



# Evaluation of parameters affecting nitrate adsorption by sawdust of beech tree using analytical hierarchy process

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**Abstract:** Inorganic anions are such as toxic substances that can be harmful to humans and animals at low concentrations. In the meantime, nitrate ions are considered as a serious threat to surface water and groundwater resources due to their high solubility. Nitrate contamination of water can be caused by the discharge of municipal and agricultural wastewater, the unhealthy disposal of industrial and sanitary waste. Among the effective parameters on the nitrate adsorption process by natural adsorbents are adsorbent mass, initial concentration of nitrate, pH and adsorbent contact time with solution. The main purpose of this study is to evaluate the parameters affecting nitrate adsorption by sawdust of beech tree using analytical hierarchy process. To determine the most important parameters affecting the nitrate adsorption, four parameters pH, contact time, adsorbent mass and initial concentration of nitrate were studied, each of which has four levels. Expert Choice software was used to evaluate the most important parameters and their levels. The results of this study showed that the contact time parameter had the most effect on the nitrate adsorption process from aqueous solutions and pH parameter had the least effect on this process. The results of ranking the levels of each criterion showed that with increasing adsorbent mass, initial concentration of nitrate, pH and contact time to optimum point increased nitrate adsorption. Also, after passing through optimum point, with increasing adsorbent mass, initial concentration of nitrate, pH and contact time decreased nitrate adsorption.

**Keywords:** Nitrate adsorption, sawdust of beech tree, Analytical hierarchy process, Expert Choice software

## INTRODUCTION

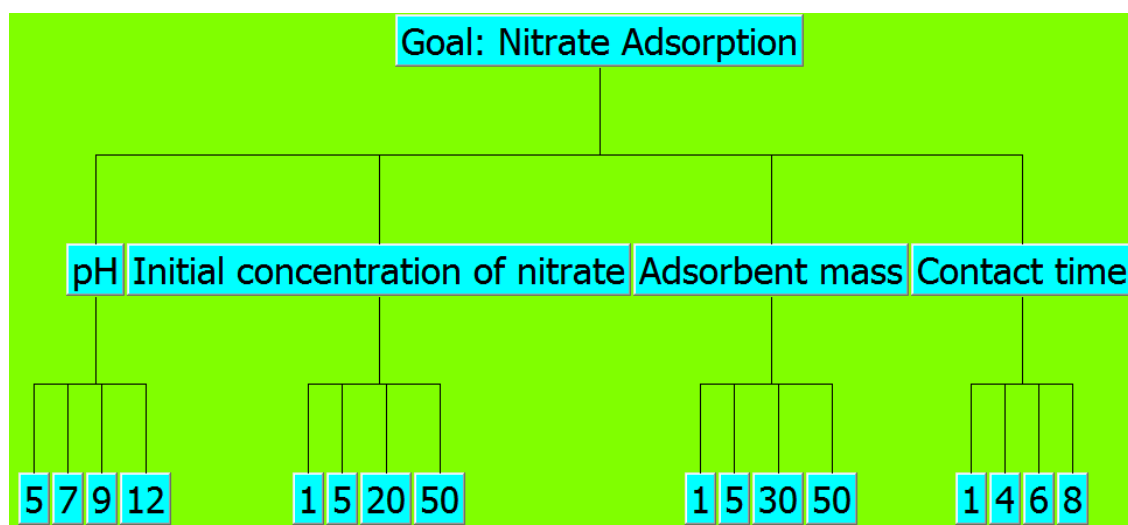
Inorganic anions are one of the most important toxins materials that are also harmful to humans and animals at low concentrations (Ganesan et al, 2013). Among these anions, nitrate due to its high solubility in water of the most important sources of pollution of surface water and groundwater (Bhatnagar et al, 2010). This ion enters water sources due to the entry of industrial and agricultural wastewater and human raw sewage (Divband et al, 2014). Nitrate ion is an indicator of the occurrence of groundwater contamination. The high concentration of this ion in water, in addition to toxicity, can lead to microbial contamination, so that the increase in nitrate concentration in water is not detectable by taste (Ganesan et al, 2013). Revitalization of this ion to nitrite by microorganisms poses more serious health risks. Until now, various methods including

