



## Investigating Regenerative Characteristics and Equilibrium Studies of Clinoptilolite, A Natural Zeolite Used in Ammonia Removal from Wastewater

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### Abstract

Wastewater treatment for water reuse is one of the main concerns in oil refineries since it can lead to high economic and environmental benefits. This paper deals with treatment of Ammonia effluent through ion exchange method, which Clinoptilolite was selected as a natural adsorbent. The effect of Zeolite's preconditioning on adsorption capacity as well as Zeolite's regeneration efficiency and the best isotherm models fitted to the isothermal equilibrium data were examined for two particle size ranges 1-3 mm and 3-10 mm. In the case of this project the exchanger zeolite is initially in the Na<sup>+</sup> form, and the influent contains NH<sub>4</sub><sup>+</sup> ions. During a cycle, the NH<sub>4</sub><sup>+</sup> ions will displace the sodium ions and after some time, breakthrough will begin to occur. Then adsorption process stopped and regeneration begins. The results after 9 consecutive regeneration stages were a decrease of 2.41% for 1-3 mm and 2.9% for 3-10 mm in Ammonium uptake capacity. In addition, preconditioning with an alkaline mixture of NaCl and NaOH results in a better affinity for Ammonium uptake and there was an increase in maximum capacity by 6.75%-8.07%. Finally, an adsorption isotherm, which is a relation curve between adsorption equilibrium capacity and equilibrium concentration, is illustrated. Results of all equilibria were modelled by fitting the Langmuir isotherm and the Freundlich isotherm alike to the experimental data. It was observed that Langmuir isotherm was the best fit to the experimental data due to assumptions made in deriving this isotherm model.

**Keywords:** Wastewater Treatment, Ammonia, Clinoptilolite Zeolite, Ion Exchange, Preconditioning Isotherms, Regeneration

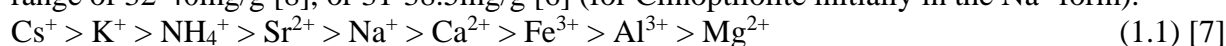
### 1. Introduction

Ammonia removal is a significant problem in a range of wastewater treatments. The municipal wastewater industry generates large volumes of Ammonia contaminated water after primary and secondary treatment. The land based aquaculture industry and the oil refining industry also produce significant volumes of Ammoniacal wastes. In all these cases reliable removal technologies believe a high standard of treated wastewater is required [1,2,3,4]. Ion exchange via Zeolite is the method examined in this study.

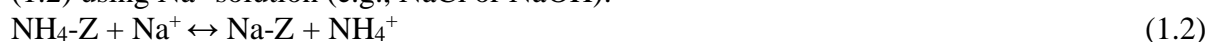
A Zeolite is a 3-dimensional aluminosilicate consisting of AlO<sub>4</sub>/SiO<sub>4</sub> tetrahedra, and cations. Each aluminium or silicon tetrahedra is connected by shared oxygen atoms and therefore



carries an overall negative charge, which is balanced by the cations [5]. Uses of Zeolites include: Gas phase adsorption of CO<sub>2</sub> and H<sub>2</sub>O, Oil absorption for spills, Fertiliser, Catalysts in the petroleum industry and Ion exchange (water softening, heavy metal removal, NH<sub>4</sub><sup>+</sup> removal). The particular ion exchanger of interest in this study is Clinoptilolite, which is known to have a high affinity for Ammonium ions [6,7,8] and is an abundant Zeolite found in nature as well. The cations found in natural Clinoptilolite are Na<sup>+</sup>, Ca<sub>2</sub><sup>+</sup>, some K<sup>+</sup>, Mg<sub>2</sub><sup>+</sup>, and traces of metals such as Fe<sub>3</sub><sup>+</sup>, Sr<sub>2</sub><sup>+</sup>, and Ba<sub>2</sub><sup>+</sup>. Zeolites with a high Al/Si ratio (high charge density) prefer small, highly charged ions such as Ca<sub>2</sub><sup>+</sup>. High Si/Al ratio (low charge density) will favour lower charged ions such as NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> [7]. As can be seen from the selectivity order in Equation 1.1, monovalent ions are preferred over the multivalent ions. Clinoptilolite is a silica-rich Zeolite, therefore it has a lower capacity than many other Zeolites, though having a number of other properties such as a high selectivity for NH<sub>4</sub><sup>+</sup> ions, and resistance to degradation by acidic solutions. Typical Ammonium ion capacities for Clinoptilolite are in the range of 32-40mg/g [8], or 31-38.5mg/g [6] (for Clinoptilolite initially in the Na<sup>+</sup> form).



