Modification of Clinoptilolite by Chitosan and Application in the Removal of Nitrate

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Abstract*—The modification of clinoptilolite was performed by coating it with chitosan in order to use it as an adsorbent material for nitrate removal from waste water. The characterization of the modified clinoptilolite was done by Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The results obtained showed that the removal of the nitrate from wastewater is strongly dependent on initial concentration, contact time, adsorbent dosage, pH and contact time. It was found that the initial concentration of 25 mgL^{-1}, contact time of 120 minutes, adsorbent dosage of 2 g, pH 10 and temperature of 45°C (318K) are better conditions for nitrate removal from wastewater. The equilibrium sorption isotherms were analyzed by the Langmuir and Freundlich isotherms and the results indicated that Freundlich isotherm describes better the adsorption process. Thermodynamic parameters such as Gibb's free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were studied. The results revealed that the process was spontaneous and exothermic in nature. The pseudo-first and second order model were used in analyzing kinetic data for nitrate. The experimental data were fitted well with the pseudo second order model. It was concluded that a modified clinoptilolite with chitosan is a highly efficient and economic adsorbent material and can be utilized in the removal of nitrate from environmental wastewater.

Keywords: Clinoptilolite, Chitosan, Modification, Nitrate, Removal, Wastewater

I. INTRODUCTION

The existence of nitrate in ground waters represents a serious problem for humans and the environment. The pollution of water is caused mainly using excessive quantities of fertilizers but also by human and animal wastes [1]. Pietersen [2] reported that South African groundwater regularly has high concentration of nitrate standards, which go beyond 50 mg·L^{-1}, the limit mentioned by the world Health Organization. High nitrate concentration in drinking water would cause a serious threat to human health such as cancer, methemoglobinemia in newborn infants and liver damage [3]. Therefore, nitrate concentration reduction in drinking water to acceptable levels is mandatory. Several techniques such as reverse osmosis, ion exchange, biological denitrification, electrochemical reduction and catalytic reduction had been developed for nitrate removal from waste water [1]. Among these techniques, adsorption was known such as the best abundant techniques for it simple operations, easy recovery, high efficiency and cost effectiveness [4]. While numerous studies have been conducted for the nitrate concentration deduction from wastewater by adsorption techniques using varieties of adsorbents [5], a literature review revealed no published report on the modification of clinoptilolite by chitosan. Clinoptilolite has been selected as a low-cost absorbent material for the removal of nitrate from wastewater [6]. Clinoptilolite is the most abundant zeolite in natural form ($Na_6Al_6Si_6O_{12}.24H_2O$). Clinoptilolite is a crystalline hydrated aluminosilicate formed by a tetrahedral extensive network of AlO_4 and SiO_4. The structural framework of clinoptilolite is negatively charged for it isomorphic substitution of Al^{3+} and Si^{4+} [7]. Mažeikiene et al. [3] indicated that clinoptilolite has low nitrate removal efficiency due to negative charge network at its structure. Its negatively charged aluminosilicate lattice not only attracts different metal cations but it can also exhibit an affinity towards anions by suitable modifications. Hence, charging anionic contaminants such as nitrates on its surface is only just possible, for it columbic repulsive forces [8]. Thus, to enhance the adsorption performance of clinoptilolite appropriate for the elimination of anionic contaminant from aqueous solutions, its surface charge property must be transformed using suitable charge reversing chemical species [9]. Modification of the negatively charged clinoptilolite surface can be conducted by forming layers of adsorbed cationic surfactant allows the retention of anions such as nitrate by adsorption. Some modified techniques [5] were useful to enhance their absorption of nitrate. However, some modifiers had a potential hostile effect on environment. Chitosan has received vast interest due to its specific characteristics such as low cost, good adsorption performance, biodegradability environmental friendly and the presence of the amount of reactive hydroxyl (-OH) and amino (-NH_2) [10].