surface adsorption and ion exchange, chemical deposition, reverse osmosis, nitrate depletion and electro dialysis have been used to purify nitrate from water sources (Khajavi-Shojaei et al, 2019). Surface adsorption and ion exchange methods have attracted the attention of researchers because of their high efficiency, cheapness, ease of use and being environmentally friendly (Yin et al, 2018). Hitherto, many studies have been done on the removal of nitrate from aqueous solutions with different adsorbents, which some of them are referred to here. Khajavi-Shojaei et al (2019) investigated the nitrate adsorption kinetics and isotherm by common reed (*Phragmites australis*) biochar from aqueous solution. In this study, reed (*Phragmites australis*) biochar was prepared at 500°C and its properties were measured. The effect of some effective parameters on the nitrate adsorption process by reed (*Phragmites australis*) biochar including initial concentration, contact time, pH and amount of reed biochar were studied on a batch experiment. Nitrate adsorption by reed biochar reached equilibrium after 480 minutes. The optimum pH for nitrate removal was 3. Nitrate removal efficiency increased with increasing contact time and adsorbent amount. The pseudo second order kinetic model provides a well description for the adsorption process of nitrate ( $r^2 = 0.97$ ). The Freundlich model ( $r^2 = 0.99$ ) showed the best fit for the nitrate data. In general, the results of this study showed the high ability of reed biochar for nitrate adsorption (73.5 mg/g). Therefore, reed biochar after nitrate adsorption due to its proper capacity to supply part of the nitrogen needed for plants, has a good potential as a soil modifier. Mikhak beiranvand et al (2019) studied nitrate removal using pumice aggregate coated with zeolite nanoparticles modified by cationic surfactant from synthetic aqueous solutions. In this study, zeolite nanoparticles were fixed on the substrate of pumice aggregates after modification by CTAB surfactant. The physical and structural properties of the adsorbent prepared by XRD, EDAX and SEM techniques were investigated. In this study, the response surface methodology based on Box-Behnken design was used to evaluate the effect of independent variables pH (5–9), temperature (15–45°C) and adsorbent amount (5–15g) on response performance. Also, the response level method based on Box-Behnken design was used to predict the best value response. The results showed that the maximum nitrate removal efficiency under optimum conditions predicted by the model (temperature 34°C, pH 5 and adsorbent amount 15g) was 52.26%. The rate of nitrate removal also increased with increasing adsorbent content and contact time, but with increasing pH and initial nitrate concentration reduced nitrate removal efficiency. Finally, the results indicated that pumice aggregates coated with zeolite nanoparticles can be used as an effective and available adsorbent for the removal of contaminants. Amininejad et al (2019) evaluated of nitrate removal from aqueous solution by nanostructure of *Conocarpus*. In this study, powder of nanostructure *Conocarpus* leaf was prepared in nanometer dimensions. To enhance nitrate removal capability, chemicals were loaded onto the adsorbent surfaces of the amine groups. Batch adsorption experiments were performed to determine the optimum pH, equilibrium time, optimum adsorbent content and optimum nitrate concentration. Kinetic and isotherm models were studied to describe the adsorption behavior and quantitative calculation of nitrate removal. The optimum pH value of 3 and the equilibrium time of 90 minutes was determined. The optimum amount of adsorbent consumed was 0.6 g/L and the optimum initial nitrate concentration was 100 mg/l. The optimum amount of removal efficiency in optimal conditions was 47% and adsorption capacity of 79 g/mg. Investigation of adsorption isotherms showed that Freundlich isotherm with 0.96 correlation coefficient more consistent on nitrate adsorption by nanostructure of *Conocarpus* leaf. Also, kinetic model of Ho et. al. with correlation coefficient 0.99 compared to Lagergren model and intraparticle diffusion showed a good match with experimental conditions. Ahmadpari et al (2019) investigated the models of kinetics and isotherms for nitrate adsorption from aqueous solution by wheat straw. In this research, potassium nitrate salt was used to make nitrate solutions. NaOH and HCl with 0.1 mole/L concentration was used to adjustment amount of the solutions pH. The pH of the solution was in the range of 4 to 13. To describe the data, the kinetics models of Ho et al and Lagergren were used. To describe the data, the isotherm models of Langmuir and Freundlich were used. The results indicated that the most nitrate adsorption by wheat straw observed in pH=6 and contact time 140 minutes. Langmuir and Freundlich models as equilibrium models and Ho et al. and Lagergren models as non-equilibrium models were used to study the adsorption process. Determination

