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Removal of Nitrate from Groundwater by Zeolite – A Batch Study

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Abstract: ***Nitrate is one of the most widespread chemical contaminant found in groundwater across the globe. It may be naturally present in groundwater due to geological formation or due to anthropogenic activities. This contaminant, even if harmless to some extent, can be dangerous beyond the standards of drinking. According to various drinking water standards, Nitrate should not exceed beyond 45 mg/L as NO_3 & 10 mg/L as NO_3-N. To remove the Nitrate contaminants from drinking water, various technologies are available, however adsorption is one of the most reliable and cost effective method. It was observed that, at an adsorbent dosage of 10g/L of natural zeolite at pH 7, temperature 30°C and 240 minutes of contact time was able to give 66.05% removal efficiency. Acid-$FeCl_3$ modified zeolite reduced the adsorbent dosage to 1.5 g/L which provided removal efficiency of 62.5% at pH 7, temperature 30°C and 180 minutes of contact time. Adsorbent dosage of 10 g/L of Acid-$FeCl_3$ modified zeolite increased the removal efficiency to 92.82% for Nitrate in the filtrate solution.***

Keywords: Water, nitrate, adsorption, groundwater

1. Introduction

Water is one of the most important, valuable, life saving and indispensable natural resource present in earth. It is a free gift of nature. However the availability of fresh water is very less. Groundwater, which is one of the purest forms of water, is mostly used for domestic purposes including drinking in developing country like India. India acquires an average of 4000 cubic kilometres of rains annually that is 1700 cubic meters of fresh water per person per year. However, the spatial and temporal variations make it non-uniformity in water resources in every state. Even with more than average rainfall, large area of the country lies with less or drought prone regions. Almost 90% of the water demand is met with surface interstate rivers. India mostly relies excessively on ground water supplies for domestic water demand in many regions. Nitrate is one of most common contaminant that is present in groundwater.

Nitrate contamination of drinking water source causes various health defects. Nitrate in itself is harmless; however it converts into more toxic nitrites. Study shows that almost 7% of the nitrate consumed converts into nitrites. Remaining converts lower in the intestine; prevent its adsorption into bloodstream. Methemoglobinemia is another dangerous and most common ill-affect of nitrate intake of more than 45 mg/L affecting infants of less than 42 weeks. Other serious diseases that are found in various studies are chronic inflammatory, cancer, enema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions. Increase in concentration of Nitrate in water bodies leads to eutrophication, which houses various harmful algal blooms which make the water unfit for use[12].

Nitrate contamination is an increasing problem worldwide. Majority of European countries have higher levels of Nitrate, which is more than 50 mg/L NO_3-N. Many places in Western and Central America, a Nitrate concentration ranging 10-30 mg/L is found. In South Africa, Namibia, Bostwana, the highest nitrate concentration has found to be 500 mg/L NO_3-N [2].

In India, more than 25 states are contaminated with Nitrate in groundwater which easily exceeds 45 mg/L. In Maharashtra, places like Nagpur, Amravati, Wardha Aurangabad, Buldana, Jalgaon, have shown a Nitrate concentration of 250-380 mg/L in groundwater [7]. Due to serious effects of groundwater contamination by nitrate and their occurrence in various parts of the world, treatment of water for their removal is a necessity. Though there are various processes available, adsorption is one of the most common and a very effective method for removal of Nitrate. Various researchers have been working on this for a very long time. The focus in this treatment process should be on using cheap and efficient adsorbents like banana peel, clay, activated carbon, bentonite clay, rice husk zeolite, silica etc [5],[9],[4],[14],[8],[13]. These adsorbents have also succeeded in removal of Nitrate. In this study we have studied the removal of Nitrate by using surface modified natural zeolites.

2. Methodology

2.1 Preparation of Materials and Characterization

Natural zeolite, Heulandite, has been obtained from mines in Maharashtra. The zeolite crystals where the crushed and powdered. Then the powder was sieved and the matter retained on the 150µm was separated for the experiments. This powder was washed with 0.1N HCl for removing impurities and dried at 105°C for 24 hours. Modification of the natural zeolite was carried out by using $FeCl_3$ and concentrated Hydrochloric acid. Ferric chloride is used for etching purpose from olden times and it provides suitable modification of the zeolite surface. For the modification of natural zeolite, zeolite was agitated with 0.03M $Fecl_3$

solution for 24 hours and dried at 150°C. The sample was washed with distilled water till the pH of filtrate was neutral. The composition of modified zeolite was characterized with X-ray Fluorescence, X-ray Diffraction and Fourier Transform Infrared Spectroscopy.