II. MATERIALS AND METHODS

A. Preparation of Materials

Clinoptilolite was washed with 20 Vol % HCl and then with deionized water. Resulting material was dried in an oven at 80°C for 24 hrs, crushed in 1-2 mm mesh sizes for the experiments, while some of it was pulverized into

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powder with average particle size of 75 µm for the characterization. The XRD, XRF, FTIR and SEM equipment were used to characterize the clinoptilolite. The synthetic solution was prepared by dissolving $NaNO_3$ in distilled water at pH 6.5. Chitosan powder (10g) was dispersedly dissolved into 1000 mL of 3.0% (w/w) acetic acid solution, and then stirred at 150 rpm at room temperature for 2hrs. Afterwards steadied for 1h, the hydrogel beads from the process were detached, washed with deionized water and dried at 50°C for 8hrs. The dried hydrogel beads remained absorbed in deionized water at 25°C for 4hrs. The enlargement consequence happened during the involvement which would improve the adsorbent surface property and promote the adsorption capacity. After this process, granular chitosan was obtained and stored at 25°C for further study. The prepared clinoptilolite was soaked for 4 hrs into glutaraldehyde (25wt %). The coated clinoptilolite was filtered and added into Na_2CO_3 for 1 hr to fix and solidify the coating. The clinoptilolite-chitosan was saturated in 150mL $NaBH_4$ (0.1M) for 12hrs at 25°C to eliminate residual formyl groups and glutaraldehyde which didn’t react. Lastly, the coated clinoptilolite was widely washed with distilled water and dried in oven at 40°C for 12hrs.

B. Experimental Procedure

Batch trials were directed to determine different parameters such as of pH, initial concentration and adsorbent dosage. In separately item, 10g of modified clinoptilolite was mixed with 250 mL of synthetic solution and held in a closed polyethylene flask at 90◦C for 24 hrs. The adsorbents were then separated from the synthetic solution by using a funnel, filter. 50 ml of synthetic solution was analyzed using AAS to control the nitrate concentration in the synthetic solution after handling. All the trials were showed in triplicate and the results stated the average values and deviation of ± 0.002.

The effect of pH was agreed at the value of 2-12, adsorbent dosage of 0.5-5.0 g, initial concentration 25-75 mgL^{-1}.

Kinetic and isotherm studies were granted at different nitrate concentrations (20, 50 and 100 mg NO_3^--N L^{-1}) and (20, 30, 40, and 200 mg NO_3^--N L^{-1}), respectively. Thermodynamic studies were conducted at 15, 25, 35, 45 and 55°C. The equilibrium capacity of chitosan was calculated using Eq. (1) [11]:

$$q_e = \frac{\left(C_0 - C_e\right)}{M} xV \qquad (1)$$

Where q_e (mg. g^{-1}) is the quantity of nitrate adsorbed at equilibrium, C_e (mg L^{-1}) and C_o (mg L^{-1}) are equilibrium NO_3^--N and initial concentration in aqueous solution, respectively. V (L) is the volume of synthetic solution and M (g) is the mass of coated clinoptilolite.

III. RESULTS AND DISCUSSION

A. Characterization of Clinoptilolite

A.1. Scanning electron microscope (SEM)

The scanning electron microscope images of natural and modified clinoptilolite presented in Fig. 1a and Fig. 1b display the apparent casing of the clinoptilolite with chitosan, i.e., surface area is linked to the adsorption capacity of the adsorbent. The change in surface zone offers more binding sites for the adsorbate to be adsorbed can be credited to the adsorption as a surface marvel. The microscopy surface of modified clinoptilolite as revealed in Fig. 1b has established more pores and softened structure than the natural clinoptilolite in Fig.1a was for the occurrence of swelling effect. This observation approves the coating of chitosan onto the clinoptilolite surface.