coefficients of Ho et al model was 0.97 ( $R^2= 0.97$ ) and the value of this index for the Lagergren model was 0.91( $R^2= 0.91$ ). Comparing the determination coefficients between measured data and obtained amount from Ho et al. and Lagergren models indicated that the model of Ho et al. describes experimental data better. Determination coefficients of Freundlich isotherm was 0.98 ( $R^2= 0.98$ ) and the value of this index for the Langmuir isotherm was 0.83( $R^2= 0.83$ ). comparing the Langmuir and Freundlich isotherm for nitrate adsorption by wheat straw indicated that Freundlich isotherm was more suitable than Langmuir isotherm in describing adsorption process. The aim of this study was to investigate the nitrate removal using woodchips of beech tree and determining the adsorption isotherms and kinetics. The main purpose of this study is to evaluate the parameters affecting nitrate adsorption by sawdust of beech tree using analytical hierarchy process.

## Materials and Methods

In this study, sawdust of beech tree was used as adsorbent for nitrate adsorption. To determine the most important parameters affecting the nitrate adsorption, four parameters pH, contact time, adsorbent mass and initial concentration of nitrate were studied, each of which has four levels. Expert Choice software was used to evaluate the most important parameters and their levels. Figure 1 shows the parameters and their levels. In this figure, criteria are included the initial concentration of nitrate (milligrams per liter), contact time (hour), adsorbent mass (grams) and pH.



**Figure 1:** Hierarchical structure of nitrate adsorption process by sawdust of beech tree

After determining the criteria and sub criteria in Expert Choice software, pairwise comparisons tables were prepared for each extracted factor. The results of these comparisons were entered into the Expert Choice software as raw data. Finally, weighting and ranking of criteria and sub criteria were performed to maximize nitrate adsorption by sawdust of beech tree using this software. The basis of Expert Choice software work is method AHP (Analytical Hierarchy Process). The AHP method is one of the most well-known multi-criteria decision making methods that has been welcomed in a variety of applied fields. In general, it can be stated that the AHP method consists of three main steps, which are described here.

- 1) Creating hierarchical structure
- 2) Pairwise comparison of elements a hierarchical structure
- 3) Scoring of criteria

According to the AHP approach, the subject of decision making has a tree whose first level will be the target, the last level of competing options. Also, the intermediate level or levels will be decision indicators. Then, to collect the data, the elements at each level must be evaluated from the lower to the highest levels in relation to all the relevant elements at the higher levels. In the AHP method, if the basis of evaluation is qualitative, the evaluation is performed as pairwise comparison. With research conducted by Saaty and Vargas (1991), a range for comparison of criteria has been proposed, comprising numerical values of 1 to 9 (Table 1).

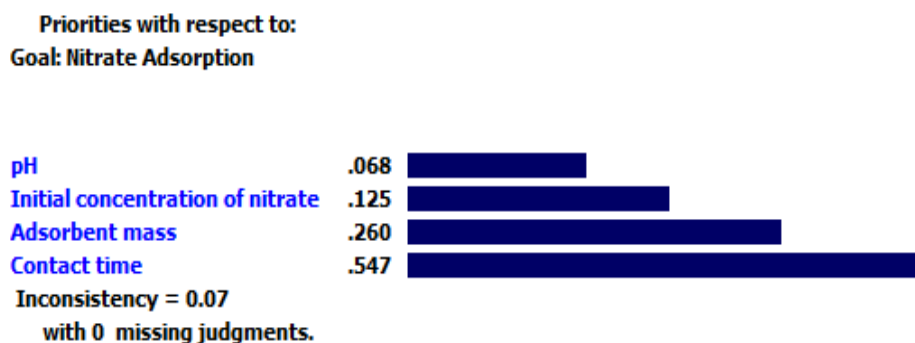
**Table 1:** Table presented by Saaty and Vargas