Table 1: Chemical composition of modified zeolite from X-ray Fluorescence analysis

Composition	Percentage (%)	Composition	Percentage (%)
Na_2O	1.13	Cr_2O_3	0.008
MgO	0.05	NiO	0.006
SiO_2	63.21	CaO	6.73
Al_2O_3	10.98	MnO_2	0.005
P_2O_5	0.006	BaO	0.001
SO_3	0.02	K_2O	0.2
Fe_2O_3	0.98	TiO_2	0.01

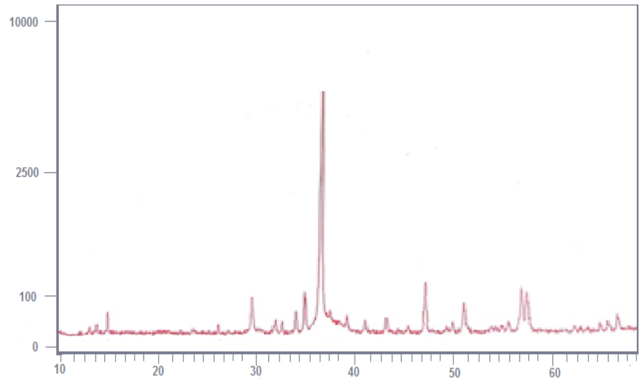


Figure 1: X-ray Diffraction graph of the modified zeolite.

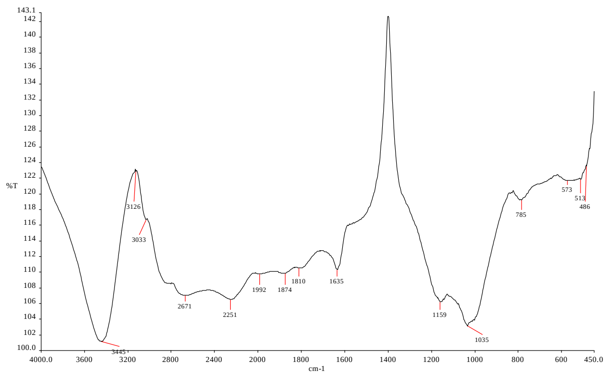


Figure 2: FTIR spectrum of the modified zeolite.

2.2 Adsorption Batch Studies

The study is carried out on the basis of the principles of adsorption and filtration widely referred to as adsorptive filtration. All synthetic samples of nitrate contaminated water were prepared in lab. The chemicals used were of analytical grade and the distilled water was from the laboratory distillation plant. Experiments on various parameters were carried out to study the adsorptive capacity of the natural zeolite.

3. Result and Discussion

3.1 Effect of Adsorbent dose

The effect of adsorbent dose of unmodified (natural) and modified zeolite on nitrate removal efficiency is shown in fig. the pH was kept neutral and temperature 30°C. The removal efficiency increased when dose was increased in both adsorbents. The modification has considerably increased the adsorption capacity for nitrate uptake. This is to be expected because for a fixed initial solute concentration, increase in total dose present a greater surface area and increase adsorption potential. For unmodified zeolite, after 10g/L almost equilibrium achieved. For the modified zeolite, the removal efficiency was increasing with increasing dosage. However, 1.5g/L of modified zeolite for further studies was adopted for further studies of parameters.

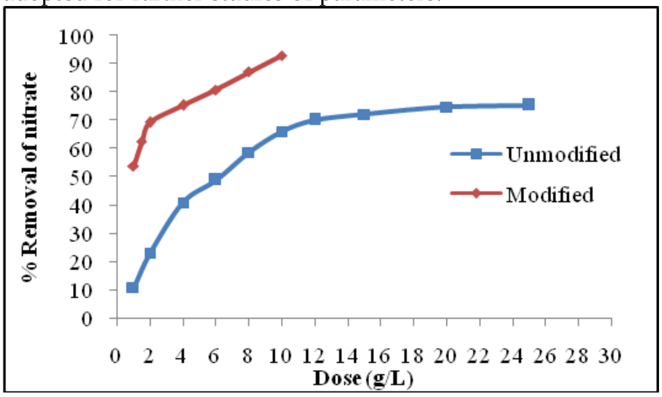


Figure 3: Effect of dosage of umodified (natural) and modified zeolite on removal efficiency of nitrate