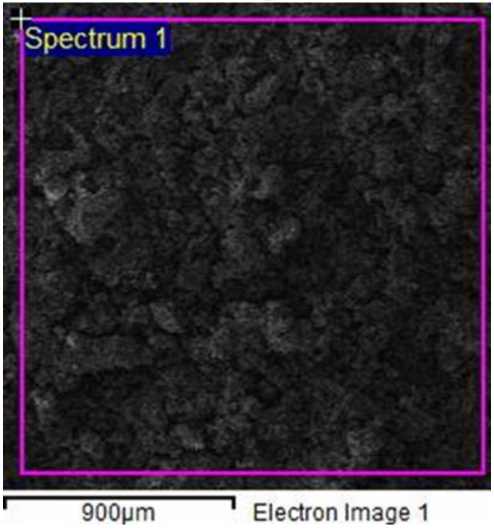


Fig. 1a. SEM images of natural Clinoptilolite

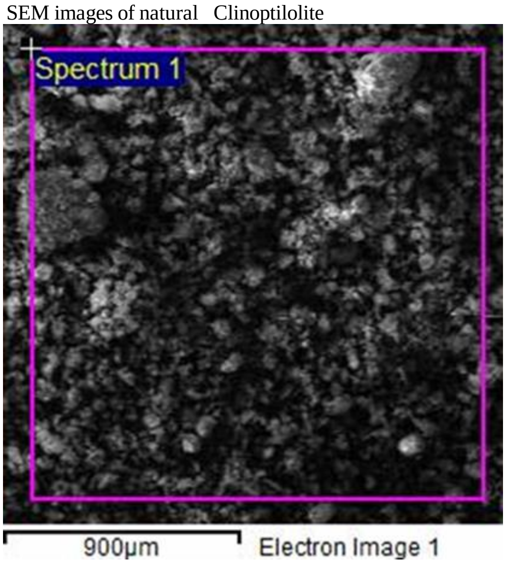


Fig. 1b. SEM image of modified Clinoptilolite

A.2. Scanning electron microscope (SEM)

The XRD pattern of the modified clinoptilolite with chitosan in Fig. 2 shows the characteristic peaks. The crystalline peak of clinoptilolite was not detected after 2θ = 40°, signifying that chitosan-clinoptilolite showed amorphous nature. The crystallinity increases in the intensity at 2θ = 22°. This is attributed to increase in intermolecular hydrogen boundary for the existence of more free NH_2 groups within the molecular structure involved in the reaction. Intensity decreases are due to the crystalline chains during the process. Around 2θ = 30°, intensity of diffraction peaks of clinoptilolite decreases due to the broad bond of poorly crystallized chitosan. The results show that modification has effect on the crystal structure of the clinoptilolite when compare to the XRD spectra result of natural clinoptilolite presented by Mamba et al. [12]. An examination of XRD patterns of natural and modified shows a little change in peak intensities at $2\theta = 40^{o}$, 34 and 30^{o}.

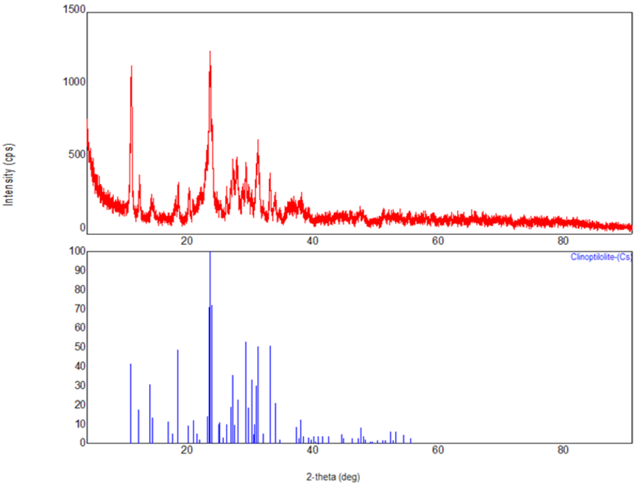


Fig. 2. X-ray diffraction pattern of natural and modified clinoptilolite

A.2. X- Ray Fluorescence (XRF)

Tables I shows the XRF analysis of natural and modified clinoptilolite. The elemental composition results revealed the composition (%) of amorphous SiO_2 in the natural clinoptilolite was 74.0% and decreased to 65.0% after modification. The decrease in the composition (%) of SiO_2 after modification for it dissolution possibility of amorphous SiO_2. The XRF results also shows the reduction in percent composition of other elements such as Al_2O, K_2O, Fe_2O_3, CaO and MgO after modification. The presence of NH_2 was observed in modified clinoptilolite, this can be explained by the presence of amine groups in the chitosan.

