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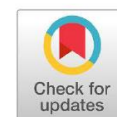
Original Research article

NH₃ Removal from Sour Water by Clinoptilolite Zeolite: A Case Study of Tabriz Refinery

Hassan Esmaeilzadeh[a], Ebrahim Fataei[b, *], Hossein Saadati[c]

[a] Ph.D. Student, Department of Environmental Sciences and Engineering, Ardabil Branch, Islamic Azad University, Ardabil, Iran

[b] Associate Professor, Department of Environmental Sciences and Engineering, Ardabil Branch, Islamic Azad University, Ardabil, Iran

[c] Assistant Professor, Department of Environmental Sciences and Engineering, Ardabil Branch, Islamic Azad University, Ardabil, Iran

### ARTICLE INFORMATION

ABSTRACT

Sour water (SW) is one of the refinery effluents that is very dangerous for the environment and humans. In refineries, the use of conventional methods to remove contaminants, including ammonia (NH₃), from SW is not very effective. This study proposes a method to remove NH₃ from the refinery's SW and reduce its associated risks. In this study, for the first time, using the adsorption method and clinoptilolite adsorbent, the concentration of NH₃ in SW decreased and reached the standard limit, which could be as an innovation for this research. The effect of pH, adsorbent dose, initial pollutant concentration, contact time, and temperature were investigated. Thermodynamics, kinetics, and isotherms were studied. The results were used to remove NH₃ from the SW of Tabriz refinery. The optimal values of the aforementioned parameters were 11, 1 g/100 mL, 50 mg/L, 30 min, and 25 °C, respectively. The results of the thermodynamic analysis showed that the adsorption process was exothermic, reversible and spontaneous in the test conditions. Experimental data were fitted better to the pseudo-second-order kinetics model and Langmuir isotherm model. After passing the SW through two consecutive fixed substrates, the NH₃ concentration decreased from 400 mg/L to 2.3 mg/L, and the R% was 93.4%. According to the results of this study the proposed method can be used as a suitable method and suitable adsorbent to remove NH₃ from the SW of refineries and effluents, due to its simplicity and high efficiency and the clinoptilolite due to its cheapness, abundance and ability to resuscitation.

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Corresponding author: E-mail: eafataei@gmail.com, Associate Professor, Department of Environmental Sciences and Engineering, Ardabil Branch, Islamic Azad University, Ardabil, Iran, Tel: 0914354900

Graphical Abstract
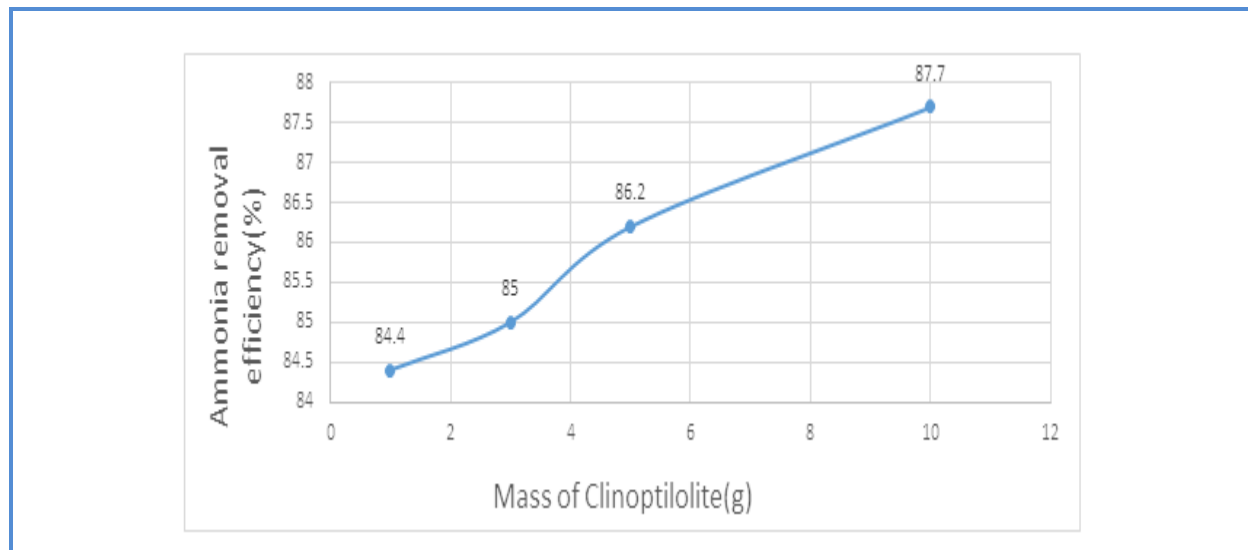
Introduction

The activity of industries such as the oil industry and refineries to meet human needs cause environmental pollution and damage to community health [1]. Ammonia is a material synthesized and manufactured in 1906 by Fritz Haber and Carl Bosch on an industrial scale. This substance, which is basically the main raw material of chemical fertilizers, has saved many people in the world from starvation. However, the residual excess in the environment later caused environmental pollution [2]. Today, ammonia has been introduced into groundwater and surface water as the most important nitrogen pollutant and can cause bad odor and reduce dissolved oxygen and cause great damage to the environment. Ammonia accelerates eutrophication of water resources ecosystems and enhances algae growth and has significant negative effects on fish and human health [3]. Due to the activity of microorganisms, ammonia nitrogen causes nitrate (NO_3^-) to change into nitrite (NO_2^-) and nitrite is combined with the proteins of the human body and becomes a very dangerous and carcinogenic substance called nitrosoamine. The presence of nitrate in drinking water and vegetables has caused blue baby syndrome, called methemoglobinemia [4, 2]. As ammonia concentrations in the atmosphere rise above 35 ppm, it will affect human and animal health [5]. Oil refineries are one of the industries that produce ammonia into the environment and water resources due to the production of wastewater contaminated with ammonia called sour water. Conventional wastewater treatment methods cannot always standardize ammonia nitrogen concentration, thus causing substantial problems when large volumes of wastewater enter the

