

# Comparative Evaluation of Natural Zeolites for Ammonium Removal from Aqueous Solutions

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## ABSTRACT

Ammonia nitrogen, present in water as ammonium ( $\text{NH}_4^+$ ) and ammonia ( $\text{NH}_3$ ), is a toxic pollutant that contributes to eutrophication and aquatic life degradation. This study investigates the potential of three natural clinoptilolite zeolites-sourced from Kamloops, BC (Canada), and Preston and Sheaville, ID (USA)-for ammonium removal from aqueous solutions. The zeolites were characterized using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) to confirm their crystalline structure and functional groups. Batch adsorption experiments were conducted at pH 5.4 and 20 °C with initial ammonium concentrations ranging from 2 ppm to 45 ppm. Results showed that all zeolites maintained structural integrity after adsorption and followed the Langmuir isotherm model, indicating monolayer adsorption on uniform sites. The maximum adsorption capacities ( $q_{\text{max}}$ ) were 3.7, 3.4, and 2.8 mg  $\text{NH}_4^+$ /g for Preston, Kamloops, and Sheaville zeolites, respectively. These findings suggest that locally available natural zeolites, particularly those from Preston and Kamloops, are promising, low-cost, and environmentally sustainable adsorbents for the removal of ammonium from low to moderately contaminated waters.

**Keywords:** Ammonium Removal, Natural Zeolite, Adsorption Isotherm, Water Treatment

## Introduction

Ammonia nitrogen, which exists in equilibrium in aqueous solutions as ammonium ( $\text{NH}_4^+$ ) and ammonia ( $\text{NH}_3$ ) is classified as a toxic substance in water bodies under the Canadian Environmental Protection Act (CEPA 1999), Canadian Water Quality Guidelines for the Protection of Aquatic Life and USEPA [1-5]. According to USEPA 1985e ammonia nitrogen is toxic to aquatic organisms in concentrations between 0.5 to 23 mg/L for some invertebrate species and from 0.88 to 4.6 mg/L for fish [5]. This ion is found in surface waters due to discharges from municipal, industrial, and agricultural wastewaters and contributes to eutrophication, causes oxygen depletion, negatively affects fish and invertebrate growth and increases fish mortality [1,2,6-9].

Chemical, physical and biological methods are being used and developed to address the problems caused by ammonia nitrogen in aquatic ecosystems. Some of these technologies include biological nitrification, chemical precipitation, chlorination, and adsorption using activated carbon and clay minerals which

can be expensive and contribute to production of sludge which needs further management. The use of zeolites as an alternative technology is attracting attention due to their ease of operation, safety, low cost and availability [6,10,11].

Zeolites are porous, crystalline aluminosilicates capable of adsorbing cations. Their crystalline structure is made up of repeated units of silica-oxygen tetrahedra, where some of the  $\text{Si}^{4+}$  atoms are replaced by  $\text{Al}^{3+}$  atoms [2,8]. The substitution creates a negative charge within the structure, which can be compensated by the sorption of cations such as ammonium [1,10,11]. This affinity of ionized ammonia for zeolite makes this technology ideal for removing ammonia from surface waters [2,7,11,12].

The adsorption of ammonia by various types of zeolites can be influenced by several parameters. These include the composition of the natural zeolite used, contact time, initial concentration of ammonia, temperature, pH, mass of zeolite used and presence of competitive ions [10,11].

Although the adsorption of ammonia by various types of modified and synthetic zeolites has been studied, there is not

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enough studies for adsorption of ammonia on natural local zeolites. Therefore, this study compares the efficiency of three types of natural zeolite from Kamloops, BC, Canada and Sheaville & Preston, ID, USA in removing ammonia from aqueous solutions. After characterizing the zeolite samples, using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), tests were conducted with various initial ammonia concentrations to determine the maximum adsorption capacity. The result of this study can help expanding the knowledge of using local natural zeolites for the adsorption of ammonium from nearby contaminated waters.

## Materials and Methods

### Zeolite Samples and Chemicals

Three types of natural zeolites were used in this study: one Canadian clinoptilolite (from Kamloops, BC) and two U.S. clinoptilolites (one from Preston, ID and the other from Sheaville, ID).

The zeolites were initially in a coarse granular state and were pulverized to enhance their adsorption by reducing the particle size. This was done in the British Columbia Institute of Technology Mining Laboratory using a grinder and then sieving using mesh sizes 200 and 325. The fraction collected ranged from 44-74  $\mu\text{m}$  in diameter.