TABLE I
XRF COMPOSITION OF THE NATURAL AND MODIFIED CLINOPTILOLITE

Oxide	Natural clinoptilolite (wt %)	Modified clinoptilolite (wt %)
SiO_2	74.0	65.0
Al_2O	12.4	11.4
K_2O	3.8	2.6
Fe_2O_3	1.5	0.9
Na_2O	1.3	1.3
CaO	1.5	0.8
MgO	1.1	0.2
TiO_2	0.2	0.2
H_2O	0.7	0.7
NH_2	0.0	3.2

This reduction in percentage composition can be credited to the reaction among these compounds and chitosan was used for the modification of clinoptilolite. The same results exposed that the percentage composition of TiO_2 and H_2O remain constant after modification, it showed that there was a few interactions between chitosan and these compounds at modification conditions. According to basic composition analysis of the natural and modified clinoptilolite, there is an inferred that the modified clinoptilolite will affect the crystallinity of clinoptilolite.

A.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were used to remove the adsorption mechanism of nitrate onto chitosan and were analyzed to identify the surface functional groups nitrate adsorption. In Fig. 3, the bonds at the range of 4000 and 3750 cm^{-1} the natural and modified clinoptilolite showed distinct stretching, typical of water adsorption. At the range 3500 and 2000 cm^{-1}, natural clinoptilolite showed a peak and yet again this could be because of washes out the non-zeolite impurities present. The major adsorption band is approximately 1979 cm^{-1} for the spectrum of pristine chitosan was attributed to intermolecular hydrogen bonds and the conjunction between O-H and N-H stretching vibration. The peaks at 1962 and 1781 cm^{-1} were attributed to C-H stretching vibration of $–CH_2$. New peak looked at 1567 cm^{-1} was assigned to the amino protonation of $–NH_2$, weak peak at 1500 indicated a double bond carbon compound. The peak intensities recorded at 1248 and 1159 cm^{-1} referred to C=O vibration stretching of acetyl group and the stretching vibration of amine group, respectively. The peaks observed at 1055 and 1052 cm^{-1} were connected to C-O-C stretch vibration. The peak at 1036 and 1012 cm^{-1} linked to the stretch vibration of C-O in chitosan molecule on the position of C-3 and C-6, respectively. It was clearly seen in Fig. 3 the peaks showed at 1000 and 960 cm^{-1} extinct for chitosan after reaction.

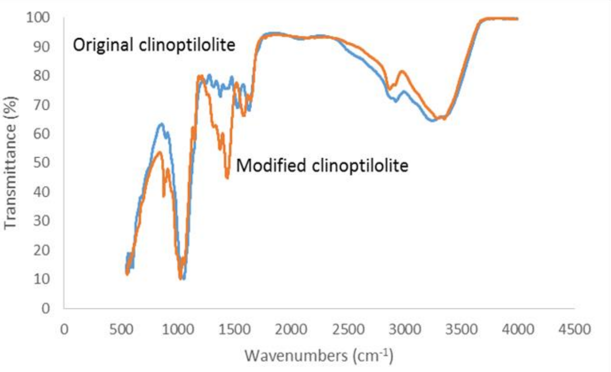


Fig. 3. FTIR spectra of Clinoptilolite

The intensity of the transmittance at 874 and 741 cm^{-1} in spectra, shows a strong C-O bond. The clino-chitosan spectra indicate weak peaks at 598 cm^{-1} indicating a double bond of carbon compound, while some small peaks around 553 cm^{-1} indicates tertiary amine bonds (CN). The presence of a secondary amine at 500 cm^{-1} and primary amine at 496 cm^{-1} was not detected in the clinoptilolite-chitosan samples. The lane pair of electrons present in O, N and S of the respective hydroxyl, amino of third group present in the chitosan was supplied to the empty atomic orbital of which makes the chitosan-nitrate complex from in the surface of the adsorbent. Amino and hydroxyl groups of chitosan may participate in removal process. Hydroxyl groups on the adsorbent surface where involved in nitrate adsorption.