environment [6]. This study aimed at removing ammonia from the sour water of Tabriz refinery to reach the allowable limit (less than 3 mg/L) and recycle large amounts of water as well as reduce air pollution in the refinery. Abundant research has been done on the removal of contaminants by surface adsorption but the ammonia absorption from the SW of Tabriz refinery using the zeolite of clinoptilolite was investigated for the first time which denotes the main novelty of this paper. What follows is a review of studies done in the past. Bobonich (1995) studied the effect of chemical modification on clinoptilolite in the removal of polar molecules and found that this natural zeolite has good adsorption capacity for hydrogen sulfide [7]. Mohammed *et al.* (2013) applied the surface response methodology (RSM) to remove COD and ammonia nitrogen and 4,2-dichloro phenol from pilot-scale paper mill reclaimed wastewater using granular activated carbon in a batch biofilm reactor. The results were successful [8]. Studying the absorption of ammonia by porous aluminum oxide by molding, Chanjoo and Younghun (2017) found that with increasing temperature, removal efficiency (R%) and adsorbent capacity (q) decreased [9].

 In refineries, as a result of using a lot of water in the oil purification process, a large volume of sour water is produced. Therefore, the removal of ammonia and other pollutants from the sour water will result in the recycling of large quantities of water, reducing environmental pollution and refinery air pollution. Consequently, the environment will have less pollution for the activity of refinery staff and local residents. There are currently methods such as stripping, chemical oxidation, reverse osmosis, activated sludge, nitrification and denitrification, ultrafiltration, microfiltration and ion exchange, *etc*. to remove ammonia from effluents [10, 11, 31]. Pollutant removal technology by surface adsorption method, also the focus of this study, is one of the methods of removing organic and inorganic pollutants in wastewater. One of the benefits of this method is its ability to be reabsorbed, easy to operate and affordable, *etc.* [12]. In this study, a zeolite called clinoptilolite was used as an adsorbent because it is abundantly and cheaply found in many parts of Iran such as Semnan, Mianeh and *etc.* On the other hand, due to the polar nature of ammonia, the ability of zeolite to adsorb of ammonia is high [13].

Experimental

Adsorbent

This is an experimental and laboratory study. In this study, a natural Iranian zeolite called clinoptilolite, which is abundant in Iran, was used to remove NH₃ from aqueous solutions and SW of Tabriz refinery. Clinoptilolite was purchased from Iranian zeolite export company located in Semnan in 1-3 mm size. Clinoptilolite material were washed several times with distilled water to

remove any impurities and dried at 105 °C for 24 h in laboratory oven. Figure 1. shows the clinoptilolite appearance.

Figure 1. Clinoptilolite appearance

SW and chemical reagent

The SW solution was sampled from Tabriz refinery. NH_3 concentration in SW refinery was different at different times, so three samples of SW were considered at three different times. Next, NH_3 concentration was determined and the sample with higher concentration was used for experiments. SW is a mixture of different pollutants, but the purpose of this study was to remove NH_3 from SW. The concentration of NH_3 in the concentrated sample was 400 mg/L and pH=10.5. 10 literes polyethylene containers were used for sampling. The samples were immediately transferred to the laboratory and were kept in the refrigerator until the experiments.

To adjust the pH, solutions of 0.1 mol/L hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used. One liter of 50 mg/L NH_3 solution was prepared in the laboratory. All sample bottles and glass wares were cleaned, rinsed with deionized water, and then oven dried at 60 °C.

Method

In this study surface adsorption method was selected due to its possibility to resuscitation, easy to operate, affordable, and simple design [12, 27].

The optimum conditions including pH, adsorbent dose, initial pollutant concentration, contact time and temperature for removal of NH_3 from 50 mg/L solution were investigated. Then thermodynamics, kinetics, and isotherms of the adsorption process were studied. After that, the results were used to remove NH_3 from the SW of the Tabriz refinery. Nesler test and DR 5000 spectrophotometer were applied to measure NH_3 concentration. Experiments were carried out in 250 mL erlenmeyer flasks and the sample volume was 100 mL. A magnetic mixer was used to stir the mixtures, and a Whatman 42 filter paper was utilized to separate the adsorbent from the mixtures.

Eqs. 1 and 2 were used to calculate the removal efficiency (R%) and adsorbent capacity (q) in mg/g [9, 25].

$$\%R = \frac{100(C_o - C_e)}{C_o} \tag{1}$$

$$q = \frac{(C_o - C_e)V}{W} \tag{2}$$

Where C_o and C_e in (mg/L) are the initial and the equilibrium concentration of NH_3 in solution, respectively. W in gram (g) is the mass of the adsorbent and V denotes the volume of the used solution in a liter (L).

In this research, the classical and common methods were used to design the experiments. That is, all independent variables were kept constant and the desired variable was changed in a certain range and its effect on the process response (R% and q) was determined.

Determination of optimum pH and dose

100 mL of 50 mg/L NH_3 solution was poured into five erlenmeyer adjusted pH of solutions to (3, 5, 7, 9, 11) and the adsorption was performed in four steps in the presence (1, 3, 5 and 10 g) of the adsorbent for 60 min. Then the adsorbent was separated from the mixture and the NH_3 concentration in the solutions was read, and optimum pH and optimum dose of adsorbent were determined.

Determination of optimum initial contaminant concentration on the adsorption process

100 mL of NH_3 solution was poured into five erlenmeyer to concentrations of (100, 75, 50, 25 and 10 mg/L) and adsorption process in the presence of 1 g adsorbent and pH = 11 for 60 min was performed. The effect of initial NH_3 concentration on the adsorption process and optimum initial concentration of NH_3 was determined.

Determination of optimum contact time

The adsorption was performed of NH_3 solution with different time durations of 15, 30, 60, 90, 120 and 150 minutes and optimum conditions (pH = 11, adsorbent dose = 1 g/100 mL solution and initial NH_3 concentration = 50 mg/L). Then the concentrations of NH_3 in the solutions were read and optimum contact time was determined.

Determination of optimum temperature

An NH_3 solution sample was selected at optimum conditions (pH = 11, adsorbent dose = 1 g/100 mL, initial NH_3 concentration = 50 mg/L and contact time = 30 min), adsorption was performed at 25, 35 and 45 °C, equilibrium concentration (C_e) was read for each temperature and the optimum temperature was determined.

