, 2009) and are hydrophilic which makes them inappropriate for the removal of anionic and hydrophobic pollutants. In order to improve the water contaminant remediation performance of zeolites, cationic surfactants have been successfully used to modify their surface properties (Apreutesei *et al.*, 2008; Sullivan, 1998).

The major increases in N use by agriculture during the last decades in developed and some part of Asia have been associated with large rises in N losses both as  $\text{NO}_3^-$  in drainage water and gaseous emissions. In Iran, agricultural land may be considered to be the main source of  $\text{NO}_3^-$  where intensification in the last 30 years has increased  $\text{NO}_3^-$  leaching from soils into both surface and ground waters (Jalali., 2005). The focus of this study was to investigate the nitrate removal using the organic and inorganic materials. Organic materials were prepared of the available agricultural and wood industry waste (Barley straw and Sawdust). Inorganic material used to absorb nitrate was Semnanzeolite. Experiments were carried out in 5 steps with intervals

of two hours, the ability of the nitrate absorption was measured for each media. Removed Nitrate were measured in the first, third and the fifth two hours. Composition of the duplex, triplex and quadruple of Barley, zeolite, saw dust and sand that formed treatments for nitrate removal of the drainage poultry manure were compared.

## MATERIALS AND METHODS

In recent years, many researchers have tried to remove nitrogen species by using sorption media (Kim *et al.*, 2003; Guo and Ullrich, 2005; Hsieh and Davis, 2005). Absorption is taking place for high surface area and some media have special affinity for specific species of nitrogen. Organic matter (OM) might be very effective in nutrient removal and coarse media might not be able to retain the nutrient in repetitive loading due to small surface area (Hsieh and Davis, 2005). On this basis the performance of filters of Sandston-Sand with organic materials (Barely straw and Sawdust) and inorganic materials (zeolite Semnan), in order to reduce nitrate and Electrical Conductivity (as a measure of salinity) in agricultural drainage water, such as poultry manure drainage water, have examined.

### A. Absorptive Materials

Sand with a particle size of 1 to 1.5 cm have been washed with distilled water and was poured into columns. The Sand was a fine-grained Aeolian Sand, which have been used between filters. Semnan natural zeolite has a particle size of 0.2 to 0.8 mm and 0.5 mm effective size. Zeolite was prepared from mines of Semnan. Barely straw was collected from a field near the university and was crushed to the size of 1 to 2 cm. The Sawdust in the columns was prepared by timber industry. The absorptive material characteristics showed in Table 2. To determine the electrical conductivity (EC) and pH of adsorbents, 25 ml of distilled water added to 5 g of sample. The solutions were mixed in a shaker for 2 h. EC and PH were measured after passing the solutions through the filter paper.

**Table 1: Some of absorptive material characteristics.**

Sawdust	Barely straw	Zeolit	Sand	Parameters
8.8	9.58	6.5	8.75	EC ds/m
6.9	5.98	7.06	7.88	PH
0.85	0.7	0.01	0	% organic nitrogen
50.63	22.5	0.19	0.4	% Organic carbon

### B. Experiment columns

This study was performed by 10 treatments in three replicates (Table 1) in a completely randomized design and under greenhouse conditions in a greenhouse located in Isfahan (Khorasgan Branch), Islamic Azad

University, Isfahan in Iran. A laboratory column test method is a physical model, or microcosm, which attempts to simulate, on a small scale, a portion of the real world subsurface environment under a controlled set of experimental conditions.

The column height is important for the removal of nitrate. Hashemi *et al* (2010) showed that the average nitrate reduction is in treatments by 300 mm and 600 mm height 63.49% and about 69.97% respectively. So filter columns made from 62 cm diameter Polyethylene pipe (PE), with 100 cm height (Fig. 1). 20 cm from each column was dedicated to the absorbing materials; height was divided equally by the number of absorbing materials in each column. 50, 70 and 90 cm pipe have been used for the treatments of double, trial and Quad respectively.