B. Effect of Initial Nitrate Concentration and contact time

The effect of initial concentration for nitrate removal was determined at the following conditions: nitrate concentration from 25 to 75 mgL^{-1}, adsorbent dosage of 2.0

g, contact time 120 minutes and temperature of 25°C (298K). The nitrate removal on modified clinoptilolite decrease from 82% to 77% with an increased in the initial concentration from 25 to 75 mgL^{-1}. For the lowest initial concentrations, maximal removal reached 82% as shown in Fig. 4. This may be attributed to the more active site available in sites than the number of adsorbate species.

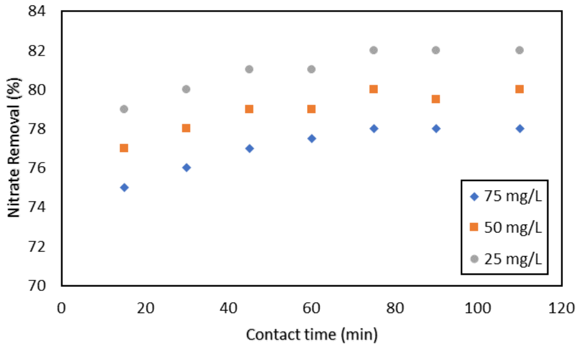


Fig. 4. Effect of initial concentration on removal of Nitrate

C. *Effect of Adsorbent Dosage*

The effect of adsorbent dosage on nitrate removal was vigorous parameter influencing adsorption capacity and effluent concentration. The effect of adsorption dosage was studied at the following conditions: nitrate concentration 25 mgL^{-1}, adsorbent dosage 0.5 g, 1.0 g, 2.0 g and 5.0 g, temperature 25°C (298K) and 120 minutes. The nitrate removal percentage increased from 75% to 81% with an increased in adsorbent dosage from 0.5 to 5.0 g as depicted in Fig. 5. The increase was attributed to the availability of active sites and high surface area at greater dosage [13]. The increase reaches equilibrium after 120 minutes, this may be due to binding of almost all nitrate into clinoptilolite. The equilibrium establishment between the ions bond to the clinoptilolite suggested that the adsorption rate of nitrate from solution increases with increasing the amount of adsorbent.

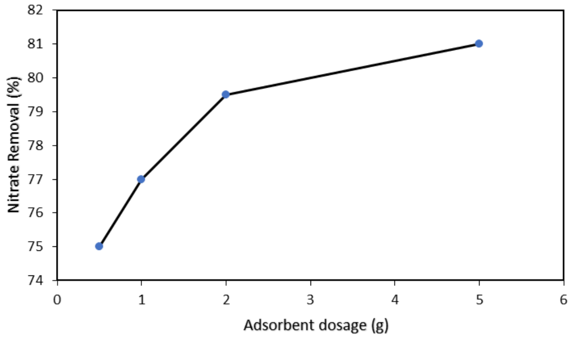


Fig. 5. Effect of adsorbent dosage

D. *Effect of Temperature*

The effect of temperature was conducted at the following conditions: temperatures 298-318K, nitrate concentration 25 mgL^{-1}, adsorbent dosage 2.0 g and contact time 120 minutes. At higher temperature, the electrostatic interaction becomes weaker which causes the anions to become smaller promoting the adsorption of ions onto the surface of clinoptilolite with nitrate removal of 82% at 318K (see Fig. 6).