A 1000 ppm Hach standard Nitrogen-Ammonia solution ( $\text{NH}_3\text{-H}$ ) purchased from Fisher Scientific, Canada was used as a stock solution to prepare the solutions with different initial concentrations. To adjust pH levels, 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH) purchased from Fisher Scientific, Canada were used.

### Ammonium Analysis

The ammonium concentrations were measured using the Hach® Salicylate Method (Method 10031), which includes the Ammonia Salicylate and Ammonia Cyanurate reagents. The DR 2700 Portable Spectrophotometer was used at 655 nm for all absorbance measurements. It should be noted that before each reading, the solutions were filtrated two times. First, samples were filtered under vacuum using a 5  $\mu\text{m}$  glass fiber filter to remove suspended solids. Then, 1 mL aliquots were further filtered through 0.45  $\mu\text{m}$  syringe filters to avoid turbidity and ensure correct readings using the spectrophotometer.

### Adsorption Experiments

For the adsorption experiments, 0.25 g of each zeolite type was weighed and solutions of initial ammonium concentrations ranging from 2 ppm to 45 ppm were prepared from a stock solution of ammonium (1000 ppm). The zeolite samples were then placed in contact with the prepared ammonium solutions (2 ppm, 10 ppm, 20 ppm, 30 ppm, and 45 ppm) in 50 mL Erlenmeyer flasks. The mixtures were agitated on an orbital shaker (OS-20Pro) at 150 rpm for 20 hours to ensure that equilibrium was reached (preliminary experiments showed that equilibrium can be reached in less than 20 hours). The pH of the samples was adjusted at 5.4 and experiment were performed at room temperature of 20° C. After finishing with the experiments, samples were filtrated and analysed as described above. All experiments were performed in triplicates.

### FTIR Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Cary 630 FTIR Agilent Technologies in a wavenumber region from 400 to 4000  $\text{cm}^{-1}$  to characterize functional groups, chemical bonds, and cation ( $\text{Si}^{+4}$  by  $\text{Al}^{+3}$ ) of three clinoptilolite zeolite samples before and after the ammonium adsorption [1].

### X-Ray Diffraction Characterization

The XRD characterization was conducted using a Bruker (D8 Advance) diffractometer with  $\text{CuK}\alpha$  radiation.

X-ray diffraction was employed to characterize and analyse the crystalline structure of three natural zeolites samples. The diffraction data were compared with the International Zeolite Association-Structure Commission (IZA-SC) database to identify crystalline phases in the samples [2]. The measurements were performed at values of  $2\theta$  angles from 5° to 90°.

## Results and Discussion

### Characterization of Zeolites

The FTIR spectrum of three zeolite samples before the ammonium adsorption experiment is shown in Figure 1.

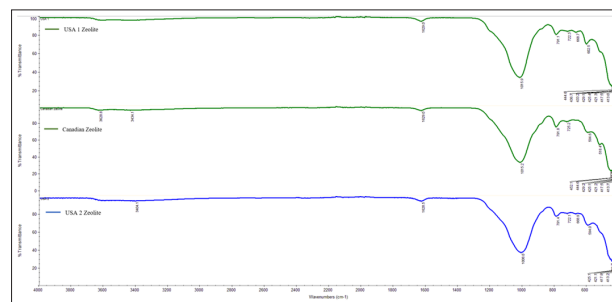


**Figure 1:** FTIR spectrum in a wavenumber region from 400 to 4000  $\text{cm}^{-1}$  of three different zeolites before ammonium adsorption (USA1: Preston, ID, USA2: Sheaville, ID, Canada: Kamloops, BC)

FTIR results demonstrate that the three samples have a similar structure characteristic of a clinoptilolite zeolite type [6]. The band from 3700 to 3500  $\text{cm}^{-1}$  is attributed to the water absorbed by the zeolite. Specifically, these peaks result from the vibration of OH- groups of the water and Si-OH-Al bridges [8]. The band in 1620  $\text{cm}^{-1}$  is attributed to water molecules bound to Na and Ca cations in the channels in the zeolite structure [10].