Coarse sand (Geravel) with basalt stones were placed in the lowest layer of the column to a depth of 10 cm, this will improve drainage and prevent the outflow of geravel and sand. Mesh filter was installed at the

bottom of each column to prevent the outflow of rubble and sand. The nitrate removal is also done by deferent processes rather than only biological process. If the nitrate removal is only by biological process, all the media should get almost same removal but different media get different removal. So it might be a combined effect of adsorption and biological process.

Apreutesei *et al* (2008) and Sullivan (1998) modified the ziolite surface to improve its efficiency to remove water contaminants. The treatments of this experiment (Table 1) were combinations of organic materials (Sawdust and Barely straw), mineral material (Semnan zeolite) and sand (windy sand) with Sandstone (particle size of 1 to 1.5 cm).The Sandstone particles were washed with distilled water and placed in the columns.

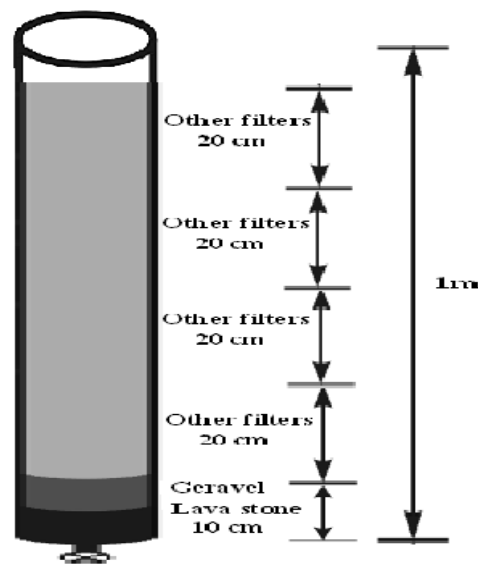


Fig. 1. Diagram the experimental filter columns

### C. Performance Experiment

In order to stability of hydraulic conditions, the distilled water was added to the columns after installing filters. The degree of saturation of the column was determined depending on the filter type. The salt solution of the sodium chloride (as a source of salt) and the potassium nitrate (as a source of nitrate) in 5 steps were added to each filter in the two-hour time intervals, to achieve the appropriate conditions of statistical and saturated the columns. Treatments were saturated at intervals of 2-3 hours once with a solution of potassium nitrate in distilled water, input and output water samples were transported to the laboratory to determine the qualitative component. The electrical conductivity (EC) and nitrate concentration of artificial

drainage water input to the treatment were 20 ds/m and 80 mg/L respectively. At the end of each stage a sample with volume of approximately 50 ml of the bottom of each filter and also Drainage water from the inlet samples were collected in special containers. Electrical Conductivity and nitrate concentrations of the samples were measured in the laboratory. Treatments were named as Table 3.

### D. Quality of water input and output

Water quality input and output of the treatments were assessed with the nitrate concentration and electrical conductivity (EC). The electrical conductivity of treatments was assessed by salinity meter with accurately 0.0001ds/m and nitrate concentrations were determined using Kjeldahl.

**Table 2: Treatments and naming.**

Replication			
3	2	1	
SS <sub>3</sub>	SS <sub>2</sub>	SS <sub>1</sub>	Sandston- Sand
SZ <sub>3</sub>	SZ <sub>2</sub>	SZ <sub>1</sub>	Sandston -zeolite
SB <sub>3</sub>	SB <sub>2</sub>	SB <sub>1</sub>	Sandston -Barely straw
SW <sub>3</sub>	SW <sub>2</sub>	SW <sub>1</sub>	Sandston -Sawdust
SBZ <sub>3</sub>	SBZ <sub>2</sub>	SBZ <sub>1</sub>	Sandston - Barely straw-zeolite
SWZ <sub>3</sub>	SWZ <sub>2</sub>	SWZ <sub>1</sub>	Sandston -sawdust-zeolite
SSB <sub>3</sub>	SSB <sub>2</sub>	SSB <sub>1</sub>	Sandston-sand- Barely straw
SSBZ <sub>3</sub>	SSBZ <sub>2</sub>	SSBZ <sub>1</sub>	Sandston -Sand- Barely straw- Zeolite
SSWZ <sub>3</sub>	SSWZ <sub>2</sub>	SSWZ <sub>1</sub>	Sandston -Sand-sawdust-Zeolite
SSWB <sub>3</sub>	SSWB <sub>2</sub>	SSWB <sub>1</sub>	Sandston - Sand - - Barely straw