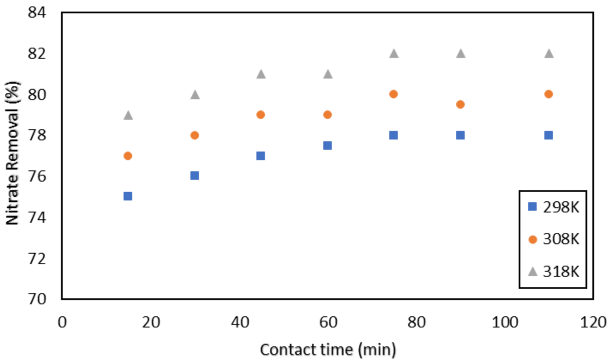


Fig. 6. Effect of temperature

E. *Effect of pH*

The pH is apparently as a significant variable for the nitrate removal from wastewater [6]. To examine the effect of pH, the experiments were conducted by varying the pH values in the range of 2 -12, nitrate concentration 25 mgL^{-1}, adsorbent dosage 2.0g, contact time 120 minutes and temperature 273K. It shows in Fig. 7 that the nitrate removal increases with an increased in pH. This implying that electrostatic attraction among negatively charged nitrate ions and positively charged anime groups of chitosan were not a unique mechanism of nitrate removal [14]. The maximum nitrate removal percentage of appeared at pH 10 was attributed to the competition between hydroxide and nitrate ions for adsorption sites and an increase in diffusion resistance of nitrate case by abundant hydroxide ions [15]. It can be concluded that the nitrate removal could be well performed in basic condition. The minimum nitrate removal (75%) at low pH value of 2 was due to the presence of H^+ and H_3O^+ in the solution can compete with the negatively charged nitrate ions for the available adsorption sites in chitosan which are positively charged by amine groups (NH_2 becomes NH_3^+) by electrostatic attraction [16].

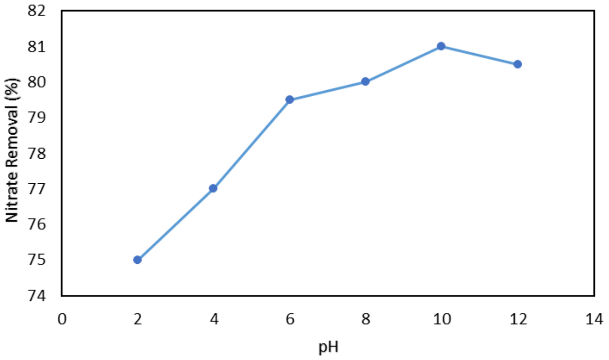


Fig. 7. Effect of initial concentration on removal of Nitrate

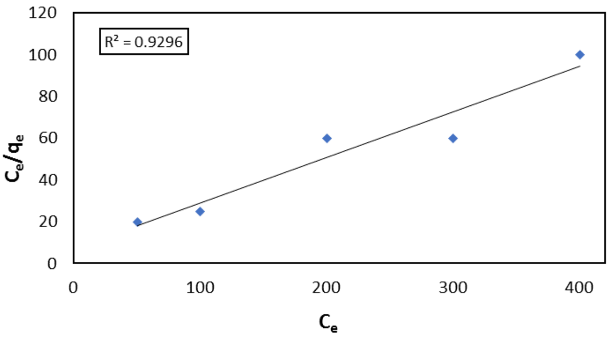
F. *Adsorption equilibrium*

Adsorption isotherm is an important and essential factor required to design an adsorption process. To obtain a model that will describe an adsorption process, it is required to establish an appropriate correlation for the equilibrium adsorption curve. Various adsorption isotherm models have been employed to analyze experimental data and describe the equilibrium of adsorption. Eqs. (2) and (3) described the Langmuir and Freundlich models, respectively.