3.2 Effect of Contact time

The effect of contact time experiment on modified zeolite was carried out to obtain optimum contact period for adsorption process. The removal efficiency is presented in figure 4, for different time periods of 30, 60, 90, 120, 240 minutes and so on with one hour interval for 7 hours. The highest efficiency of nearly 64.47 % was observed for contact time of 180 min; however the removal efficiency for contact time of 420 minutes was also nearly the same. Hence, 180 minutes was taken for further experiments.

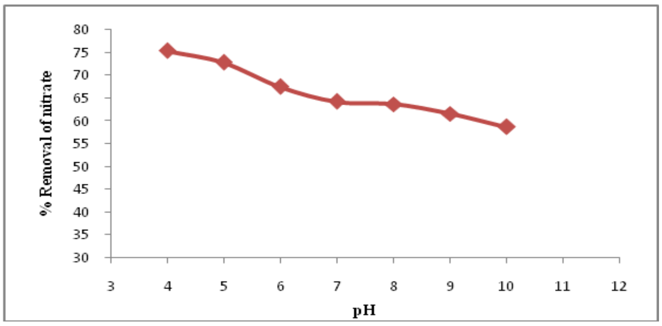


Figure 4: Effect of contact time on removal efficiency of nitrate

3.3 Effect of pH

The pH of water samples were adjusted from pH 4 to pH 10 using 0.1N HCl and 0.1N NaOH. The study showed that at acidic medium, adsorption capacity improved and reduced with increase in alkalinity. However, due to the neutral pH of drinking water, pH 7 was adopted as optimum pH. The result may be due to the excessive presence of OH^- ions in the water sample, which hamper the adsorption of nitrate ions on the available sites by competing for the active available sites.

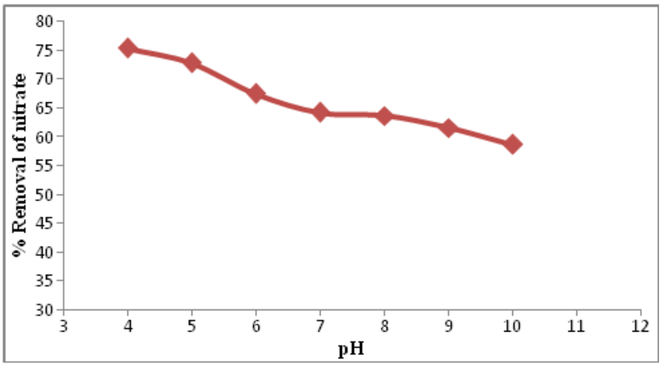


Figure 5: Effect of pH on removal efficiency of nitrate

3.4 Effect of temperature

Temperature is an important factor in adsorption process; hence temperature studies were carried of 20, 25, 30, 35, 40°C. It is seen that removal efficiency decreases with the increase in temperature. This shows the exothermic nature of adsorption taking place. It may be due to increase in solubility of nitrate ions in water with increase in temperature.

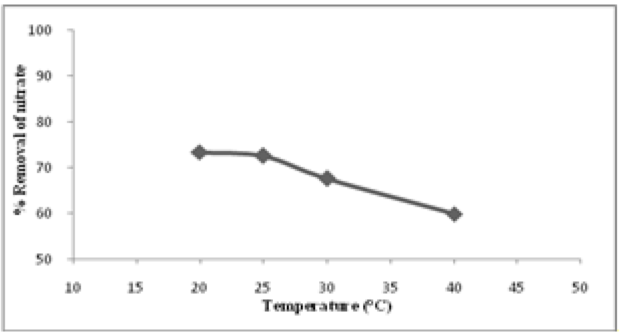


Figure 6: Effect of temperature on removal efficiency of nitrate

3.5 Effect of varying Initial concentration

The varying initial nitrate ion concentration was carried out to study the effect on adsorption by modified zeolite. Initial concentration of 75 mg/L, 100 mg/L, 150 mg//L, 200 mg/L, 250 mg/L and 300 mg/L were studied. It is observed that with the increase of nitrate ions in the water sample, the removal efficiency decreases gradually. It is concluded that decrease in efficiency was due to the exhaustion of the active sites for nitrate adsorption on the modified zeolite surface. Thus it is observed that treating nitrate contaminated groundwater with the modified zeolite will not bring the concentration below the drinking standards.