### E. Data analysis

The effect of nitrate removal at different time intervals using statistical analysis (by Duncan test) was evaluated. The next step investigated the ability of different media in the nitrate removal, so that the ability of the media was compared with each other by Duncan test. Salinity reduction (electrical conductivity) by the media was examined by Duncan test. The analysis was performed in the software SPSS 19.

## RESULT

### A. The nitrate removal in drainage water output of the three stages

At first the solution of potassium nitrate salt (as source of nitrate 80 mg/L) and sodium chloride salt (To get the salt solution to 20 ds/m) added to the columns of experiment in 5 steps to reach the saturation level.

The table 3 shows the results of data analysis of nitrate concentrations in drainage water output of treatments in the 3 sampling time (first, third and fifth two hours). Significant differences were showed in the treatment of sand - sandstone (SS) between the SS1 compared with SS2 and SS3. The most of the reduction of nitrate concentrations in the drainage water treated with sandstone- sand was up to 59.89% that occurred in the third two hours. Significant differences were observed between the first stages in the treatment of sandstone - zeolite (SZ1) compared with (SZ2 and SZ3) the second and third stages of sampling. In the second stage, the

maximum nitrate concentrations reduced up to 47/19% by SZ2. Analysis of variance of the output of treated water drainage with sandstone - barley straw (SB) showed significant differences between the three stages of sampling. The second stage, with the reduction of nitrate up to 54.32% showed the greatest impact. Water drainage outlet of sandstone - sawdust treatment (SW) created significant difference between the three stages of sampling, the most of nitrate reduction (64.38%) was related to the second stage of sampling. The output data of treated drainage water with sandstone - Barely straw - zeolite (SBZ), sandstone - Sawdust - zeolite (SWZ) and sandstone - Sand- Barely straw (SSB) indicated significant difference between every three stages sampling. These treatments reduced the maximum nitrate concentrations in the second stage of sampling respectively up to 66.55%, 64.38% and 69.97%. Drainage water treated with Quad media such as; Sandstone - Sand - Barley straw - zeolite (SSBZ), Sandstone - Sand - sawdust - zeolite (SSWZ) and Sandstone - Sand - sawdust - Barley straw (SSWB) caused significant difference between every three stages sampling, the most nitrate reductions of Quad media were respectively up to 67.91%, 73.13% and 78.72% that were related to the second stage of sampling. The variances of the nitrate concentrations data in the drainage water output treatments in every three sampling have been showed in table 3.

Table 3.

Treatment		N	Subset		
			1	2	3
SS	1.00	3	53.7167		
	3.00	3		58.8370	
	2.00	3		59.8944	
	Sig.		1.000	.072	
SZ	1.00	3	43.8074		
	3.00	3		46.6315	
	2.00	3		47.1926	
	Sig.		1.000	.268	
SB	1.00	3	49.8537		
	3.00	3		52.1185	
	2.00	3			54.3220
	Sig.		1.000	1.000	1.000
SW	1.00	3	57.7167		
	3.00	3		62.7463	
	2.00	3			64.3870
	Sig.		1.000	1.000	1.000
SBZ	1.00	3	59.3796		
	3.00	3		63.1833	
	2.00	3			66.5519
	Sig.		1.000	1.000	1.000
SWZ	1.00	3	57.7167		
	3.00	3		62.7463	
	2.00	3			64.3870
	Sig.		1.000	1.000	1.000
SSB	1.00	3	64.8574		
	3.00	3		67.2130	
	2.00	3			69.9704
	Sig.		1.000	1.000	1.000
SSBZ	1.00	3	64.5733		
	3.00	3		67.1989	
	2.00	3			69.9141
	Sig.		1.000	1.000	1.000
SSWZ	1.00	3	69.5944		
	3.00	3		70.8944	
	2.00	3			73.133
	Sig.		1.000	1.000	1.000
SSWB	1.00	3	74.4333		
	3.00	3		76.4889	
	2.00	3			78.7241
	Sig.		1.000	1.000	1.000