Preferences(qualitative concept of privileges)	Amount of quantitative
Quite a reference or quite importantly or quite favorable	9
Very strong preference or importance or desirability	7
strong preference or importance or desirability	5
A little reference or slightly importantly or slightly favorable	3
Equal preference or importance or desirability	1
Preferences between above intervals	2, 4, 6, 8

One of the benefits of the analysis hierarchical process (AHP) is decision compatibility control. In other words, in the analysis hierarchical process can be calculated the degree of compatibility of the decision and judged about the good and bad of being rejected or accepted. Also, if the compatibility rate is greater than 0.1, then in the judgment should be revised (Saaty, 1990).

## Results and Discussion

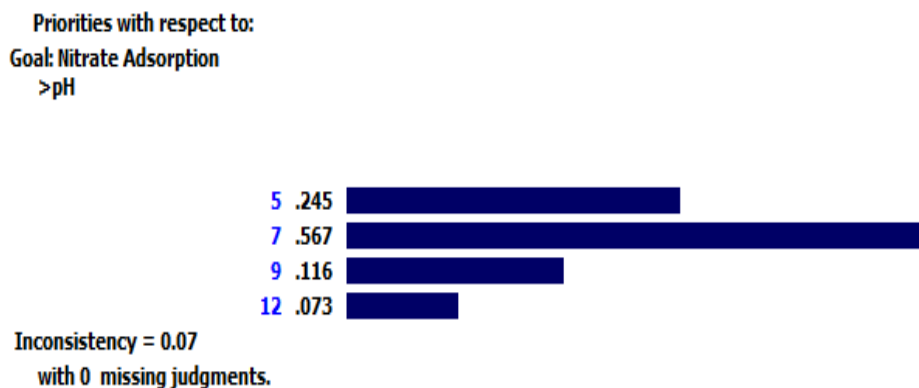
Figure 2 shows the weighting diagram and comparison main dimensions of the project with the main goal of the project. Figure 2 shows that the contact time parameter with the weight equal to 0.547 is allocated the highest priority. Also, the adsorbent mass parameter with the weight equal to 0.260 after contact time parameter has the highest priority. Nitrate initial concentration parameter with the weight equal to 0.125 has the third priority among the investigated parameters in the field of nitrate adsorption by sawdust of beech tree. The pH parameter with a weight of 0.068 has acquired the last priority among criteria. The value of the inconsistency index is also 0.07, which is less than 0.1 and is at the accepted level.



**Figure 2:** Weighting diagram and comparison main dimensions of the project with the main goal of the project

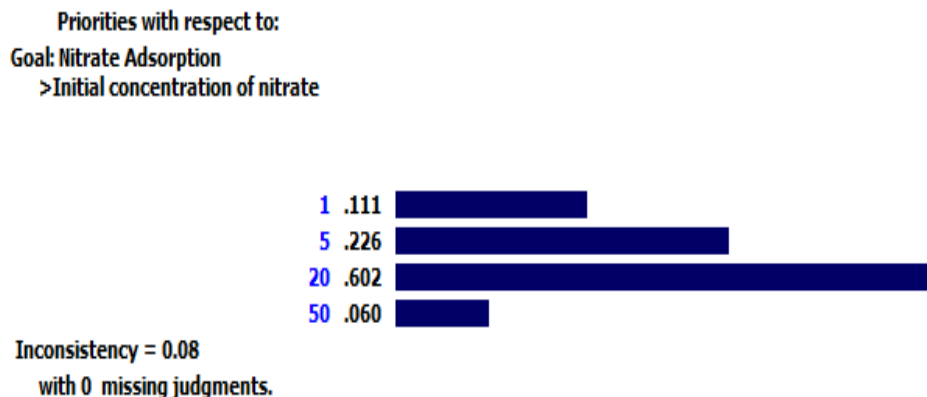
Figure 3 shows the weighting diagram and comparison of the solution pH parameter with the main goal of the project. Figure 3 shows that the pH=7 with the weight equal to 0.567 is allocated the highest priority. Also,

the pH=5 with the weight equal to 0.245 after pH=7 has the highest priority. The pH=9 with the weight equal to 0.116 has the third priority among the investigated levels in the field of nitrate adsorption by sawdust of beech tree. The pH=12 with a weight of 0.073 has acquired the last priority among levels. The value of the inconsistency index is also 0.07, which is less than 0.1 and is at the accepted level.