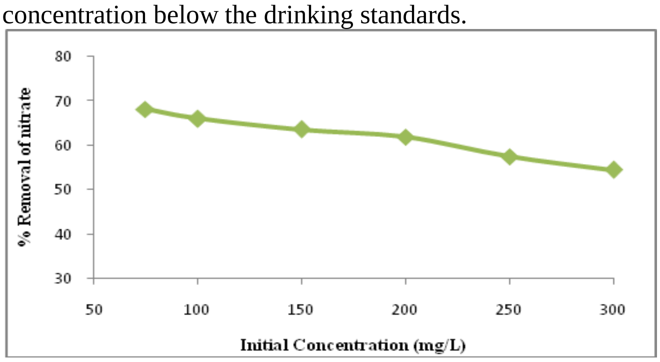


Figure 7: Effect of initial concentration of nitrate ions on removal efficiency of nitrate

3.6 Effect of Co-existing ions in the aqueous solution

Contaminated groundwater generally consists of various other co-existing ions along with nitrate. These ions may interfere with the adsorption of nitrate taking up the active adsorption site. Thus to investigate the interference of the co-existing ions in the water, the study was performed. The cations and anions most commonly found in groundwater are studied in various concentrations.

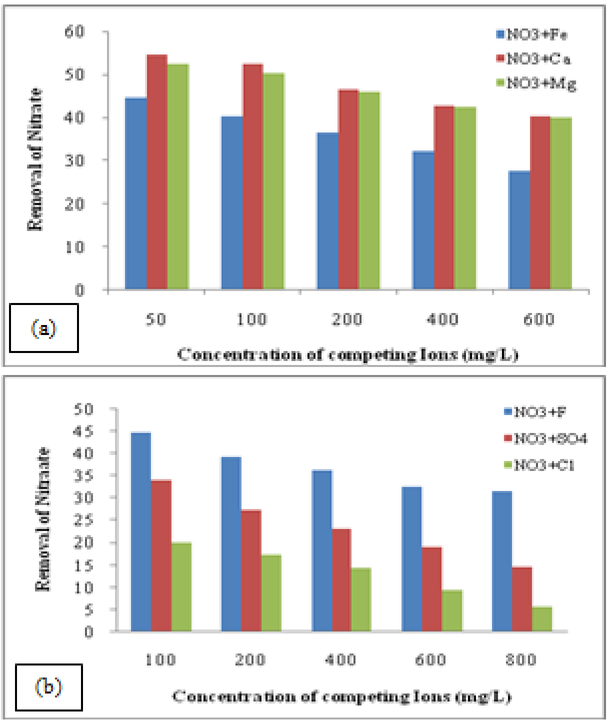


Figure.8. Effect of different cations on the adsorption of nitrate onto modified zeolite (a); Effect of different anions on the adsorption of nitrate onto the modified zeolite (b).

The result indicated that the anions had an adverse effect on removal of nitrate from aqueous solution. The presence of chloride ions affected the removal potential by 71.2% at 100mg/L of Cl^- ions. Also, fluoride ion showed least interference with the nitrate uptake, which is consistent with the study of adsorbent, PAN-Oxime-Fe_2O_3 [11]. The hydrating radius of nitrate is much greater than other anions used, reducing the chance of nitrate ion adsorption.

4. Adsorption Studies and Kinetic Modeling

Adsorption isotherm is a vital factor for designing the adsorption systems. It shows the separation of contaminant ions from liquid phase by adsorbent in the equilibrium balance as a function of the contaminant concentration. The Langmuir isotherm assumes monolayer adsorption on the surface consisting of finite number of active sights. According to the results of the present study, adsorption data followed Langmuir isotherm model because of a higher R^2 value of 0.97.