*B. The nitrate concentration of treatments in the first stage of sampling*

Analysis of variances (Table 4) showed significant differences between treatments in the first stage of sampling. In accordance with this table, the best performance in the nitrate reduction is related to the filter 10, the treatment of sandstone - Sand - Barely straw - zeolite (SSBZ1), the treatment reduced nitrate concentration up to 74.43%. The lowest performance is related to the filter 2 or the treatment sandstone -

zeolite (SZ1). The treatment could be reduced nitrate concentration up to 43.8% only. In the first stage of sampling, there were not significant differences between treatments sandstone - Sand (SS1), with sand - barley - zeolite (SBZ1) treatment. Treatment sandstone - Sawdust - zeolite (SWZ1) showed no significant difference compared with the sandstone - Sand - Barley straw (SSB1). There the treatments were significantly different from the first stage of sampling.

**Table 4. Analysis variance of the treatments in the first two hours of sampling.**

Duncan <sup>a,b</sup>									
Treatment	N	Subset for alpha = 0.05							
		1	2	3	4	5	6	7	8
2.00	3	43.8074							
3.00	3		49.6685						
5.00	3			53.2630					
1.00	3			53.7167					
4.00	3				57.7167				
7.00	3					59.2667			
6.00	3					59.3796			
8.00	3						64.8574		
9.00	3							69.8648	
10.00	3								74.4333
Sig.		1.000	1.000	.339	1.000	.810	1.000	1.000	1.000

*C. The nitrate concentration of treatments in the two third hours of sampling*

Significant differences have been observed by analysis of the variances (Table 5) between treatments in the second stage of sampling. However, there was observed not significant differences between treatments of sandstone - Sand (SS2) with sandstone - barley straw - zeolite (SBZ2) treatment. Treatment sandstone - Sawdust (SW2) showed no significant difference compared with the treatment sandstone - Sawdust - zeolite (SWZ2). At this stage drainage water treated with Sandstone- zeolite (SZ2) with the nitrate concentration of up to 47/13% and drainage water treated with Sandstone- Sand- Sawdust- Barely straw (SSWB2) with the reduction of the nitrate

concentration up to 78/38% indicated the lowest and highest performance respectively.

*D. The nitrate concentration of treatments in the fifth two hours of sampling*

Analysis of variances (Table 6) showed significant differences between the treatments in the third stage of sampling. However, in the stage, there was no statistical difference between treatment sandstone - Sand (SS3) compared with drainage water treated with sandstone - Sand- Zeolite (SBZ3). Drainage water treated with Sandstone- Sawdust, Sandstone- Sand- Barely straw (SSB) and Sandstone- Sawdust- Zeolite (SWZ3) showed no significant differences in reduction of nitrate concentrations.

**Table 5: Analysis the variances of the treatments in the fifth two hours of sampling.**

Duncan <sup>a,b</sup>									
Treatment	N	Subset for alpha = 0.05							
		1	2	3	4	5	6	7	8
2.00	3	47.1926							
3.00	3		54.3241						
5.00	3			59.3796					
1.00	3			59.8944					
4.00	3				64.3870				
7.00	3				64.8537				
6.00	3					66.5519			
8.00	3						69.9704		
9.00	3							73.2667	
10.00	2								78.9194
Sig.		1.000	1.000	.308	.354	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 2.857

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

**Table 6: Analysis the variances of the treatments in the fifth two hours of sampling.**

Duncan <sup>a,b</sup>								
treatment	N	Subset						
		1	2	3	4	5	6	7
2.00	3	46.6315						
3.00	3		52.1185					
5.00	3			58.7241				
1.00	3			58.8370				
4.00	3				62.7463			
6.00	3				63.1833			
7.00	3				63.5741			
8.00	3					67.2130		
9.00	3						71.0389	
10.00	3							76.4889
Sig.		1.000	1.000	.808	.103	1.000	1.000	1.000

At this stage the lowest and highest performance for reduction of the nitrate concentration are related to drainage water treated with Sandstone-Sand- Barely straw- Sawdust (SSBW3) up to 76.48% and Sandstone - Zeolite (SZ3) up to 46.63% respectively.