Thermodynamics analysis

The thermodynamics parameters, such as changes in Gibb's free energy (ΔG) in (kJ/mol) enthalpy (ΔH) in (kJ/mol), and entropy (ΔS) in (kJ/mol/K), were determined in order to understand the reaction changes during the process using the following Eqs. (3-5).

$$LnK_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(3)

$$K_C = \frac{C_{ad}}{C_e}$$
(4)

$$\Delta G = -RTLnK_c$$
(5)

Where R = 8.314 (J/mol/K) is the general constant for gases, T is the absolute temperature in (K) and K_c is the equilibrium constant and C_{ad} and C_e are the adsorbed NH_3 and the equilibrium NH_3 concentration in (mg/L), respectively [14, 16, 28].

The LnK_c inear graph relative to 1/T was plotted. The graph slope was ΔH/R and the width of the origin was ΔS/R. The value of *ΔG* was calculated from Eqs. (4-5).

Adsorption kinetic modelling

In kinetic studies, pseudo-first-order and pseudo-second-order equations were used to investigate the factors affecting the rate of adsorption process [21, 22]. Eqs. (6-7) which are pseudo-first-order and pseudo-second-order kinetic equations, respectively, were used in this study [20, 28].

$$Ln(q_e - q_t) = Lnq_e - k_1t$$
(6)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$
(7)

Where k_1 in (min^{-1}) and k_2 in (g/mg^{-1}/min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order equations, respectively. q_e and q_t, are the adsorbent capacity at equilibrium time and t time (mg/g), respectively.

The adsorption rate constant, k_1 can be calculated from the plot of *ln (q_e_q_t)* vs *t* and the values of k_2, and q_e can be calculated by the plot of (t/q_t) vs t.

Adsorption isotherm models

In the adsorption isotherm studies, Langmuir and Freundlich isotherm models were used. The Langmuir isotherm assumes that adsorption occurs as a monolayer on homogenous surfaces, while the Freundlich model is applicable on heterogeneous surfaces with different adsorption energies

and on non-identical sites [13, 29]. Eqs. (8-9) which are Langmuir and Freundlich equations, respectively, were used in this study.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{8}$$

$$Ln q_e = Ln K_f + \frac{1}{n} Ln C_e \tag{9}$$

Where K_L (L/mg) and K_f (mg$^{(1-1/n)}$/L$^{1/n}$/g) are Langmuir and Freundlich constant. q_e (mg/g) q_m (mg/g) and C_e (mg/L) are the equilibrium adsorbent capacity, the maximum adsorbent capacity, and equilibrium concentration of contaminant, respectively [19]. n is called the surface heterogeneity constant. If n is less than 1, adsorption is undesirable, but if n is between 1 and 10, adsorption is desirable [24].

To express the main feature of the Langmuir isotherm, a dimensionless constant called the equilibrium parameter (R_L) is used, which is defined by Eq (10).

$$R_L = \frac{1}{1 + K_L C_o} \tag{10}$$

Where K_L (L/mg) and C_o (mg/L) are the Langmuir constant and the maximum initial concentration of pollutants, respectively. If the R_L values are between zero and 1, it indicates that the adsorption process is desirable [24, 30].

Investigation of NH₃ removal from SW of Tabriz refinery

According to the results obtained from previous steps, removal of NH₃ from the SW solution of Tabriz refinery was studied. In the first experiment, the effect of NH₃ concentration in SW on R% was investigated. To do this, 100 mL of SW with NH₃ concentrations equal to 40, 80, 100, 200 and 400 mg/L was poured in five erlenmeyer, then 10 g of adsorbent was added, stirred for 30 minutes, then filtered and the NH₃ concentration was read. In the second experiment, the effect of contact time on the R% was investigated. 100 mL of SW was poured in an erlenmeyer, 10 g of adsorbent was added and the adsorption was performed and the NH₃ concentration was read at 10, 30, 45, 60, 90, 180 and 240 min. In the third experiment, 100 mL sour water was selected and passed through two consecutive fixed beds each containing 65 g of clinoptilolite. NH₃ concentration was measured in the outlet solution of each fixed bed.

Results and discussion

XRF analysis of clinoptilolite

Sequential XRF[1] spectrometer with Rh anticathode was used for XRF analysis. The XRF analysis of clinoptilolite used in this research was shown in Table 1. It is observed that more than 69% of the mass of the constituents of clinoptilolite is SiO_2.

Table 1. XRF analysis of Semnan, Iran clinoptilolite

Constituents	Mass percentage	Constituents	Mass percentage
SiO_2	69.9	TiO_2	0.32
Al_2O_3	12.3	SrO	0.3
CaO	5.3	Cs_2O	0.25
K_2O	3.2	CuO	0.15
Na_2O	2.9	SnO_2	0.12
Fe_2O_3	2.1	MnO	0.12
MgO	1.5	Sb_2O_3	0.11
P_2O_5	0.37	BaO	0.12
		Insignificant material	0.94

XRD analysis

For XRD[2] analysis, Philips device model 3710 with cobalt anticatode was adopted. The XRD analysis of clinoptilolite used in this research was shown in Figure 2. The results showed that Semnan clinoptilolite sample had a high purity.
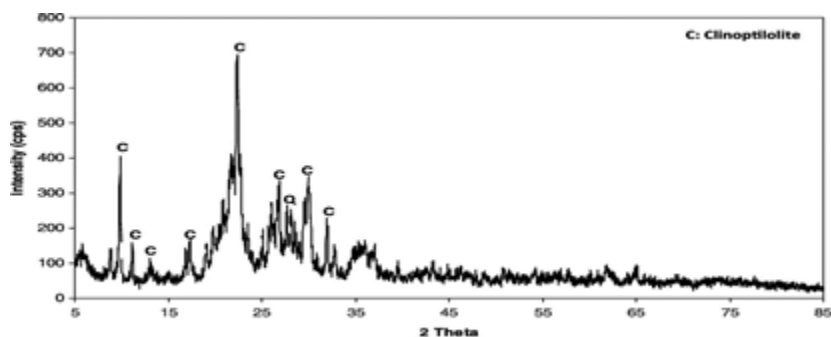
Figure 2. XRD spectrum of Semnan clinoptilolite