**Figure 3:** Weighting diagram and comparison of the solution pH parameter with the main goal of the project

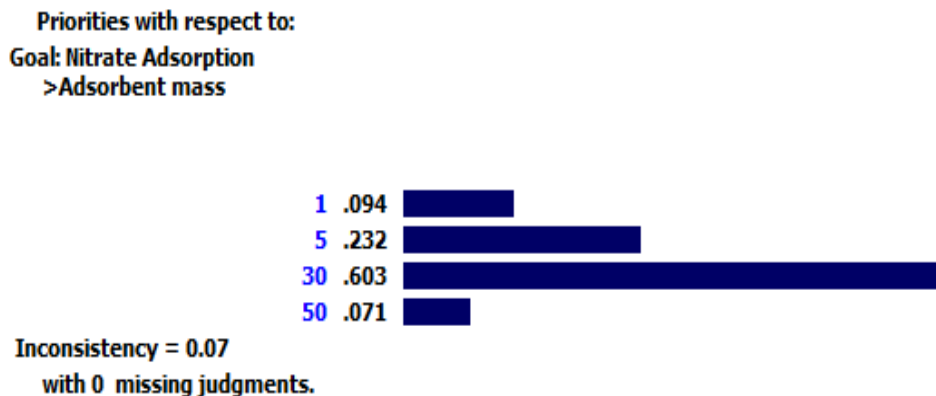
Figure 4 shows the weighting diagram and comparison of the nitrate initial concentration parameter with the main goal of the project. Figure 4 shows that the initial concentration of nitrate about 20mg/lit with the weight equal to 0.602 has the highest priority. Also, the initial concentration of nitrate about 5mg/lit with the weight equal to 0.226 after concentration of 20mg/lit has the highest priority. The initial concentration of nitrate about 1mg/lit with the weight equal to 0.111 has the third priority among the investigated levels in the field of nitrate adsorption by sawdust of beech tree. The initial concentration of nitrate about 50mg/lit with a weight of 0.060 has acquired the last priority among levels. The value of the inconsistency index is also 0.08, which is less than 0.1 and is at the accepted level.



**Figure 4:** Weighting diagram and comparison of the initial concentration of nitrate parameter with the main goal of the project

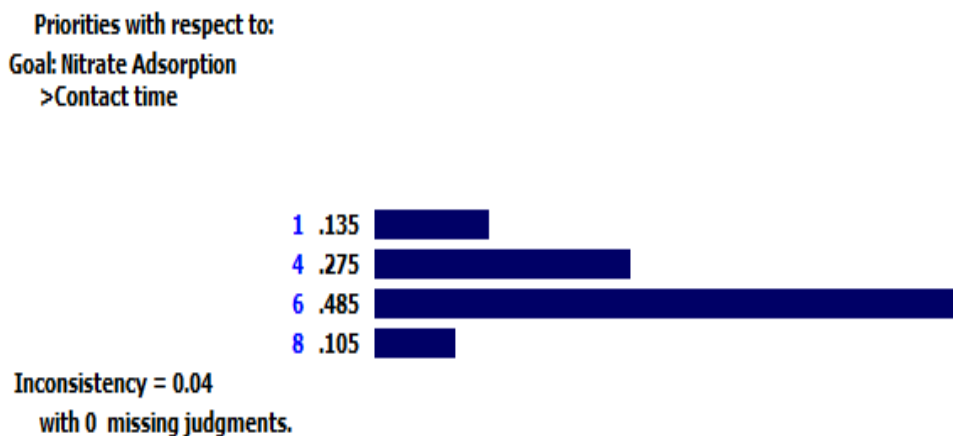
Figure 5 shows the weighting diagram and comparison of the adsorbent mass parameter with the main goal of the project. Figure 5 shows that the adsorbent mass about 30g with the weight equal to 0.603 has the highest priority. Also, the adsorbent mass about 5g with the weight equal to 0.232 after adsorbent mass of 30g has the highest priority. The adsorbent mass about 1g with the weight equal to 0.094 has the third priority among the investigated levels in the field of nitrate adsorption by sawdust of beech tree. The