An intensive peak is observed at 1010  $\text{cm}^{-1}$ , corresponding to the stretching vibration of the main crystalline structure tetrahedral (TO4) of ammonium-silicate, where T represents Si and Al, and the position of this band depends on the Al/Si ratio and indicates the number of Al per unit [1]. The bands of 790 and 460  $\text{cm}^{-1}$  are attributed to the stretching vibration of O-T-O groups and bending tensions of the T-O bond [1].

Figure 2 shows the FTIR spectra of the three clinoptilolite zeolites after exposure to 45 ppm of ammonium for 24 hours at 150 rpm. The FTIR spectra for the three zeolites remain almost the same after the ammonium absorption experiment; however, a new small vibration band appears at around 1400  $\text{cm}^{-1}$ . This band is attributed to the stretching vibration of the ammonium ion exchanged [7,12]. This indicates that the zeolite structure

absorbed the ammonium without any changes in the framework bands, suggesting that the zeolite structure remains intact during ammonium absorption.

The XDR patterns for the Canadian, Preston, and Sheaville, zeolites showed that the range from 5° to 40° was the most relevant due to several intense peaks' characteristic of clinoptilolite natural zeolite [11].

Figure 3 shows the XDR diffractogram comparing the theoretical XDR patterns of a clinoptilolite zeolite and the Canadian zeolite. The most intense peaks in the range of 2θ angle were observed at 9.85°, 11.15°, 17.31°, 22.38°, 25.03°, 28.02°, 30.07°, 31.98°. According to Zendelska and coworkers, an intense peak at an angle of 22° represents clinoptilolite zeolite, confirming that the sample primarily consists of this crystalline phase [4]. However, minor additional peaks were observed at 20.86°, 26.02°, and 37°, which may indicate the presence of trace secondary minerals such as quartz, which is common in natural zeolite deposits [11].

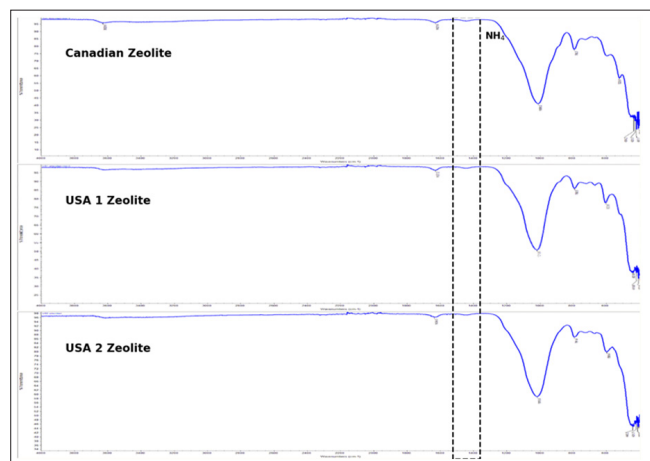


**Figure 2:** FTIR spectrum in a wavenumber region from 400 to 4000 cm<sup>-1</sup> of three different zeolites after the ammonium adsorption (USA1: Preston, ID, USA2: Sheaville, ID, Canada: Kamloops, BC)

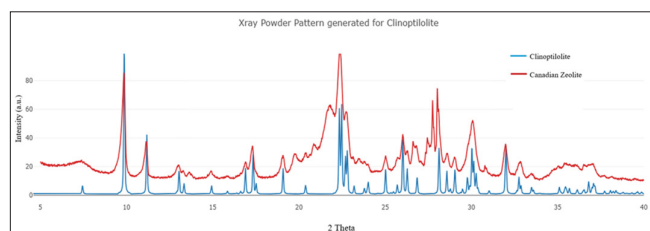


**Figure 3:** Comparison of real and experimental XRD Patterns for Clinoptilolite zeolite

As seen in Figure 4, the X-ray diffraction analysis for the USA zeolites revealed similar diffraction patterns, indicating that all samples share the same crystalline phase (Clinoptilolite). These results showed differences in peak intensities and a slight shift in peak position in all zeolites. For the Preston, ID zeolite, the most intense peaks were observed at 9.81°, 11.13°, 17.26°, 22.36°, 25.01°, 28.13°, 30.06°, 31.95°, while for Sheaville, ID zeolite the most intense peaks were 9.82°, 11.12°, 17.26°, 22.35°, 25.01°, 28.09°, 30.02°, 31.95°, as well as some peaks that represent secondary minerals such as quartz.