Spectrometric surface morphological analysis

To examine the morphology of clinoptilolite, SEM[3] (S 360 Cambridge) was applied, and the image shown in Figure 3. indicated that naturally clinoptilolite has adequate pores that are crystalline

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1. X- Ray Fluorescence
2. X-Ray Diffraction

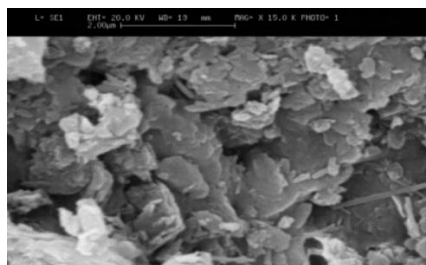structure. This pore structure is required as a place for adsorbed pollutant trapped in the internal surface of the sorbent**.**

Figure 3. SEM analysis of Semnan clinoptilolite

Determination of the optimum pH

The effect of pH on R% for the values of adsorbent (1, 3, 5, 10 g) was shown in Figures 4-7.
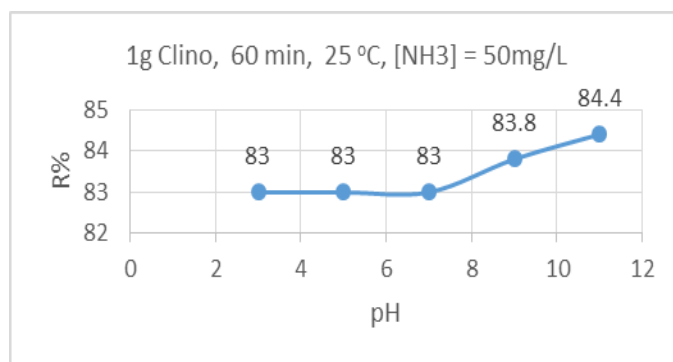

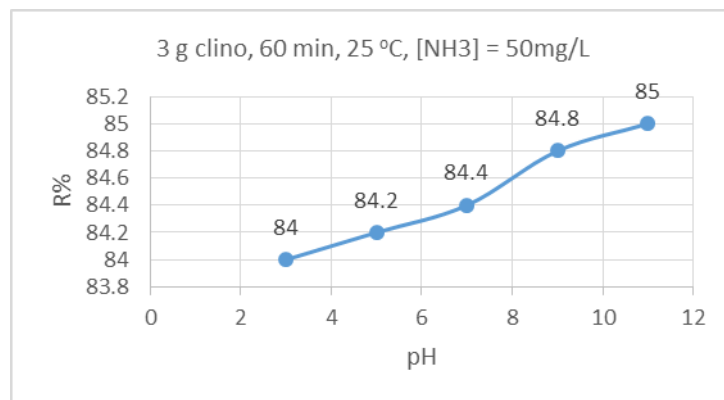**Figure 4**. The effect of pH on R% (1 g Clino)
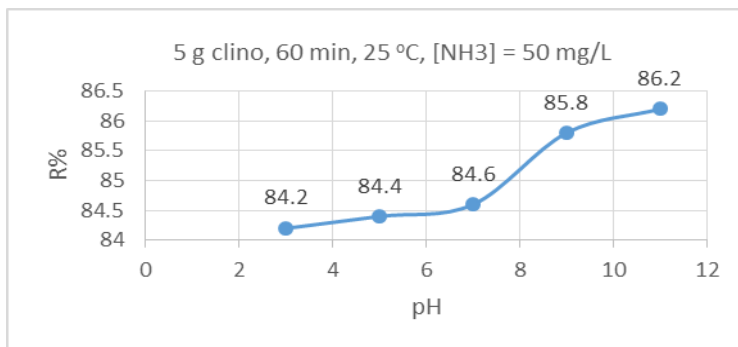

Figure 5. The effect of pH on R% (3 g Clino)

3. Scanning electron micrograph

Figure 6. The effect of pH on R% (5 g Clino)
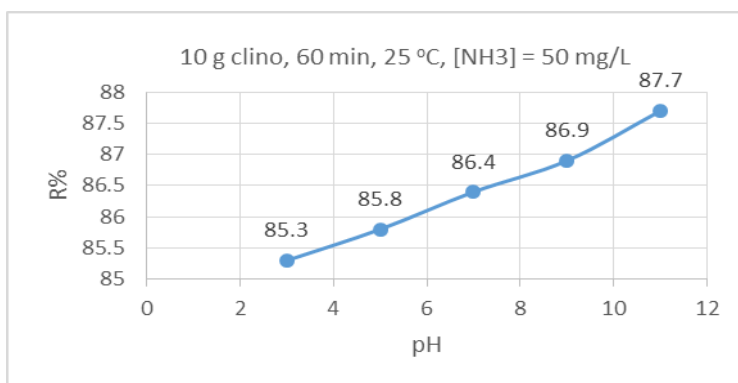
Figure 7. The effect of pH on R% (10 g Clino)

The results showed that by increasing the pH and the amount of adsorbent, the removal efficiency (R%) increased. The reason is that in the adsorption process, two hydroxide ion (OH^-) and hydronium ion (H^+) determine the surface charge [14]. NH$_3$ is also in equilibrium with ammonium ion (NH_4^+) in aqueous solutions. The zeolite surface is negatively charged due to the presence of silicate and aluminate anions. At low pHs, the concentration of H^+ is high, which makes the adsorption sites and adsorbent surface more positive. Therefore, this surface prevents better absorption of NH_4^+ ion and consequently reduces R%. At high pHs the negative charge of adsorbent and R% increases [11]. These results are similar to those of Guo *et al.*, on adsorption of ammonia nitrogen to activated carbon prepared from palm shells impregnation with H$_2$SO$_4$ [1]. Because increasing pH led to a rise in the ammonia adsorption efficiency (R%), so optimum pH = 11 was selected.