Regeneration is the process by which the Ammonia ions adsorbed on the Zeolite exchange sites during the water treatment phase are removed before the Zeolite can be reused. Chemical regeneration aims at replacing Ammonium ions from Zeolite with other monovalent cations (e.g., Na<sup>+</sup>), which allows exhausted Zeolite to have exchangeable sites for Ammonium ion again. The chemical regeneration process is often based on the following reaction equation (1.2) using Na<sup>+</sup> solution (e.g., NaCl or NaOH):



Many studies have used sodium chloride in a range of 0.17–1 M NaCl [9,10,11,12] for chemical regeneration. The volume of NaCl brine needed for satisfactory regeneration of the exhausted Zeolite was varied and depended on the NaCl concentration of the brine. pH can affect the chemical regeneration process because Ammonium nitrogen will be transformed to dissolved Ammonia under alkaline pH, which can improve the regeneration. Odegaard [13] recommended a mixture of sodium chloride and sodium hydroxide as the regeneration brine for increasing the pH to improve the regeneration efficiency [13]. As a result, a mixture of NaOH along with NaCl was applied into this study.

Adsorption is another important unit operation used in water treatment and is when an adsorbate from a liquid or gaseous phase attaches itself to an interface. There are two types of adsorption, physisorption and chemisorption. There are a number of different models for adsorption but the two most commonly applied are the Langmuir isotherm and the Freundlich isotherm. These two models relate liquid phase concentration to solid phase concentration for equilibrium processes [14,15]. The Langmuir and Freundlich isotherms can also be used to model ion exchange. The Langmuir isotherm has been found to be suitable for ion exchange, as some of the assumptions used in deriving it include the following:

- There are a fixed number of sites.
- Only one solute molecule per site

Both of these assumptions work well with ion exchange.

## 2. Experimental

### 2.1. Preconditioning of Clinoptilolite

The Clinoptilolite was provided from the Zaminkav Company located in Semnan-Iran. The Zeolite was sieved to 1-3 mm and 3-10 mm, then all samples were washed with distilled water to remove any fines. In the next step, these samples were dried for 24 hours at 90 °C. During preconditioning, the Clinoptilolite was soaked in the NaCl (1M) and NaOH (0.1 M) solution



for 10 hours with regular agitation by shaker speed of 150 rpm. The Clinoptilolite was then rinsed with distilled water to remove excess NaCl and NaOH.

To quantify the effect of preconditioning on the Ammonia adsorption efficiency of Clinoptilolite, a test was conducted using Zeolite that was only washed with distilled water and immediately contacted with the Ammonia solution. The same particle sizes (1-3 mm and 3-10 mm) were used to obtain Ammonium concentration in untreated Clinoptilolite. There were two replicates for each particle size.

Since the capacity of Zeolites is greatly influenced by chemical and physical treatments that are usually applied to activate the Zeolite, performing this step (preconditioning) plays an important role in improving the efficiency.

Preconditioning with acid or heat treatment was not employed as these methods change the structure.  $H^+$  ions can remove impurities such as  $CO_3^{2-}$  from pores, but  $H^+$  can also dealuminate the structure and cause a loss of capacity. Heat treatment can reduce the affinity for  $NH_4^+$  ions [6]. Alkali treatment is not believed to cause any structural changes.

## **2.2. Determination of Ammonia Concentration**

The method adopted for Ammonia determination is classical one and employs a spectral method based on classical Nesslerisation. According to the Nessler's method, specified amount of mineral stabilizer, polyvinyl alcohol and Nessler's reagent was added to each sample and forms a coloured complex with Ammonia. The concentration of Ammonia in the solution was determined by measuring the absorption by spectrophotometer [16].

## **2.3. Isothermal Equilibria Experimental Conditions**

Ion exchange equilibration measurements were carried out by contacting 10g of each size of Zeolites with 100ml of various initial concentration of Ammonia solution in a sealed bottle. Each bottle and glassware were thoroughly cleaned and washed with distilled water. From this section on, all experiments were carried out at  $30^\circ C \pm 1^\circ C$ . time spans required for equilibration were 4 days and 5 days in 1-3 mm and 3-10 mm Zeolite size experiments respectively; nevertheless, in order to reach a perfect equilibrium, the given periods extended from 4 to 6 days and from 5 to 7 days. The containers were sealed and the mixture was shaken by 100 rpm speed. Tests were replicated two times for each size of adsorbent (1-3 and 3-10 mm), using new material for each test.