*E. The reduction of nitrate concentration of the dual media in the second stage of sampling*

Analysis the variances of the dual treatments (Table 7) showed significant differences between all treatments. Treatment of 4 (Sandstone - Sawdust) (SS2), with 64.38% absorption of the nitrate concentration showed the highest performance. Treatment of 2 (Sandstone -

Zeolite) (SZ2) with 47.19% showed the lowest performance to reduce the nitrate concentration.

*F. The reduction of nitrate concentration of the triple media in the second stage of sampling*

Analysis of the variances (Table 8) showed a significant difference between the triple treatments. The treatment of 6 (Sandstone - Zeolite - Sawdust) (SZS2) with absorption of 66/55% and the treatment of 5 (Sandstone - Barley straw- Zeolite) with 59.37% absorption indicated the maximum and minimum impact on the reduction of the nitrate concentration.

**Table 7: Analysis the variances of the dual treatments in the second stage of sampling.**

Duncan <sup>a,b</sup>					
Treatment	N	Subset			
		1	2	3	4
2.00	3	47.1926			
3.00	3		54.3241		
1.00	3			59.8944	
4.00	3				64.3870
Sig.		1.000	1.000	1.000	1.000

**Table 8. Analysis of the variances of the triple treatments in the second stage of sampling.**

Duncan <sup>a,b</sup>				
treatment	N	Subset		
		1	2	3
5.00	3	59.3796		
7.00	3		64.8537	
6.00	3			66.5519
Sig.		1.000	1.000	1.000

### G. The Reduction of nitrate concentration of the Quad media in the second stage of sampling

Analysis of the variances (Table 9) showed a significant difference between Quad treatments. Treatment of 10 (Sandstone - Sand - Sawdust -

Barley straw) (SSSB2) with 72/77% and the treatment 8 (Sandstone - Sandstone - Barley straw - Zeolite) (SSBZ2) with 54.05% showed the highest and lowest impact on nitrate absorption.

**Table 9: Analysis of the variances of the Quad treatments in the second stage of sampling.**

treatment	N	Subset		
		1	2	3
8.00	3	69.9704		
9.00	3		73.2667	
10.00	3			78.7241
Sig.		1.000	1.000	1.000

### H. Reduction of salinity (EC) of the 5-stage sampling

There was no significant difference related to the reduction of salt by the treatments, therefore the average of the three stages in the 10 treatments were compared (Figure 6). The highest performance was associated with a decrease in the salinity of the treatment 9 (Sandstone - Sand - Sawdust - zeolite) with the absorption of 72.92% and the performance was the lowest for treatment 3 (Sandstone - Barley straw) with the absorption of 50.94%.

## DISCUSSION

Significant differences were observed for the reduction of nitrate concentrations in the three stages of sampling (first, third and fifth two hours) by the treatments. The first stage of sampling the treatments of Sandstone - Sand (SS1) and Sandstone - Zeolite (SZ1) showed significant difference with the second and third stages of sampling (SS2, SS3, SZ2 and SZ3). The drainage water treated with organic media makes significant difference for removal nitrate between the three stages of sampling given these findings; the ability of sand and zeolite particles remains constant over time. There was not a constant process of nitrate removal with the organic media, so the ability of organic carbon for nitrate removal varied over time.