Determination of the optimum dose

The effect of adsorbent dose on removal efficiency (R%) and adsorbent capacity (q) at optimum pH were shown in Figures 8 and 9.
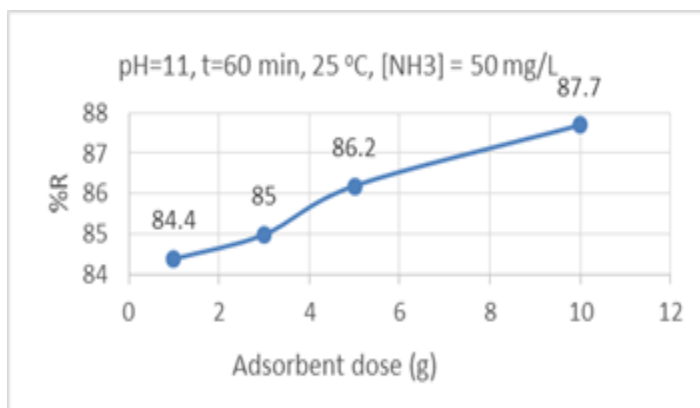
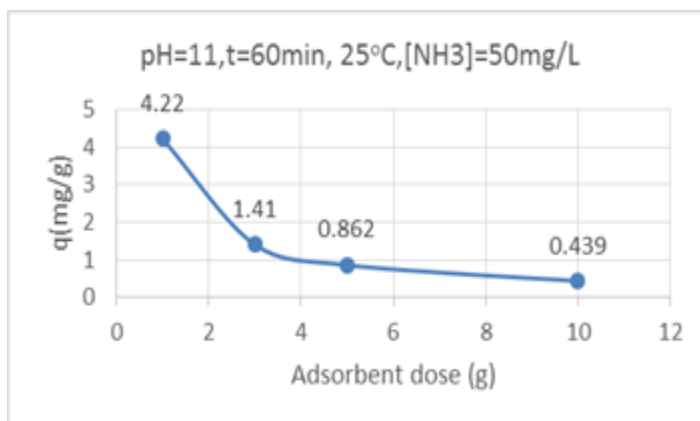**Figure 8**. The effect of adsorbent dose on R%

Figure 9. The effect of adsorbent dose on q

The results showed that when the adsorbent dose increased, R% increased and q decreased. This is because as the adsorbent dose increases, the active adsorbent surfaces increase and the adsorbed particles reach the adsorption sites, However, an excessive increase in the amount of adsorbent reduces the active adsorption levels due to the high density of the adsorbent particles and as a result does not cause much change in R% [15]. The reason for the decrease in q is that by increasing the amount of adsorbent, the adsorption sites increase, thereby reducing the amount of contaminant absorbed by the unit of mass of the adsorbent [16]. Since the %R increase was not very high, because of issues such as disposal problems, adsorbent resuscitation, transportation, economic and environmental, the optimum dose of adsorbent 1 mg/g was determined.

Determination of the optimum initial contaminant concentration on adsorption process

The effect of initial concentration of ammonia on removal efficiency (R%) and adsorbent capacity (q) at optimum pH and optimum adsorbent dose are shown in Figures 10 and 11.
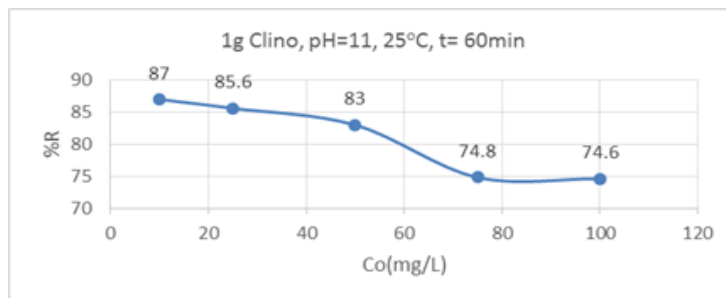
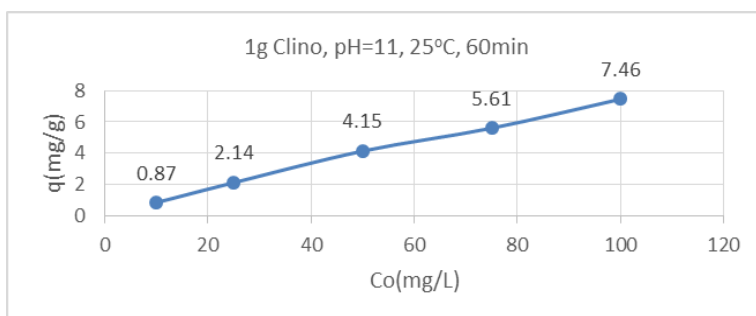**Figure 10**. The effect of initial concentration of ammonia on removal efficiency (R%)

Figure 11. The effect of initial concentration of ammonia on adsorbent capacity (q)

The results showed that, the highest and lowest R% were observed at concentrations of 10 mg/L and 100 mg/L ammonia, which were 87% and 74.6%, respectively. The optimum initial concentration of the ammonia was considered to be 50 mg/L. As the ammonia concentration increased from 10 mg/L to 100 mg/L the adsorbent capacity(q) increased from 0.87 mg/g to 7.46 mg/g. In 2006, Sprinsky *et al.,* research on the efficacy of clinoptilolite for the removal of heavy metals showed that as the concentration of pollutants increased, q increased, similar to the results of this study [17].