After The containers were shaken by a 100 rpm-speed shaker, a sample of the solution from each container was analyzed for its Ammonia content. The Clinoptilolite was then contacted with Ammonia solution again. This procedure was repeated until there was no difference between initial and final Ammonia concentrations after shaking, implying that the Zeolite exchange sites were saturated with Ammonium ions.

The solid concentration (mg of  $NH_4^+$  per gram of Clinoptilolite) was calculated from the decrease in liquid concentration and the amount of Clinoptilolite added at the start. It was assumed that all  $NH_4^+$  lost from solution exchanged with  $Na^+$  ions onto Clinoptilolite. Ammonium concentration in fluid phase was analysed by Nesslerization [16]. Results of all equilibria were modelled by fitting either the Langmuir isotherm or the Freundlich isotherm to the experimental data.

## **2.4. Regeneration Process**

In this batch study, a mixture of NaCl (0.5 M) and NaOH (0.1 M) solution with a volume of four times higher than that of saturated Zeolite was applied as a regenerant solution. The shaker's speed was 200 rpm and contact time periods for a complete desorption process were



6 hours and 8 hours for 1-3 mm size and 3-10 mm size, respectively. After regeneration, the Zeolite is subject to washing with pure water to remove loosely bound ions and traces of the regenerant solution. This was done in two steps to remove all the excess Chloride ions and in each step the volume of water was twice the volume of Zeolite and the shaker's speed was set to 150 rpm for a half an hour. The cycle of adsorption-regeneration was conducted in 9 stages in addition to the preconditioned process (stage 0) in order to assess the maximum adsorption capacity.

### 3. Results and discussion

#### 3.1. Effect of Preconditioning Process

It was observed that preconditioning improves the Clinoptilolite adsorption capacity, most likely due to the increase in the number of sites available for ion exchange. Thus, pre-treatment can be recommended in order to achieve optimal Ammonium removal Clinoptilolite Zeolite. Effect of preconditioning on the maximum amount of Ammonia adsorption is shown in figures 3.1 and 3.2 for both Zeolite sizes. 1-3 mm Zeolite had 6.75% of capacity improvement (from 31.1 to 33.2), whereas this percentage was 8.07% for 3-10 mm (from 22.3 to 24.1).

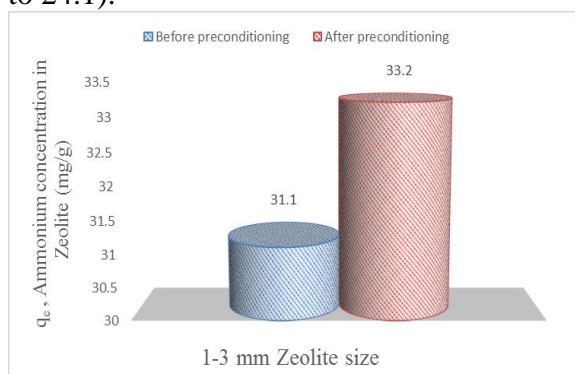


Fig 3.1- Effect of preconditioning on the maximum amount of Ammonia adsorption (1-3mm)

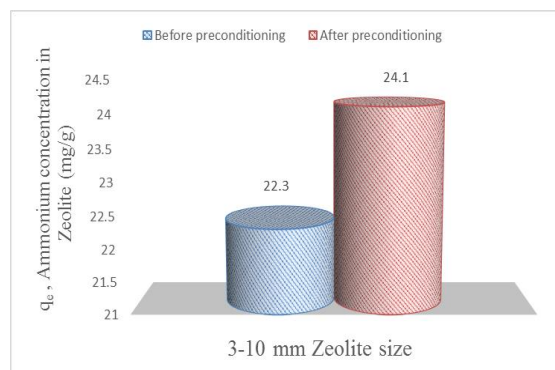


Fig 3.2- Effect of preconditioning on the maximum amount of Ammonia adsorption (3-10 mm)

#### 3.2. Adsorption Isotherm Models

As can be seen in figures 3.3 and 3.4, the Langmuir isotherm provided a very good fit to the experimental data. The Freundlich isotherm provided a very poor fit. The results obtained agree with some of the assumptions made in deriving each of the models. The Langmuir isotherm assumes that there are a fixed number of sites and that each site can only hold one molecule from the solution. Whereas the Freundlich isotherm assumes that there are an infinite number of sites. An ion exchanger only has a fixed number of exchangeable sites and only one ion per site is permissible due to charge balancing. It is therefore no surprise that the Langmuir isotherm model fits the experimental data well.