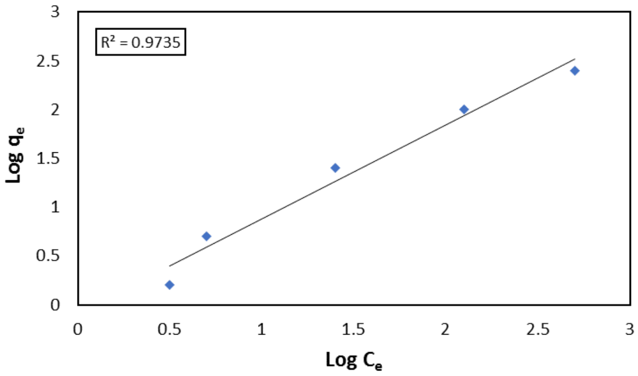
$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{2}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

Where q_e (mg.g^{-1}) is the equilibrium nitrate ions adsorption amounts on the clinoptilolite , C_e (mg.L^{-1}) is the equilibrium nitrate concentration, q_m is the fitting maximum adsorption capacity (mg.g^{-1}), K_F and b are the Freundlich and Langmuir constants respectively, 1/n is the heterogeneity coefficient. The high value of the correlation coefficient (R^2) of the adsorption isotherm values shows that adsorption of nitrate ions on modified clinoptilolite were fitted to Freundlich isotherm model as presented in Fig. 8a and Fig. 8b. This result could be due to physical as well as chemical interaction. This suggested that the adsorption of nitrate onto modified clinoptilolite was heterogeneous Freundlich compare to monolayer adsorption (Langmuir).



(a) Langmuir isotherm plots



(b) Freundlich isotherm plots

Fig. 8. Adsorption isotherm plots for nitrate adsorption (Langmuir and Freundlich)

G. *Kinetics Studies*

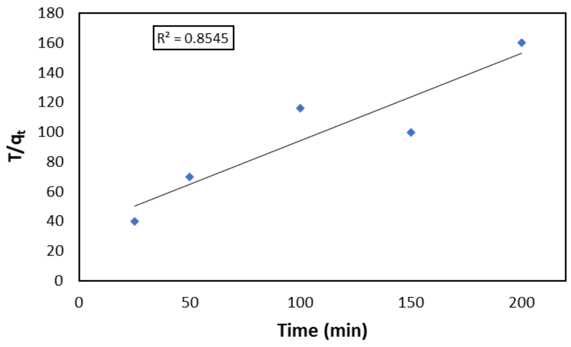
Kinetic studies are of utmost importance for an application of nitrate removal on modified clinoptilolite, it allows knowing the adsorption mechanism and its potential rate limiting steps. This can be used to determine the adsorption equilibrium and to develop a model that can aid in system design. Pseudo-first order and second kinetic models were employed to accurately reflect the trend of nitrate adsorption with time and reveal the reaction pathway of the process. The linear pseudo-first and second order kinetic models were expressed by Eqs. (4) and (5), respectively.

$$\log(q_e - q_t) = \log(q_e) - k_1 t \tag{4}$$

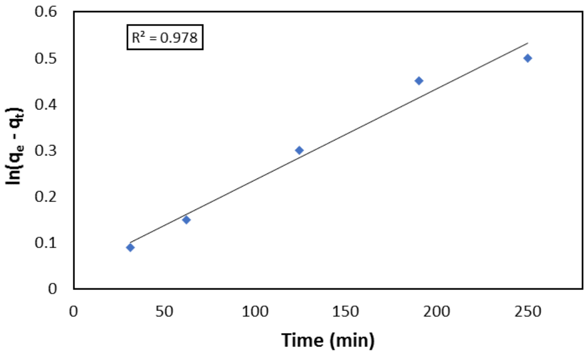
Where q_e and q_t denotes the amount of nitrate ion absorbed on the modified clinoptilolite at equilibrium and time t respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first order kinetics.

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \frac{1}{q_e} t \tag{5}$$

Where K_2 (g mg^{-1} min^{-1}) is the rate constant. The experiment data were used to study the kinetics models for nitrate adsorption onto clinoptilolite. The adsorption kinetic parameter values are presented in Fig. 9a and Fig. 9b. It was observed that the higher value of R^2 (0.978) shows the pseudo-second order model describes the nitrate kinetic study more than the pseudo-first order model. The second pseudo- order model was more suitable to describe the kinetic adsorption behavior for nitrate into clinoptilolite.