Determination of the optimum contact time

The effect of contact time on removal efficiency (R%) and adsorbent capacity (q) at the optimum conditions are shown in Figures 12 and 13*.*
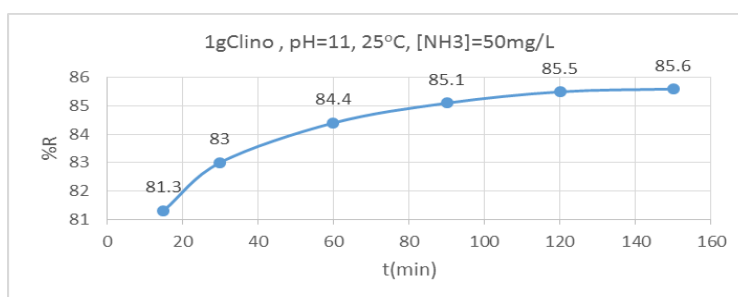

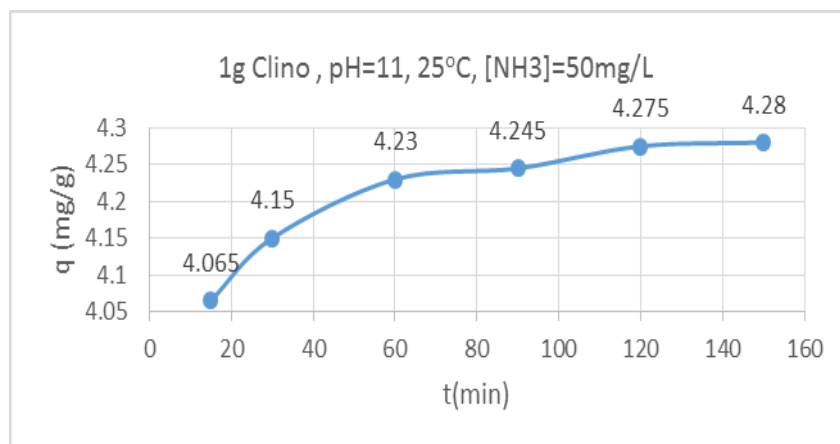**Figure 12**. The effect of contact time on removal efficiency (R%)

Figure 13. The effect of contact time on adsorbent capacity (q)

The results showed that with increasing contact time the removal efficiency (R%) and adsorbent capacity (q) increased. The slope of the charts was high at first and gradually reached zero. That is, at the start times the absorption rate was high and decreased steadily and reached a constant value at equilibrium time (t_e). Because the adsorbent active sites are larger in size, adsorption rate are high at initial times. Over time, the adsorbent active sites are filled and the adsorption rate decreases the adsorption rate decreases due to the repulsive force between the adsorbed particles and the particles present in the solution [18]. It is because the slope of the graphs gradually decreases to zero after time 120 min. Therefore, 120 min and 4.275 mg/g were determined as equilibrium time (t_e) and equilibrium adsorbed capacity (q_e), respectively. Since no significant increase was observed in R% and q over time, 30 min was selected as optimum time.

Determination of the optimum temperature

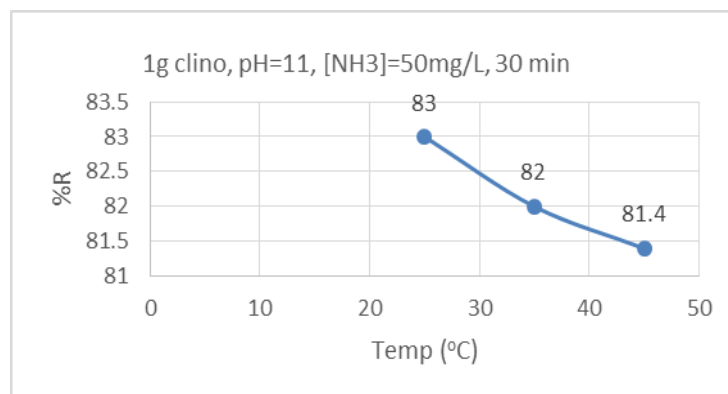The effect of temperature on removal efficiency (R%) at optimum condition was shown in Figure14.

Figure 14. The effect of temperature on removal efficiency (R%)

It was observed that increasing temperature resulted in decreasing removal efficiency (R%). That is, the adsorption process of ammonia by clinoptilolite is exothermic. A study by Changjoo and Younghun (2017) on the absorption of ammonia by porous aluminum oxide using molding also showed that with increasing temperature, R% was decreased [9]. Because of the magnitude R% at 25 °C, this temperature was determined as the optimum temperature.

Thermodynamic study of the adsorption process

The results of the thermodynamic investigation of adsorption process are shown in Figure15, representing LnKc changes relative to 1/T. The thermodynamic parameters were calculated and presented in Table 2.
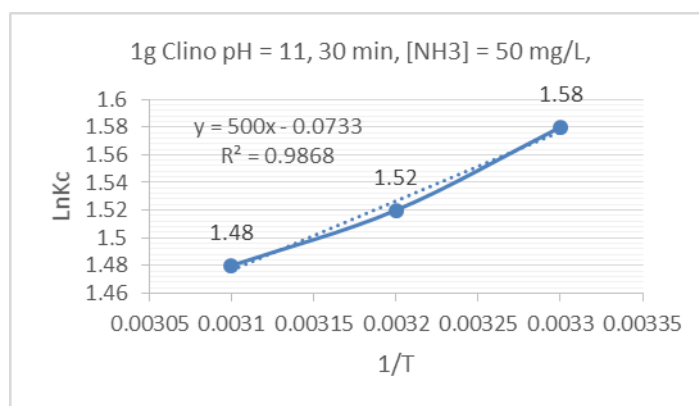

Figure 15. The LnKc changes relative to 1/T

Table 2. Calculated thermodynamic parameters for ammonia absorption with clinoptilolite

Temperature (K)	LnKc	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
298	1.58	-3.9146		
308	1.52	-3.8922	-4.157	$- 6.1 \times 10^{-4}$
318	1.48	-3.9129		

The values of ΔH, ΔS and ΔG were -4.157 kJ/mol, -6.1×10^{-4} J/mol/K and -3.914 kJ/mol, respectively (Table 2). Based on the results of Table 2, the negative ΔH and ΔS indicate respectively that the adsorption process is exothermic and entropy decreasing, and that their sign indicates that the process is reversible. The negative sign for ΔG indicates that this process is spontaneous in these conditions. In 2015, Mohammadnia and Naghizadeh studies also yielded similar results [19].