adsorbent mass about 50g with a weight of 0.071 has acquired the last priority among levels. The value of the inconsistency index is also 0.07, which is less than 0.1 and is at the accepted level.



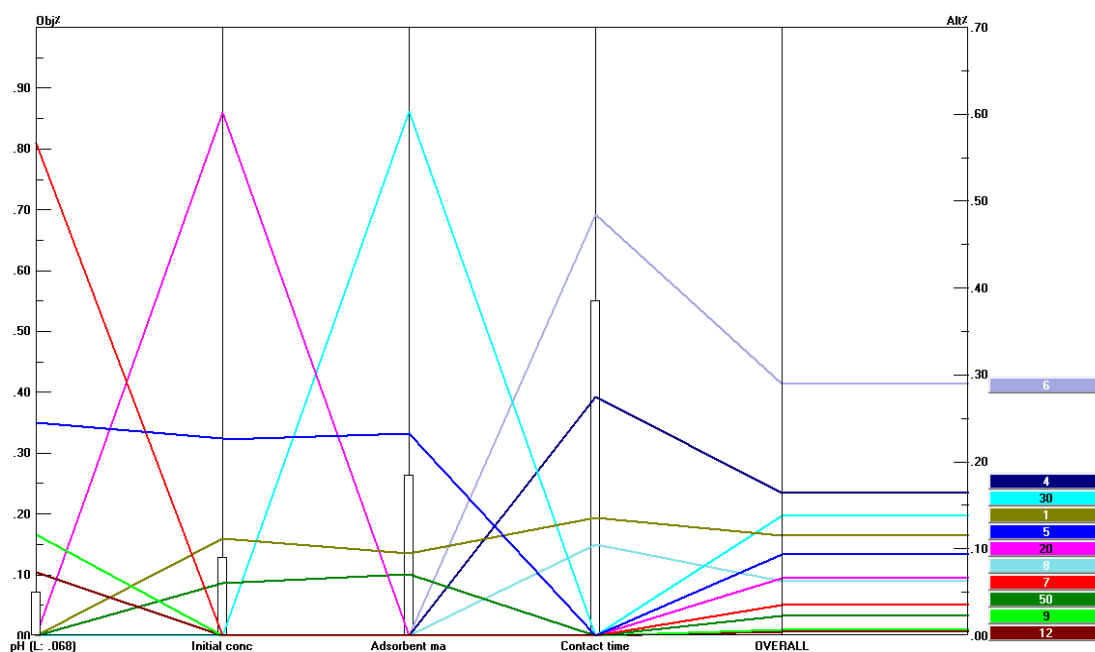
**Figure 5:** Weighting diagram and comparison of the adsorbent mass parameter with the main goal of the project

Figure 6 shows the weighting diagram and comparison of the contact time parameter with the main goal of the project. Figure 6 shows that the contact time about 6h with the weight equal to 0.485 has the highest priority. Also, the contact time about 4h with the weight equal to 0.275 after contact time of 6h has the highest priority. The contact time about 1h with the weight equal to 0.135 has the third priority among the investigated levels in the field of nitrate adsorption by sawdust of beech tree. The contact time about 8h with a weight of 0.105 has acquired the last priority among levels. The value of the inconsistency index is also 0.04, which is less than 0.1 and is at the accepted level.