(a) Pseudo First-order kinetic



(b) Pseudo Second-order kinetic

Fig. 9. Kinetic models for nitrate removal

H. *Thermodynamic Studies*

Thermodynamic studies of an adsorption were applied to determine the nature of the process (viz. endothermicity, exothermicity, randomness, or spontaneity). Thermodynamic factors such as Gibb's free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were studied. The ΔG^o (kJ mol^{-1}) value was calculated using the Eq. (6) [17]:

$$\Delta G^o = -RT \ln K_d \tag{6}$$

Where R (8.314 J mol^{-1} K^{-1}), T (K), K_d (mL g^{-1}) are the universal gas constant, temperature and distribution coefficient reflecting the selectivity for nitrate adsorption. The K_d value was calculated using Eq. (7):

$$K_d = \frac{q_e}{C_e} \tag{7}$$

The ΔS^o (J mol^{-1} K^{-1}) and ΔH^o (kJ mol^{-1}) values were estimated from the intercept and slope of linear plot of $\ln K_d$ versus 1/T, respectively using the Eq. (8):

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{8}$$

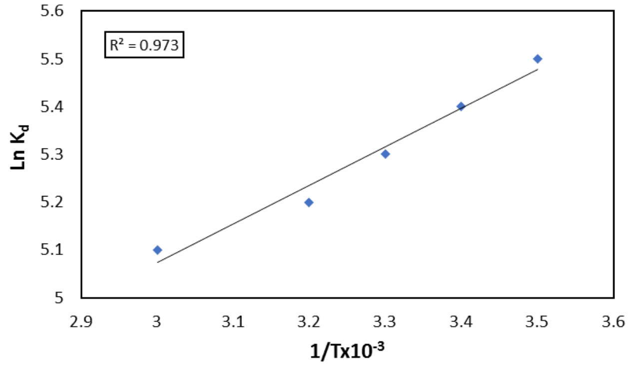


Fig. 10. ln Kd versus 1/T for nitrate adsorption

The results in Fig. 10 shows nitrate adsorption capacity increased slightly with an increased in temperature which increases the mobility of nitrate ions in solution.

TABLE II
THERMODYNAMIC PARAMETERS FOR NITRATE ADSORPTION

Temperature (K)	q_e (mg/g)	R^2	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o(J/mol.K)
288	2.05		-11.86		
298	2.01		-11.88		
308	2.00	0.973	-12.25	-5.01	26.54
318	1.96		-13.50		
328	1.94		-13.86		

Table II presents the thermodynamic parameter process for nitrate adsorption process. It was observed that the negative value ΔH^o confirms the exothermic nature of process. The negative value of ΔG^o indicates the spontaneous process and thermodynamics feasible adsorption process. The negative of ΔG^o with the higher temperature confirmed the nitrate adsorption on coated clinoptilolite was likely to occur when temperature decreases. The positive value of ΔS^o clearly showed the affinity of nitrate ions and randomness during the adsorption process.

IV. CONCLUSION

Clinoptilolite was successfully modified using chitosan to increase the nitrate removal efficiency. The results showed nitrate removal efficiency increases due to an increase in pH and adsorbent dosage. For the lowest initial concentration, the maximum removal is achieved. It was also found that the pH 10, initial concentration of 25 mgL^{-1} and adsorbent dosage of 2 g are the best removal conditions for nitrate from wastewater. Freundlich isotherm model described better fit the adsorption process. A kinetics adsorption study was effectively described by pseudo-second-order model. The thermodynamic investigation reveals spontaneous and exothermic nature of nitrate ion onto modified clinoptilolite. It was concluded that a modified clinoptilolite with chitosan is a highly efficient and economic adsorbent material for the removal of nitrate from waste water.

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