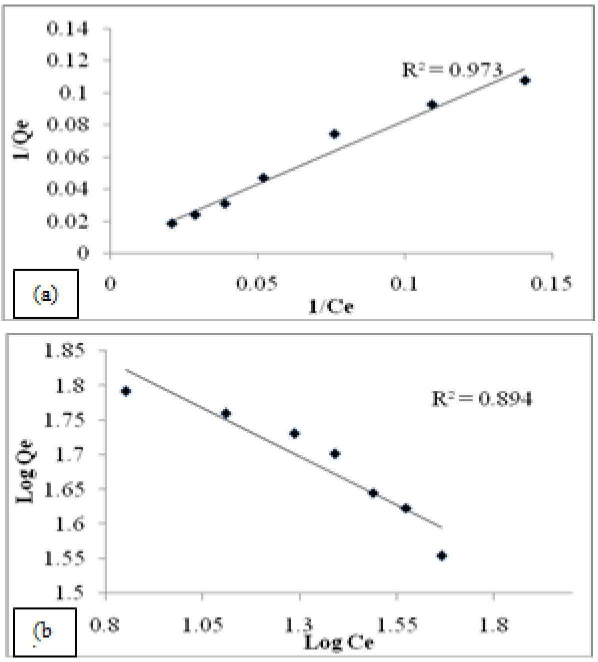


Figure 9: Langmuir plot (a), Freundlich plot (b) for adsorption of nitrate onto modified zeolite.

Table 2: Langmuir and Freundlich Isotherm data

Isotherm	Parameter	Values
Langmuir	R_L	0.874
	Q_m (mg/g)	34.48
	K_L	0.009
	R^2	0.973
Freundlich	Q_m (mg/g)	39.258
	K_f	0.0308
	R^2	0.894
	n	0.50

From table it can be seen that the value of n = 0.50 that it is not in range set by Freundlich model which is between 1 and 10 showing unfavourable adsorption of nitrate on the modified zeolite surface. On the other hand, the separation factor R_L is found to be 0.874, which is in the range $0 < R_L < 1$, indicating a favourable adsorption process. In view of correlation coefficient, R^2, values for Langmuir more close to 1 than the value for Freundlich models and thus the data best fit with Langmuir model. This is also supported by the study carried by activated bentonite for nitrate removal [14].

The thermodynamics parameters, changes in enthalpy and entropy are obtained by plotting Ln K versus 1/T, where, K is adsorption constant at various temperatures from Langmuir plot; T is temperature in Kelvin [10].

From the temperature range of 293 to 323 K, the negative value of the enthalpy showed that the adsorption of nitrate onto modified zeolite was exothermic in nature. Thus, adsorption of nitrate onto surfactant modified zeolite is more enhanced at lower temperatures. The negative value of the Gibb's free energy change indicated that the adsorption process was spontaneous in nature.

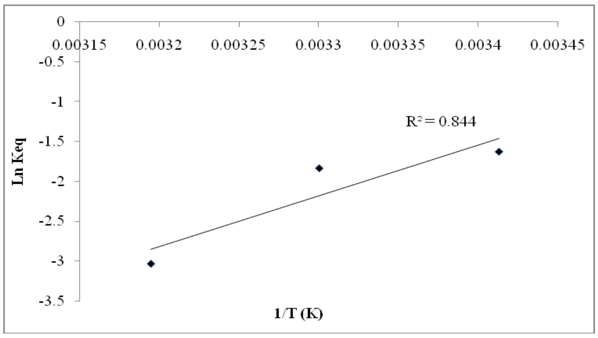
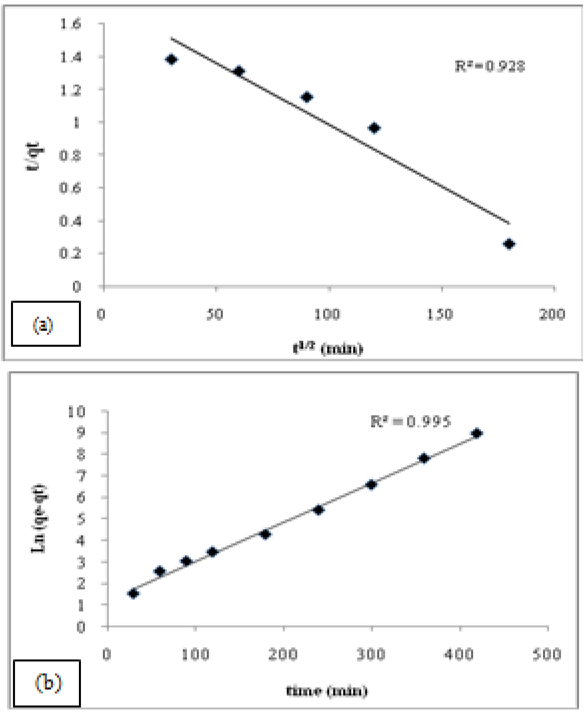