The maximum uptake, according to the Langmuir isotherm, is 33.92 and 24.36 mg of  $\text{NH}_4^+$  per gram of Clinoptilolite for 1-3 mm size and 3-10 mm size, respectively. Previous studies have found capacities of 32-40mg/g [8], or 31-38.5mg/g [6].

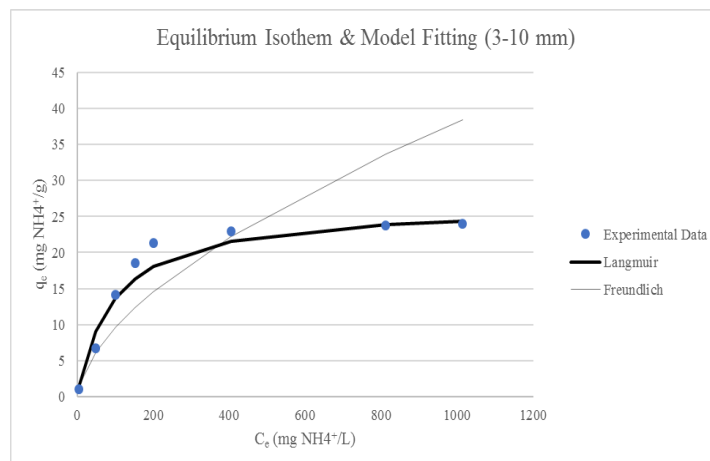
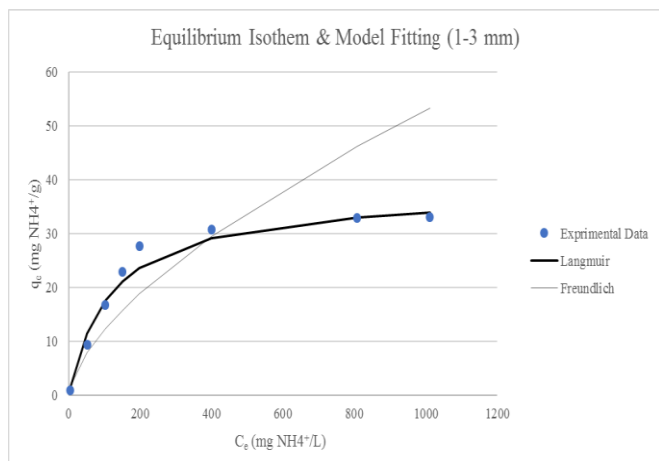


Fig 3.3- Equilibrium Isotherm and Model Fitting (1-3 mm)

Fig 3.4- Equilibrium Isotherm and Model Fitting (3-10 mm)

The equilibrium for the adsorption of Ammonium by natural Zeolite was applied to the Langmuir and Freundlich model for the purpose of providing a simple relationship between the equilibrium Ammonium concentrations in the solution and solid phases. General form of Langmuir and Freundlich equations are shown in table 3.1.

Where  $q_e$  is the equilibrium Ammonium uptake by Zeolite ( $\text{mg NH}_4^+/\text{g Zeolite}$ ) and  $C_e$  is the equilibrium Ammonium concentration in the solution ( $\text{mg NH}_4^+/\text{L}$ ). The empirical constants  $a$ ,  $b$ ,  $x$  and  $y$  for figures 3.3 and 3.4 are given in Table 3.1.

Table 3.1: Langmuir and Freundlich equation constants for both Zeolite sizes

Parameter	Langmuir Equation		Freundlich equation	
	$q_e = a.C_e / (1+b.C_e)$		$q_e = x (C_e)^y$	
	1-3 mm	3-10 mm	1-3 mm	1-3 mm
a	0.3185	0.2798	-	-
b	0.0084	0.0105	-	-
x	-	-	0.6436	0.6029
y	-	-	0.6384	0.6005

### 3.3. Zeolite Regeneration

Chemical regeneration theoretically requires 1 to 1 molar ratio of  $\text{Na}^+$  to  $\text{NH}_4^+$ , but a large concentration of sodium ion is essential to accelerate the regeneration reaction rate. In other words, washing with caustic solutions can only work if the regenerant solution has a concentration of counter ions (generally sodium ions) greater than that of the Ammonia ions being replaced. In most other regeneration situations, a high concentration of regenerating ions is required to displace the ions attached during the service cycle due to the higher affinity for these ions over the regenerant ions. However, in this case  $\text{NH}_4^+$  ions are easily removed because at high pH the displaced  $\text{NH}_4^+$  ions are converted to  $\text{NH}_3$  molecules (according to equation 3.1). The  $\text{NH}_3$  molecules cannot exchange back onto the Zeolite. The disappearance of  $\text{NH}_4^+$  ions from solution favours the equilibrium to drive more  $\text{NH}_4^+$  ions off the ion exchange. Therefore, alkaline regeneration (a mixture of  $\text{NaOH}$  and  $\text{NaCl}$ ) requires a smaller volume of regenerant than  $\text{NaCl}$  only regeneration.