Investigation of the adsorption kinetics

In kinetic studies, pseudo-first order and pseudo-second order equations were used to investigate the factors affecting the rate of adsorption process [21, 22].
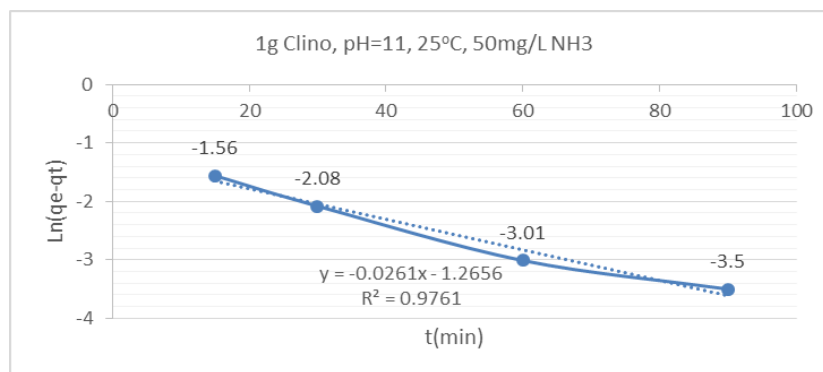
Figure 16. Matching the adsorption process with the pseudo-first order kinetic model

In Figure 16, to match the pseudo-first order kinetic model, the $Ln(q_e - qt)$ graph was plotted relative to time. According to the slope and width of the origin of the graph, $k_1 = 0.0261$ and q = 0.28, and the regression coefficient $R^2 = 0.97$ were obtained.
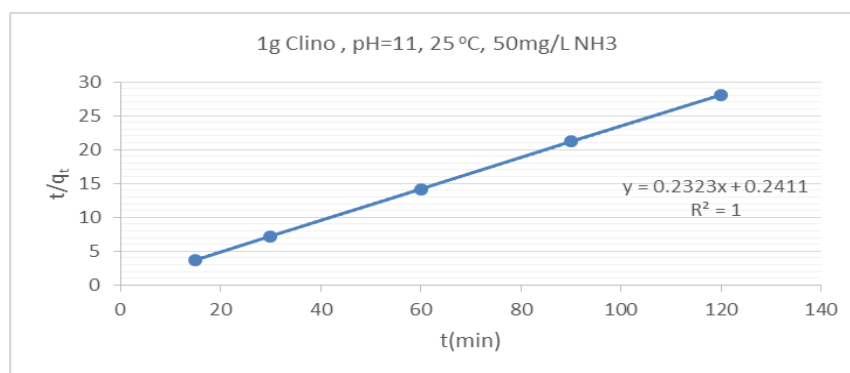

Figure 17. Matching the adsorption process with the pseudo-second order kinetic model

As can be seen in Figure 17, to match the pseudo-second order kinetic model, the graph of t/q_t relative to time was plotted, the slope and width of origin, $q_e = 4.3$ and $k_2 = 0.007$, and the regression coefficient $R^2 = 1$ were obtained. The results are presented in Table 3.

Table 3. Results of pseudo-first order and pseudo-second order kinetic equations

Pseudo-first order			Pseudo-seconed order			
R^2	q_e (cal)	k_1	R^2	q_e (cal)	k_2	q_e (exp)
0.97	0.28	0.0261	1	4.3	0.007	4.275

According to Table 3. in the pseudo-second order kinetic model, the calculated q_e (Cal) corresponded more to the experimental q_e (EXP), and the R^2 regression coefficient was larger in the pseudo-second order kinetic model, so the experimental data were fitted better to the pseudo-second order kinetics model. This result is in line with that of Eskandarian *et al.* [22]. Therefore, the

adsorption process depends on the concentration of the pollutant and most of the adsorption is done by chemical adsorption [23].

Investigation of the adsorption isotherm

In the adsorption isotherm study, Langmuir and Freundlich isotherm models were used. The Langmuir isotherm assumes that adsorption occurs as monolayer on homogenous surfaces, while the Freundlich model is applicable on heterogeneous surfaces with different adsorption energies and on non-identical sites [13].
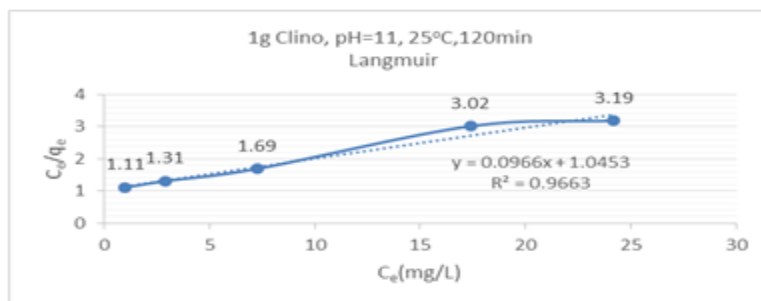

Figure 18. Matching the adsorption process with the Langmuir model

Based on Figure 18, to match the Langmuir isotherm model, the C_e/q_e graph was plotted relative to C_e. According to the slope and width of the origin of the graph, q_m = 10.4 and K_L = 0.09 and R^2 = 0.97 were obtained.
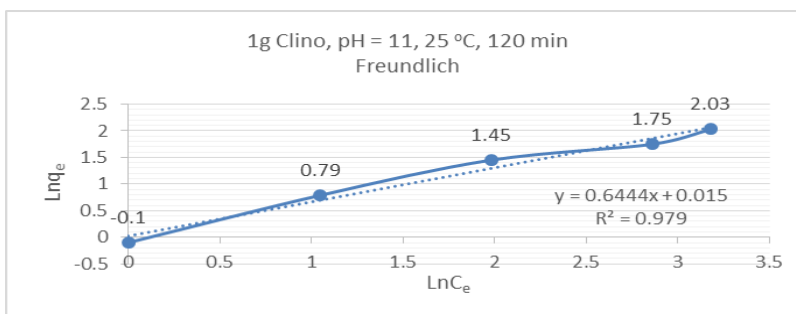

Figure 19. Matching the adsorption process with the Freundlich model

As can be seen in Figure 19, to match the Freundlich isotherm model, the graph of Lnq_e relative to LnC_e was plotted. According to the slope and width of the origin of the graph, K_f = 1, n = 1.55, and R^2 = 0.98 were calculated. The results are presented in Table 4.

