# REMOVAL OF AMMONIUM IONS FROM WASTEWATER BY MODIFIED ZEOLITE AND USE AS SLOW AMMONIUM RELEASING FERTILIZER

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Abstract: Ammonia (NH<sub>3</sub>) is the most abundant nitrogen component in the liquid phase and that can exist either in unionized form (NH<sub>3</sub>) or ionized form (NH4<sup>+</sup>). If Ammonia is not properly removed, the ionized form can cause adverse effects on the environment such as eutrophication, reduction of dissolved oxygen, and acidification. Therefore, the removal of ammonium ions by using environment-friendly adsorbent materials and the employment of such composites as slow-releasing Nitrogen-rich fertilizers would open a new avenue in the field. The major objectives of this research were to investigate the effect of the pH of the solution, optimum dosage of zeolite, and initial concentrations of ammonium ions on ammonium removal using modified zeolite and use that as slow ammonium-releasing fertilizer. The XRD and FTIR analysis of the used zeolite sample revealed that the main zeolite type was Na-Zeolite. First, Na-Zeolite was modified by the acid impregnation method. The Sorption experiments of NH4+ were conducted as a function of the solution pH, dosage of adsorbent, and initial concentration of ammonium ions. All these factors affected the ammonium ion removal from an aqueous solution. Equilibrium modeling data were well-fitted to linear Langmuir and Freundlich models. Adsorption was optimum around pH 6 - 8, and the optimum dosage of zeolite was 20 g/L. Under the optimum conditions, the Ammonium removal efficiency of the modified zeolite was found to be 82.5 %. Modified Zeolite has significant potential for removing ammonium ions from aqueous solutions and is used as slow ammonium-releasing fertilizer.

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## 1. Introduction

The hydrosphere contains surface water, groundwater, as well as atmospheric water. It is about 70% of the earth, covered by water, and more than 97 % of all water is found in the oceans and seas. Even though there is a tremendous amount of water, fresh water is a resource that is in short supply. Less than 0.3% of the water is suitable for human consumption, and only 2.5% of it is found in lakes and rivers. Water Pollution can occur when harmful substances (chemicals or microorganisms) contaminate а stream, lake, river, ocean, aquifer, or other bodies of water. Water quality can be degraded and becomes toxic to humans and the environment.

Ammonia (NH<sub>3</sub>) is the most abundant nitrogen component in the liquid phase and can exist either in unionized form (NH<sub>3</sub>) or ionized form (NH<sub>4</sub><sup>+</sup>). Total ammonia nitrogen (TAN) is the sum of the two types of ammonia. The nitrogen-containing nutrient ammonia recommended is for plant development. Bacteria can transform ammonia into nitrite (NO2-) and nitrate (NO<sub>3</sub>-), later used by plants (USEPA, 2013). The more abundant form of ammonia in an aqueous medium is the ionized form (NH4+) and the less abundant form is the unionized form (NH<sub>3</sub>) of ammonia. The ratio of these species in an aqueous solution mainly depends upon the temperature and pH. In comparison to the ionized form, the unionized form (NH<sub>3</sub>) is more poisonous(USEPA, 2013).

The ionized form of ammonia can harm the environment if it is not effectively removed from the environment, such as eutrophication of aquatic ecosystems, oxygen depletion in aquatic ecosystems, toxicity aquatic life, to and contamination of groundwater by nitrate and its effect on public health. According to the World Health Organization (WHO), 2003. the average naturally occurring ammonia level in groundwater is less than 0.2 In strata with high ppm. concentrations of humus compounds, iron, or forests, higher natural levels (up to 3 mg/L) can be detected. The maximum concentration of ammonia in the surface water is 12 mg/L. Ammonia can be detrimental to some fish and other aquatic life when it is present in water at concentrations below 1 mg/L (ppm). According to the World Health Organization (WHO), 2003, long-term use of water with an ammonia content of more than 1 ppm may be damaging to internal organ systems, even if higher species like humans are less sensitive to ammonia in water. Zeolites are crystalline hvdrated alumosilicates with framework structure and a system of pores, cavities, and channels in their crystal lattice(Beebe et al., 2013). The aluminosilicate structure, which is negatively charged, attracts positive ions to balance that charge (Lebedynets et al., 2004). The structure of zeolites allows mobile cations of alkali and alkaline earth metals to be readily removed and absorbed. In Zeolites it mainly removes ammonia by ion exchange and adsorption.

Nitrogen is vital а macronutrient for plants and is a component of amino acids, which are used by plants as the building blocks for proteins and enzymes (Anas et al., 2020). Between 40–70% of the nitrogen in applied fertilizers is not absorbed plants bv and is lost to the environment by leaching, denitrification, and volatilization(Eghbali Babadi et al., 2021). zeolite has recently received a lot of attention and is now being used to deliver fertilizer to plants at a slow rate after some structural modifications (Lateef et al., 2016).