Figure 10: Van Hoff plot for nitrate adsorption onto modified zeolite at various temperatures

Table 3: Thermodynamics parameter of adsorption of nitrate

NO3 (mg/L)	ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol) [293K]	ΔG° (KJ/mol) [303K]	ΔG° (KJ/mol) [323K]
100	-53.126	-0.0022	-52.26	-52.23	-52.176

In this study, pseudo first- and second- order has been employed to interpret the adsorption data obtained under the various conditions. Lagergren's pseudo first order kinetic model has been plotted as Ln (qe-qt) versus t, where, qe and qt are adsorption capacity at equilibrium and time (t). The kinetics of adsorption of nitrate onto modified zeolite by using pseudo-second order model is plotted values of t/qt versus $t^{1/2}$ [2].



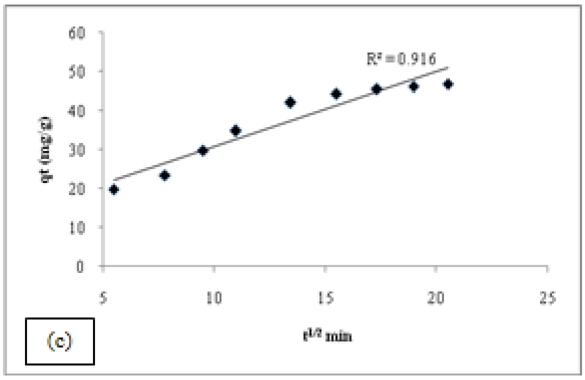


Figure 11: Pseudo-first order kinetics (a), Pseudo-second order (b) and Intra particle diffusion model (c) for adsorption of nitrate onto modified zeolite in aqueous solution.

Table 4: Kinetic data for adsorption of nitrate onto modified zeolite

Pseudo-first order kinetic model		
k (L/min)	qe (mg/g)	R^2
0.016	42.16	0.928
Pseudo-second order kinetic model		
k (L/min)	qe (mg/g)	R^2
0.000270	55.55	0.995
Intra-particle diffusion model		
Kid (mg/g*min$^{1/2}$)	C (mg/g)	R^2
1.922	11.53	0.916

It can be observed from the table 4, pseudo-first order and intra-particle diffusion model does not fit well with the experimental data. However, pseudo second-order kinetic model has shown better co-relation with the R^2= 0.995. The adsorption capacity of the nitrate ions by the modified zeolite was calculated to be 55.55 mg/g.

5. Conclusion

Zeolite has been used for treating contaminated water effectively for many years. In this study, it has been found that the natural zeolite, Heulandite, at an adsorbent dosage of 10g/L at pH 7, temperature 30°C and 240 minutes of contact time was able to give 66.05% removal efficiency. Surface modified Acid-$FeCl_3$ zeolite reduced the adsorbent dosage to 1.5g/L which provided removal efficiency of 62.5% at pH 7, temperature 30°C and 180 minutes of contact time. Adsorbent dosage of 10 g/L of Acid-$FeCl_3$ modified zeolite increased the removal efficiency to 92.82% for Nitrate in the filtrate solution.

In view of correlation coefficient, R^2, value for Langmuir is 0.973, which is higher than the value for Freundlich model and thus the data best fit with Langmuir model.

The data from the experimental study was fitted with the three models, pseudo first order, pseudo second order and intra-particle diffusion model. From the kinetic models, it has been observed that the adsorption best fit the pseudo second order with R^2 value 0.995. The calculated adsorption capacity is found to be 55.55mg/g.

From the thermodynamics study, negative value of ΔH shows the exothermic nature of the adsorption. The negative values of ΔG and ΔS show that the process is spontaneous and there is no change occurring in the internal structure.

From this study, it is found that the natural zeolite, Heulandite, has little ability to absorb nitrate from aqueous solution. However, simple modification with $FeCl_3$ has been able to reduce the nitrate concentration successfully.

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