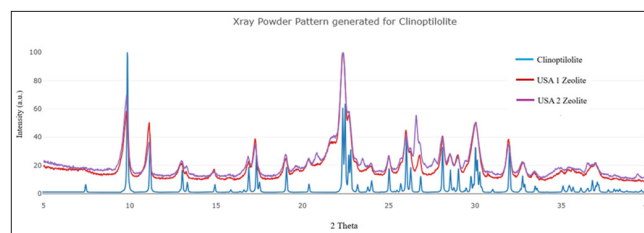


**Figure 4:** X-ray diffractogram for real clinoptilolite of Preston and Sheaville, ID zeolites. (USA1: Preston, ID, USA2: Sheaville, ID)

It was observed that the Preston, ID and Sheaville, ID zeolites exhibit more similarities in 2θ angle values when compared with Canadian zeolite; this is noticed in Figures 3 and 4, where the representative peaks at 22° show slight differences. This variation can be attributed to their differing origins and degrees of crystallinity, which, according to Pabalan and Bertetti the crystallinity and mineral impurities, can affect ion-exchange capacity [13].

Additionally, both diffractograms showed intensive reflexes of the tetrahedral crystal structure [11]. This structure presents a 3-dimensional aluminosilicate framework, which results in micropores, and channels system typically occupied by water molecules and exchangeable cations [9,3,4].

### Adsorption Isotherm

The adsorption isotherm refers to the relationship between the amount of an adsorbate (the substance being adsorbed) and the concentration of that adsorbate at a constant temperature when equilibrium is reached [14]. In this experiment, the temperature used was room temperature (20±2°C) and the initial pH of the solutions were adjusted at 5.4. Models such as Langmuir and Freundlich are used to evaluate the equilibrium behaviour of ammonium onto different zeolite samples as well as estimating parameters such as maximum adsorption capacity and adsorption intensity.

The Langmuir adsorption model is the simplest theoretical model for monolayer adsorption [15]. The Langmuir model is written as in (EQ.1).

$$\frac{1}{qe} = \frac{1}{K_L \times q_{max}} \times \frac{1}{C_e} + \frac{1}{q_{max}} \quad (1)$$

Where  $q_e$  is the adsorption capacity in mg/g,  $C_e$  is the equilibrium concentration of adsorbate in the liquid in mg/L,  $q_{max}$  is the maximum monolayer adsorption capacity of the adsorbent in mg/g and  $K_L$  is the Langmuir constant related to the affinity of the binding sites as higher values mean stronger binding [16]. For three types of natural zeolite Langmuir adsorption parameters are calculated and presented in Table1.

Freundlich model displays a semi-empirical equation, which assumes that the adsorption process occurs on a heterogeneous surface, and the adsorbents adsorption amount increases with the increase of adsorbate's concentration [16,17]. The linear form of Freundlich model is written as in (EQ. 2)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

**Table 1: Langmuir Parameters Calculated for each Zeolite**

| Zeolite       | $q_{\max}$ | $K_L$ | $R^2$  |
|---------------|------------|-------|--------|
| Kamloops, BC  | 3.4        | 1.620 | 0.9567 |
| Preston, ID   | 3.7        | 9.659 | 0.9923 |
| Sheaville, ID | 2.8        | 1.209 | 0.9851 |

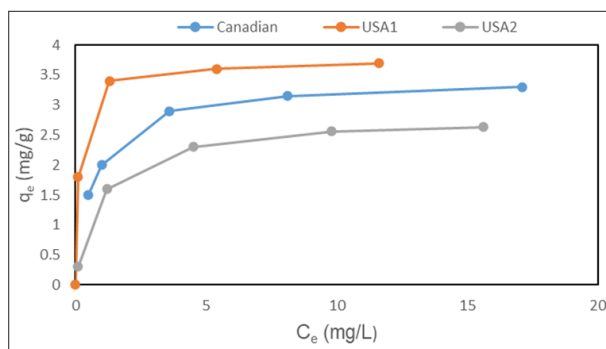
Where  $n$  is the Freundlich constant indicative of the intensity of the adsorption and  $K_F$  is Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g). For these experiments the Freundlich isotherm parameters are calculated and presented in Table 2.