**Figure 6:** Weighting diagram and comparison of the contact time parameter with the main goal of the project

Sensitivity analysis generally indicates the sensitivity of the analysis results to the change in the priority values of the criteria and sub criteria. Performance analysis was used in this study. This analysis shows that in every parameter which of the options is more important. Note that the sum of these priorities by considering the weight of each parameter leads to the final conclusion. In fact, this analysis shows how the options are ranked relative to other options according to the criteria as well as overall. Figure 7 shows the output sensitivity analysis diagram of AHP method in relation to criteria and sub criteria for maximum nitrate adsorption by sawdust of beech tree.



**Figure 7:** Output sensitivity analysis diagram of AHP method in relation to criteria and sub criteria for maximum nitrate adsorption by sawdust of beech tree

## Conclusion

One of the stable components of nitrogen in nature is nitrate. Nitrate is highly solvent and can easily enter groundwater and surface water and contaminate them. High concentrations of nitrate lead to methemoglobin, gastrointestinal cancer, heart disease, and respiratory tract cancer. In this study, we investigated the effective parameters on nitrate adsorption by sawdust of beech tree using analytical hierarchical process. To determine the most important parameters affecting the nitrate adsorption, four parameters pH, contact time, adsorbent mass and initial concentration of nitrate were studied, each of which has four levels. Expert Choice software was used to evaluate the most important parameters and their levels. The pH parameter including levels 5, 7, 9 and 12. The nitrate initial concentration parameter including levels 1, 5, 20 and 50. The adsorbent mass parameter including levels 1, 5, 30 and 50. The contact time parameter including levels 1, 4, 6 and 8. The results of this study showed that the contact time parameter had the most effect on the nitrate adsorption process from aqueous solutions and pH parameter had the least effect on this process. The results of this study on the effect of four levels of pH on nitrate adsorption showed that by increasing the pH from 5 to 7 nitrate adsorption increased and nitrate adsorption decreased after pH=7. It can therefore be said that because nitrate ions have a negative charge, at the pH of between 5 and 7 due to reactions occurring between positive surface charges and anions, the rate of nitrate adsorption is increased. Increasing the amount of hydroxide ion at high pH causes competition between the hydroxide ion and nitrate in the adsorption process and causes the nitrate adsorption is reduced. The results of this study on the effect of four levels of initial concentration of nitrate on nitrate adsorption showed that by increasing the initial concentration of nitrate from 1 to 20 mg/L, nitrate adsorption increased and nitrate adsorption decreased after 20 mg/l concentration. Thus, it can be said that up to a concentration of 20 mg/L there are many vacancies on the adsorbent that can absorb nitrate ions. By increasing the concentration after concentration of 20 mg/L increases the number of ions competing for placement in these vacancies and fills the active sites of adsorbent, which reduces nitrate adsorption. The results of this study on the effect of four levels of adsorbent mass on nitrate adsorption showed that by increasing the adsorbent mass from 1 to 30g, nitrate adsorption increased and nitrate adsorption decreased the after 30g adsorbent mass. Therefore, it can be said that with increasing the amount

of adsorbent up to a specific point, nitrate adsorption increases, because adsorption spaces (adsorption capacity) increase in this time. After a certain point (30g) with increasing adsorbent mass, nitrate adsorption is reduced, because the adsorbent particles adhere to each other and cause the adsorption spaces (adsorption capacity) decrease in this time. The results of this study on the effect of four levels of contact time on nitrate adsorption showed that with increasing contact time from 1 to 6 hours' nitrate adsorption increased and after the end of the contact time of 6 hours the nitrate adsorption is decreased. Therefore, it can be said that in the first 6 hours, there are many empty sites for nitrate adsorption, that with filling these spaces after 6 hours, adsorption of nitrate is also reduced. Therefore, the results of this study showed that the maximum nitrate adsorption by sawdust of beech tree occurs at an initial concentration of 20 mg/L, pH=7, adsorbent mass of 30g and contact time of 6h. Also, this points for each criterion are optimal points. Sub-criteria ranking results showed that with increasing adsorbent mass, initial concentration of nitrate, pH and contact time to optimum point increased nitrate adsorption. Also, after passing through optimum point, with increasing adsorbent mass, initial concentration of nitrate, pH and contact time decreased nitrate adsorption.

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