The main objective of this work is to study the effect of pH, temperature, and initial concentrations of ammonium ions on ammonium adsorption using modified zeolite and study the slow ammonium-releasing property of the ammonium-loaded zeolite.

### 2. Materials and methods

First, the Zeolite was treated with 1M ammonium chloride solution at 80 °C for 2 hours. Note that the zeolite to ammonium chloride solution will be 1 g: 100 mL. Then the residue was filtered and washed with distilled water. Then the sample was dried at a temperature of 120 °C for 4 hours. Then the above cycle will be repeated three times to get a complete exchange of sodium. As the final step, the samples will be heated at 550 °C for 5 hours to decompose to H-type zeolite (Liu et al., 2016).

#### Materials

Ammonium chloride (NH<sub>4</sub>Cl; minimum assay- 99.8%,), Hydrochloric acid (HCl; assay-36%), Sodium Hydroxide (NaOH; assay- 98-100.5%), Na A Zeolite,

### 3. Results and Discussion

#### 3.1. Characterization

#### 3.1.1. Characterization of Na-Zeolite



**Figure 3.1:** FT-IR spectrum of commercial Na-Zeolite

Characterization was performed by FT-IR in the wavelength ranging from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Figure (3.1) shows the FT-IR spectra of Na-Zeolite. Bands around 461 cm<sup>-1</sup> which is an attribute to Si-O, and Al-O bonds. The band at 548 cm-1 is known to be assignable to Ti-O species. The band at 670 corresponds cm-1 to the symmetrical stretching vibration of the Si-O-H. The band at 1242 cm<sup>-1</sup> Could be attributed to the external vibrations between SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra of Zeolite. The band at 970 cm<sup>-1</sup> could be attributed to the Si-O-Na bond.

### 3.1.2. Characterization of NH4<sup>+</sup> Adsorbed Zeolite



**Figure 3.2:** FT-IR spectrum of Ammonia adsorbed Zeolite

Characterization was performed by FT-IR in the wavelength ranging from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. Figure (3.2) shows the band at 647  $cm^{-1}$ corresponds to the stretching vibration of the Si-O-Al bond bridges. The bands at 973 cm<sup>-1</sup> are attributed to the asymmetric and symmetric stretching vibration of the zeolite framework. The band at 1440 cm<sup>-1</sup> Could be attributed to the NH4+ functional group and that confirms the adsorption of ammonium ions onto zeolite. A band at 1640 cm<sup>-1</sup> is attributed to the typical deformation band of adsorbed H<sub>2</sub>O. The bands at 3310 cm<sup>-1</sup> assigned to the stretching of H bridges are attributed to the interaction that occurs in the zeolite cavities by physically adsorbed water by the solid and surface oxygen.

#### 3.2. Optimization of Zeolite dosage



**Figure 3.3:** Graph of the effect of the Zeolite dosage on adsorption efficiency

The initial loading ammonium concentration was 100 ppm at pH 7 at room temperature. According to the graph shown in figure (3.3), the increase in the adsorbent dosage noticeable increase causes a in adsorption efficiency. The Ammonium adsorption is increasing from 57.9 % to 77.3 % with the dosage of Modified Zeolite increasing from 5.0 g/L to 20.0g/L. According to the obtained results, the optimum Modified Zeolite dosage was 20 g/L.

# 3.3. Initial Ammonium ion concentration



**Figure 3.4:** Graph of the effect of initial ammonium ion concentration on the adsorption efficiency of modified zeolite.

Figure (3.4) shows the effect of initial ammonium ion concentration on the ammonium adsorption efficiency of modified zeolite. According to the obtained results, the ammonium adsorption efficiency of the Zeolite has increased from 63.7 % to 78.77 % with the initial ammonium concentration from 50 ppm to 100 ppm. The highest ammonium adsorption efficiency was observed at 100 ppm of initial ammonium concentration.

#### 3.4. Optimum pH



**Figure 3.5:** Graph of the effect of pH of the solution for adsorption efficiency

Figure (3.5) shows the change in the ammonium ion adsorption efficiency of Zeolite at pH values of 5 - 9. Optimum ammonium adsorption efficiency is obtained when operating at a pH value of 6. pH has an obvious impact on ammonia adsorption by Zeolite. Since it can influence both the character of exchanging ions and the character of zeolite itself. At lower pH, the ammonium ions have to compete with hydrogen ions among the ion exchange sites in the zeolite structure. At lower pH, the ion exchange sites bear a negative charge that attracts the positive charge ions like NH4+ and H+ ions. At low pH, H<sup>+</sup> ion concentration

is high hence the ammonium adsorption efficiency is low. At pH 6 and 7 the highest ammonium removal occurred.