**Table 2: Freundlich Parameters Calculated for each Zeolite**

| Zeolite      | $n$ | $K_F$ | $R^2$  |
|--------------|-----|-------|--------|
| Kamloops, BC | 6.7 | 1.080 | 0.9308 |
| Preston, ID  | 4.4 | 2.649 | 0.9260 |

**Table 3: Ammonium Adsorption Capacity of Natural Zeolites (Converted to mg  $\text{NH}_4^+$  / g)**

| Zeolite Type / Origin                    | Experimental Conditions (summary)                                                                                | Reported Value (original unit)                          | Converted Capacity (mg $\text{NH}_4^+$ / g) | References |
|------------------------------------------|------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|---------------------------------------------|------------|
| Clinoptilolite (Polish natural zeolite)  | Batch adsorption of real sludge water at 295 K and 307 K; particle size 0.6–1.0 mm; pH $\approx$ 7.5             | 15.3 – 16.1 mg $\text{NH}_4^+$ / g (already reported)   | 15.3 – 16.1                                 | 18         |
| Clinoptilolite (Iranian natural zeolite) | Continuous fixed-bed column, 23 °C; influent $\text{NH}_4^+ \approx$ 50 mg $\text{L}^{-1}$ ; $\text{Na}^+$ -form | $\sim$ 15.16 mg $\text{NH}_4^+$ / g (reported directly) | 15.16                                       | 19         |
| Clinoptilolite (Swedish natural zeolite) | Batch test, synthetic wastewater, pH 7.0; initial $\text{NH}_4^+ =$ 10–500 mg $\text{L}^{-1}$                    | 2.7 mg $\text{NH}_4\text{-N}$ / g                       | $\approx$ 3.48                              | 20         |

**Figure 5:** Equilibrium isotherm for ammonium adsorption onto natural zeolites (USA1: Preston, ID, USA2: Sheaville, ID, Canada: Kamloops, BC)

## Conclusion

This study evaluated the ammonium adsorption capacity of three natural clinoptilolite zeolites originating from Kamloops, BC (Canada), Preston, ID, and Sheaville, ID (USA). The XRD and FTIR analyses confirmed that all three samples predominantly consisted of the clinoptilolite phase, with minor variations in crystallinity and the presence of secondary minerals such as quartz. FTIR spectra before and after adsorption showed that the zeolite frameworks remained structurally stable, indicating that ammonium ion exchange did not alter their crystalline integrity.

Adsorption isotherm experiments demonstrated that the ammonium uptake by all zeolites followed the Langmuir model,

|               |     |       |        |
|---------------|-----|-------|--------|
| Sheaville, ID | 2.3 | 1.171 | 0.9857 |
|---------------|-----|-------|--------|

As the adsorption isotherms follows the Langmuir model, it is plotted in Figure 5. For the Langmuir model, the Preston, ID zeolite exhibited the highest theoretical maximum adsorption capacity ( $q_{\max}=3.7\text{ mg/g}$ ) and the strongest binding affinity ( $K_L=9.659\text{ L/mg}$ ), and the maximum  $R^2$  value (0.9923). Sheaville, ID zeolite has the lowest maximum theoretical adsorption capacity as 2.8 mg/g and the Canadian zeolite maximum theoretical adsorption capacity is in between as 3.4 mg/g. In general, all three types of natural zeolite can be used for the purpose of removal of ammonium from low to moderately contaminated waters, although more experiments in terms of the effect of pH, presence of competing ions and temperature should be performed [18-20]. To compare, the ammonium adsorption capacity of some other natural zeolites in similar studies are brought in Table 3.

suggesting a monolayer adsorption process on homogeneous surfaces. Among the samples, the Preston, ID zeolite exhibited the highest maximum adsorption capacity (3.7 mg  $\text{NH}_4^+$ /g) and the strongest binding affinity ( $K_L = 9.659\text{ L/mg}$ ), followed by the Kamloops, BC (3.4 mg  $\text{NH}_4^+$ /g) and Sheaville, ID (2.8 mg  $\text{NH}_4^+$ /g) zeolites. Although these capacities are lower than those reported for certain modified or synthetic zeolites, the natural samples used in this study still demonstrated effective ammonium removal under mild experimental conditions (pH 5.4, 20 °C).

The results confirm that locally available natural zeolites—particularly the Preston, ID and Kamloops, BC types can be considered low-cost, sustainable adsorbents for ammonium removal from low to moderately contaminated waters. Future work should focus on evaluating the influence of pH, temperature, competitive ions, and regeneration potential to optimize their performance for practical wastewater treatment applications.

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