Optimum time to the reduction of nitrate concentration was the second stage of sampling by the treatments. Hashemi *et al* (2010) showed that the rate of the reduction of nitrate concentration in denitrification columns was high until the day of 12 and then the effluent nitrate concentration levelled off at  $10 \text{ mg l}^{-1}$ . Liu and Lo (2014) through column experiments, the potential of using the B.C. zeolite for ammonia removal from compost leachate was studied, stated that the hydraulic retention time, and hence the influent loading flow rate, greatly affected the zeolite column performance in terms of ammonia adsorption. Lower loading flow rates yielded higher operating ammonia adsorption capacities. This revealed that an adequate

contact time is essential to achieve a specific adsorption capacity. A hydraulic retention time of 6 hours was preferred which yielded an operating adsorption capacity of  $1.31 \text{ mg NH}_4\text{-N/g zeolite}$ . The low efficiency ( $50\% >$ ) in three stages of sampling in term to nitrate removal related to Sandston- Zeolite (SZ) treatment, moreover the efficiency of SZ treatment and Sandston - Barely straw (SB) treatment were lower compared with Sandston - Sand (SS). The optimum treatment for nitrate removal is related to Sandston-Sand-Sawdust- Barely straw (SSWB), this treatment reduced the nitrate concentration of  $80 \text{ mg /L}$  to  $20 \text{ mg /L}$  during the experiment period. The highest nitrate reduction, up to 78.39%, obtained by the treatment SSWB2 in the second stage of sampling. This ability to absorb nitrates made by abundance of organic carbon in barley straw and Sawdust that gives organic material to denitrification bacteria. This bacteria by their activation reduced nitrate contamination; moreover the Sandston and Sand with coherent structure increased the contact surface of input solution with media in the third two hours. Surface absorption of the anionic and cationic species of the adsorbent is defined on the basis of competitive adsorption of  $\text{H}^+$  and  $\text{OH}^-$  ions with adsorbent articles.

The highest nitrate concentration reduction is related to the treatment of sandstone - Sawdust (SW) that was a double media. This treatment reduced the nitrate concentration from  $80 \text{ mg/L}$  to up to  $30 \text{ mg/L}$  during the experiment period; this is equivalent to 64.37% nitrate removal. The optimal time for nitrate reduction was the third two hours of sampling. Significant differences were not between the third and fifth two hours of the sampling in the treatments of Sandston- Barely straw - Zeolite (SBZ) and Sandston- Sand- Barely straw (SSB). Barely straw on top of the sand media showed the identical ability to remove nitrate when the column made of zeolite, Barely straw and Sandston respectively.



The highest nitrate removal efficiency is related to the treatments of Sandston- Sawdust, Sandston- Sawdust- Barely straw and Sandston- Sand - Sawdust -Barely straw. High nitrate removal capacity caused with the abundant organic carbon in the Sawdust and Barely straw and increased denitrification. Moreover, Abundance of pores in Sandston and Sand modified nitrate removal.

In general a more significant role in term of nitrate removal observed by sawdust, this was due to the high consistency and abundance organic carbon. Low efficiency for nitrate removal was due to the lack of organic carbon and pore structure in the zeolite. nitrate removal showed low efficiency in the third stage of sampling by treatments, this was due to filling the pores and reduction of the organic carbon.

Reduction of nitrate concentration in drained water was different at three stages of sampling.

Due to the lack of denitrification process by bacteria and empty pores the lowest absorption occurred in the first stage of sampling. The maximum absorption related to the second stage that showed superficial absorption and increased the duration of exposure to nitrate solution with sorbents. The sampling in the fifth two hours was marked by a decrease in nitrate absorption. So filling of pores and reduction of the amount of organic carbon and adsorption were effective.

Analysis of variances showed that the nitrate removal by the treatments created the significant differences between them in the first stage of sampling. Drainage water treated with sandstone - zeolite reduced Nitrate concentrations up to 43.8 %, while the reduced nitrate concentrations reached up to 74.4% by the drainage water treated with sandstone - Sand- Sawdust- Barely straw. Analysis of variance showed significant differences between treatments in the third two hours of sampling. The nitrate concentrations reduced up to 47.1 % and 78.9% by drainage water treated with sandstone - zeolite and sandstone - Sand- Sawdust- Barely straw. Treatments in the fifth two hours of sampling reduced the nitrate concentrations with significant difference between the treatments. The reduction of the nitrate concentration was between the range of 46.6% to 76.4% by the treatments of sandstone - zeolite and sandstone - Sand- Sawdust- Barely straw. Low efficiency of sandstone - zeolite is related to the pores occupied with zeolite particles and reduction of the contact solution with absorbent.