#### 3.5. Adsorption Isotherms

The Ammonium ion exchange isotherms characterize the equilibrium of the ions and material solid phase with the concentration of the ion in solution. The ion exchange of the modified zeolite and the ammonium ion was analyzed using Langmuir and Freundlich linear isotherm model



**Figure 3.6:** Graph of Langmuir adsorption isotherm for ammonium adsorption from modified Zeolite

Figure (3.6) shows the graph of Langmuir adsorption isotherm for ammonium adsorption from the modified zeolite. The Langmuir isotherm model can be described as,

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \dots (1)$$

Another linear form can be obtained by dividing the above equation by  $c_e$ ;

$$\frac{1}{q_e} = \frac{1}{q_m c_e k_L} + \frac{1}{q_m} \dots (2)$$

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Where  $q_e$  is the equilibrium amount of NH<sub>4</sub><sup>+</sup> exchanged by modified zeolite (mg/g),  $c_e$  is the equilibrium NH<sub>4</sub><sup>+</sup> concentration in the solution (mg/L),  $q_m$  (mg/g) is the maximum uptake of ammonia exchanged and  $k_L$  is the Langmuir constant (L/mg).  $q_m$  and K<sub>L</sub> constants were calculated from the slope and intercept of the plot of/versus $c_e$ , respectively.

According to the obtained results, the data were fitted with Langmuir isotherm with a correlation coefficient value of  $R^2 = 0.9758$ . this mainly indicates that the surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent, Adsorbed molecules do not interact, all adsorption occurs through the same mechanism, and At the maximum adsorption, only a monolayer is formed(Taddeo et al., 2017).

# 3.6. Desorption of ammonium ions from zeolite



**Figure 3.7:** Graph of Ammonium released in distilled water from ammonium-adsorbed Zeolite

Figure (3.7) shows the desorption of ammonium ions from the ammonium-loaded zeolite. Adsorbed and

desorbed amount of Ammonium onto zeolite was calculated by;

$$q_t = \frac{(C_0 V_0 - C_t V_t)}{m} \dots (3)$$

Where it is the total amount of adsorbed NH4 <sup>+</sup> ions per unit weight of zeolite at time t (mg/g),  $C_0$  is the initial concentration of NH<sub>4</sub><sup>+</sup> in solution (mg/L),  $C_t$  is the concentration of NH<sub>4</sub><sup>+</sup> in solution (mg/L) at time t,  $V_0$  is the initial volume of treated NH<sub>4</sub>Cl solution,  $V_t$  is the volume of the solution at time t and m is the adsorbent mass (g).

Initially, 98.4 mg of ammonia was loaded onto the 5.0 g of zeolite. After eight consecutive days, the solution contained only 6.5 mg of ammonia. The desorption percentage was 6.6 %.

According to the published work, in slow releasing fertilizers, there should follow several requirements. Less than 15% of the nutrient should be released in the first 24 hours, less than 75 % of the nutrient should be released in 28 days, and at least 75 % of the nutrient should be released by 40 to 365 days(Trenkel, 2013). According to the observed results, the first requirement has been fulfilled.



**Figure 3.8:** Graph of first order releasing kinetic model for ammonium releasing from zeolite

Figure (3.8) shows the first order releasing kinetic model for ammonium releasing from the ammonium-loaded zeolite. The release of the Ammonium which followed first order kinetics can be expressed by the equation;

 $log C = log C_0 - kt / 2.303 \dots (4)$ 

Where  $C_0$  is the initial concentration of nutrient, k is the first order rate constant, and t is the time. The data obtained are plotted as a log cumulative percentage of nutrients remaining vs time which would yield a straight line with a slope of - K/2.303(Sciences, 2010).

According to the graph, the obtained data was well fitted with the first order releasing kinetic model. The k constant was 0.00031 min<sup>-1</sup>. This kinetic model occurs when a constant proportion of the nutrient is released per unit of time. The rate of the release is directly proportional to the amount of nutrients in the adsorbent. The higher the concentration, the greater the nutrient release per unit period.

## 4. Conclusion

All adsorption parameters such as pH, initial ammonium ion concentration, and contact time affect the removal of ammonium ions from Zeolite. The optimum dose of Zeolite for the removal of ammonium ions was 20 g/L. pH was an important parameter in the removal capacity of Zeolite. The optimum pH value for the removal of ammonium ions was pH 6 and removal efficiency was up to 82.5 %. Kinetic data fitted well with the pseudo first order model in the first 50 minutes and the pseudo second order model was fitted for the entire adsorption. Langmuir isotherm is the best-fit isotherm model for Zeolite and that can be confirmed that monolayer adsorption is taking place with ion exchange. The Linearized Thomas model was well fitted with the data obtained from the column experiment that had a 5 cm height of adsorbent.

According to the observed data, modified zeolite is a promising material to remove ammonium ions from wastewater and it can be used as a slow ammonium-releasing fertilizer.

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