Table 4. Results of Langmuir and Freundlich isotherms

Langmuir			Fruindlich		
q_m	K_L	R^2	n	K_f	R^2
10.4	0.09	0.97	1.55	1.00	0.98

Relying on Table 4, R2 = 0.98 and n = 1.55 showed that the adsorption process was better matched with the Friendlich model and R^2 = 0.97 and R_L = 0.1 showed that the adsorption process better matched with the Langmuir model. Thus, the uptake of ammonia by clinoptilolite was fitted with both Langmuir and Freundlich models and was more compatible with the Langmuir isotherm because RL = 0.1. This result is also confirmed by Eskandarian *et al.* (2017) and Mohammadnia and Naghizadeh (2016) [19, 22].

Investigation of ammonia removal from sour water of Tabriz refinery

The results showed that removal efficiency (R%) decreased with increasing initial concentration of ammonia in sour water, and increased with increasing contact time. The results of the first and the second experiment are shown in Figure 20 and Figure 21, respectively.
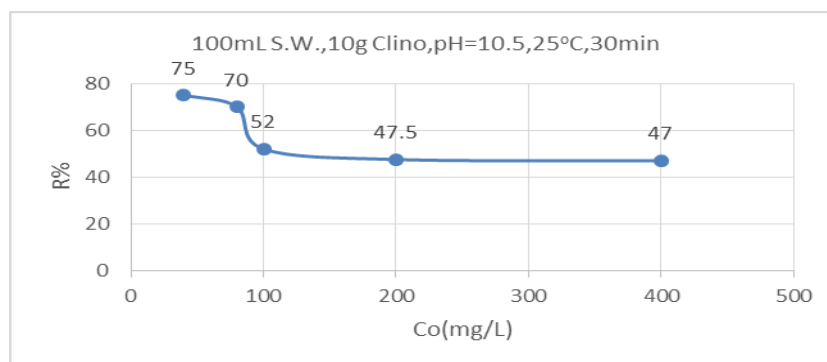

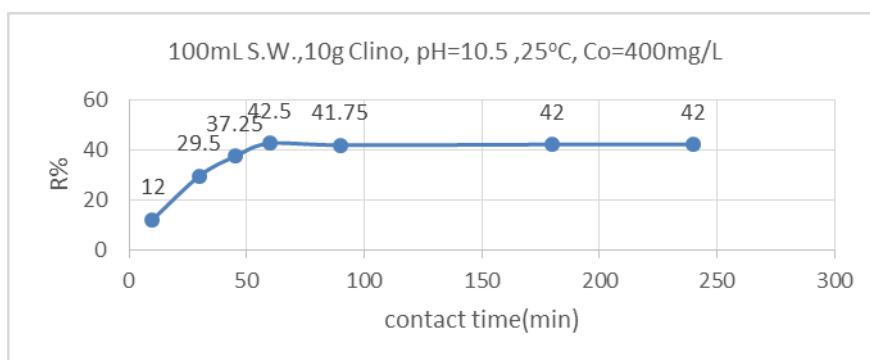**Figure 20.** The effect of NH₃ concentration in sour water on R% by clinoptilolite

Figure 21. The effect of contact time on R% from sour water by clinoptilolite

The results of the first experiment in removal of ammonia from sour water of Tabriz refinery revealed that with increasing of ammonia concentration in sour water, R% decreased. The results of Figure 17. showed that when the concentration of ammonia in sour water was initially elevated, the gradient decrease was mild, but steep in the range of 80-100 mg/L because the adsorbent

adsorption sites were filled by ammonia and other species in the sour water and the removal efficiency came down and then reached a constant amount. The results of the second experiment in Figure 18. indicated that as the contact time increased, R% increased and reached about 42% after 60 min and then remained constant. This is because the active sites of adsorbent, in addition to ammonia, with other species that are present in sour water in different concentrations are filled to reach equilibrium time. That is, the rate of absorption and desorption becomes equal. According to the first experiment R% increased with decreasing ammonia concentration. However, due to the high volume of sour water and the high concentration of ammonia, diluting the sour water to increase R% would result in excessive volume of water consumption, which is not reasonable. Therefore, due to the cheapness, abundance and reactivation ability of clinoptilolite, it is advisable to design amorphous adsorbed substrates or columns to reduce the ammonia concentration in the sour water and continue the adsorption process to the limit (Less than 3 mg/L). For optimum adsorption efficiency, the adsorbed substrates or columns should be designed so that the sour water will be in contact with the adsorbent by passing from the column for approximately 60 minutes. Accordingly, a third experiment was designed. in the third experiment, after passing the sour water through the first substrate, the ammonia concentration decreased from 400 mg/L to 35 mg/L and was R% = 91.25%. After passing the first substrate and passing from the second substrate, the concentration of ammonia changed from 35 mg/L to 2.3 mg/L. At this stage R% = 93.4%. Since in the second step the concentration of ammonia was low, so it is reasonable to increase the adsorption efficiency.

Conclusion

In refineries, utilizing conventional methods to remove contaminants, such as NH_3 and H_2S from sour water is not very effective. In this paper, a new method was proposed to decrease the concentration of NH_3 contaminants reaching the standard limitations based on the surface adsorption and clinoptilolite zeolite adsorbent. In this study, the clinoptilolite of Semnan city was used as an adsorbent for the removal of NH_3 from the aqueous solution of NH_3 and Sour water solution of Tabriz refinery. In the removal of NH_3, the optimum values of pH, adsorbent dose, initial NH_3 concentration, contact time, and temperature were obtained from NH_3 aqueous solution at 11, 10 g/L, 50 mg/L, 30 min and 25 °C, respectively. Due to thermodynamic parameters, the adsorption process was exothermic, reversible, and spontaneous. Experimental data were fitted better to the pseudo-second-order kinetics model and Langmuir isotherm model. The results of the experiments for removal of NH_3 from sour water of Tabriz refinery showed that due to its simplicity and high

efficiency and the clinoptilolite, the proposed method can be used as a suitable adsorbent because of its cheapness, abundance, resuscitation, increasing efficiency by increasing its value and also the similarity of sour water pH and optimum pH for removing of NH_3 from sour water of refineries. Finally, carrying out this research on a semi-industrial scale is suggested.

Conflict of Interest

We have no conflicts of interest to disclose.

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