The regenerant solution is usually a mixture of  $\text{NaCl}$  (provides bulk of  $\text{Na}^+$  ions) and  $\text{NaOH}$  (provides high pH). The caustic conditions also sterilise the Clinoptilolite during regeneration.



Under alkaline conditions not only is the equilibrium pushed to completion but the kinetics are much faster due to the disappearance of  $\text{NH}_4^+$  ions.

The first aim of experiments was the regeneration process to remove the adsorbed ions from the Zeolite and the second goal was to observe the efficiency of the regenerated Zeolite in its affinity for  $\text{NH}_4^+$  ion exchange after 9 stages of regeneration.

As shown in Figures 3.5 & 3.6, it can be observed that the capacity of the adsorbent after each regeneration step decrease for both sizes, this phenomenon occurs due to Zeolite aging as well as deactivation of some primary sites for adsorption. However, After 9 stages the decrease (difference between stage 0 and stage 9) was acceptable, with 2.41% for 1-3 mm and 2.9% for 3-10 mm.

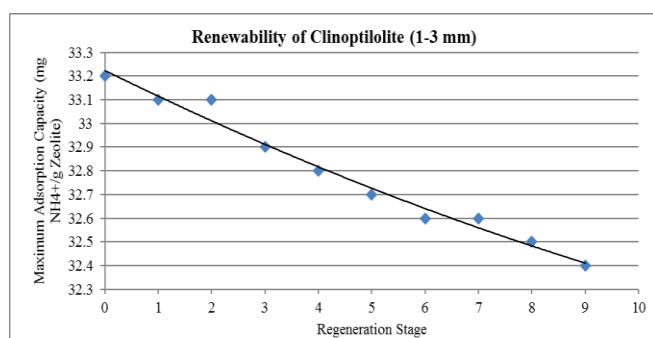


Fig 3.5- Variation of maximum adsorption capacity with regard to regeneration stage

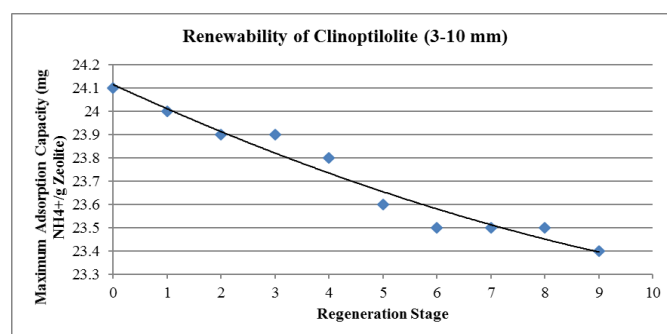


Figure 3.6- Variation of maximum adsorption capacity with regard to regeneration stage

### Conclusions

The Clinoptilolite was successfully employed to treat the wastewater including Ammonia contamination. In this paper, the performance of preconditioning and regeneration processes along with isothermal models on the Clinoptilolite Ion exchange was studied. Based on the results observed, the following conclusions can be made:

- The preconditioning of clinoptilolite with NaCl (1 M) and NaOH (0.1 M) improved the Ammonia exchange capacity of Clinoptilolite by 6.75% and 8.02% for 1-3 mm and 3-10 mm Zeolite size, respectively. Pretreatment affects the kinetics of the ion exchange process. In summary, the capacity of natural Zeolites is influenced significantly by the preconditioning the Zeolite has received. Therefore, preconditioning is necessary in order to achieve higher removal efficiencies in water treatment.
- Langmuir isotherm provided an exact fit to the experimental data compared to the Freundlich isotherm since an ion exchanger only has a fixed number of exchangeable sites and only one ion per site is permissible due to charge balancing.
- Alkaline regeneration (a mixture of NaOH and NaCl) requires a smaller volume of regenerant than NaCl brine only regeneration. As a result, using a small amount of NaOH assists both preconditioning and regeneration process.
- The renewability of exhausted zeolite after repetitive chemical regeneration is critical for engineering zeolite processes for nitrogen removal and recovery from wastewater. In this research the maximum adsorption capacity decreased only by 2.41% for 1-3 mm and 2.9% for 3-10 mm after 9 stages in a row.



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