Four treatments indicated significantly different from each other with dual media in the second stage of sampling. Reduction of nitrate concentrations was 47.1 and 64.3% by treatments of SZ2 and SW2.

The treatments that made of three media differed from each other significantly; the highest and lowest nitrate concentrations reduction were up to 59.3% and 66.5% in the drainage water treated with the three media of SBZ and SSB. Reduction of nitrate concentration by drainage water treated with quad media created the significant difference between them. The reduction nitrate concentrations were up to 69.97% and 78.7% by SSBZ and SSWB treatments. Treatments performance in Nitrate absorption increased in the multiple media. Increasing of organic matter affected the efficiency of treatments.

Guo and Ural (2005) conducted nitrate and nitrite removal from wastewater in a laboratory column experiment with three types of soil. They used sandy clay loam, loamy sand, and sandy loam and found significant nitrate and nitrite removal (>90%) in all three soils. This experiment was very important for nitrate removal by soil. It proved that some soil has an affinity for nitrate but this will vary from one kind of soil to another. Forbes et al. (2005) used lightweight expanded shale and masonry sand for the removal of phosphorus from secondarily treated municipal effluent. They found that sand was a poor candidate for retaining phosphorus and expanded shale had greater removal efficiency because of its larger surface area.

All treatments showed a high ability to reduce electrical conductivity; however, reducing the electrical conductivity was similar in all three stages for different treatments. Average of decreased salinity in the three stages sampling introduced the quad media with Sandston- Sand- Sawdust- Zeolite as the optimum treatment, it reduced EC Up to 72.92%. The lowest performance 50.94% is related to the treatment by Sandston- Barely straw. The treatments demonstrated the above 50% ability for reduction salinity. Probably, Sandstone increased the acidity (PH) of the solution through the constituent components and the formation of sodium hydroxide; this resulted in the reduction of the electrical conductivity. Zeolites are crystalline hydrated aluminosilicate with alkali metal cations and alkaline earth, Cations exchange and capability reversible adsorption is the characteristics of these compounds. The zeolite in the columns experiment, increased absorption of salt through processes of ion exchange, adsorption of surface and increased PH of the solution.

## CONCLUSION

In many countries, public concern over the deterioration of groundwater quality from nitrate contamination has grown significantly in recent years.

This concern has focused increasingly on anthropogenic sources as the potential cause of the problem. Evidence indicates that the nitrate ( $\text{NO}_3$ ) levels routinely exceed the maximum contaminant level (MCL) of 10 mg/l  $\text{NO}_3\text{-N}$  in many aquifer systems that underlie agriculture-dominated watersheds. The analysis in this study was indicative of high performance treatments to reduce nitrate and salinity of agricultural drainage water. The treatments reduced the nitrate concentration of 80 mg/ L to 50 to 20 mg/ L in the output water. In other words, the nitrate removal efficiency was 43 to 78% by the treatments. Drainage water salinity decreased from 20 dS /m to the 7 to 10 ds/m, this was equivalent to 50% to 72% reduction in electrical conductivity (EC). The media multiple treatments to remove nitrate and salinity decrease were accounted for the highest performance. Abundance of organic carbon composition of organic matter and mineral particles increased the absorption of nitrate by increasing the contact area. As a consequence, the use of agricultural waste is proposed as a practical and affordable solution for the removal of nitrate and reduction of salinity of agricultural drainage water. In this regard, the use of filters with a combination of organic and inorganic substrates showed the highest performance. Given the results of this study can be used the mineral filters (zeolite) practically to remove nitrate anions in aquatic environments with high absorption efficiency. This efficiency improved in the Sandstone - Sand filters when treated drainage water with the multiple media with different organic material and zeolite. Based on the results of this study, media of the Sandstone - Sand With organic and inorganic materials showed high efficiency in the removal of nitrate and reduction of salinity. The high efficiency for nitrate removal, that is a serious concern all over the world, requires a shorter time the maximum the few hour.

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