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Efficient Ammonium Ion Removal from the State Company of Fertilizers Wastewater through Nano Zeolite Treatment

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Abstract

One of the most significant environmental problems of the day is ammonium ion pollution of wastewater, especially from sources that produce chemical fertilizers. Higher ammonia concentrations in lakes and rivers increase eutrophication, lower dissolved oxygen levels, and ultimately cause the aquatic ecosystem to collapse. The adsorption method using one of the best adsorbent materials is one of the methods that can be used to remove ammonium ions from water with excellent results. This study aims to use adsorption technology with nano zeolite (NZ) to treat ammonium ion-contaminated water and simulate water release from the State Company of Fertilizers. The best conditions were discovered to be (2.5 g) adsorbent dose, (240 min) shaking duration, (100 ppm) starting ammonium ion concentration at pH 8.0, and constant temp. 25ºC for the efficient adsorption of NH_4^+ ammonium ions and effective removal onto NZ. The result shows that the parameters have great influence on the ammonium removal using the NZ if the removal rate reaches 98% and the maximum ammonium adsorption capacity (qe) obtained is 11.5 mg/g. The Freundlich model best describes the adsorption isotherms with a higher coefficient of determination (R^2=0.97) than the Langmuir model with a coefficient of determination (R^2=0.80). The results imply that the NZ is an efficient adsorbent for ammonium ion removal.

1. Introduction

Certainly, nitrogen compounds are one of the most important components for the survival of all living things. The existence of too many nitrogen compounds harms the ecosystem, results in toxic symptoms, and endangers the lives of sea creatures, especially fish. Monitoring its use of environmental resources is essential and crucial to maintaining public health. It is believed that nitrogen compounds (ammonia, ammonium ions.) pollute groundwater and often wastewater [1].

One of the causes of pollution with nitrogen compounds is the production of chemical fertilizers, as waste is generated during this process and drained into water sources. One of these sources is the state Company of Fertilizers, which releases untreated liquid pollutants that harm the river and aquatic life. Some remain dissolved, while others disappear due to decomposition, evaporation, transformation into another less toxic compound, deposition in the deep sea, etc. The most harmful effect is associated with the compounds that remain soluble in water, the ammonium ion (NH_4^+), a very dangerous pollutant for aquatic life because it is a nutrient for algae and others. Ammonium ion (NH_4^+) is one of the most prevalent types of reactive nitrogen in wastewater, and because of its extreme toxicity, its contamination in fish results in serious health issues [2]. The physicochemical and biochemical treatment procedures are the foundation of the technologies used to remove ammonia from wastewater, Such as biological processes, electro-oxidation, air stripping, chemical precipitation, adsorption, and ion exchange, as shown in Figure (1). Among these treatment methods, adsorption for removing ammonium ions is now acknowledged as a reliable and affordable technique [3]. A significant area of research is the search for inexpensive and accessible adsorbents to remove ammonium ions. Zeolites, typically considered low-cost materials, can effectively adsorb ammonium in wastewater. Several studies have reported on the adsorption of ammonium ions by natural or synthetic zeolitic material adsorbents. Zeolite-aluminosilicate hydrate minerals with a porous. Zeolites are hydrated, microcrystalline aluminosilicates, the structure of which contains channels and cavities of molecular dimensions (diameter 0.3-1.5 nm). Zeolites are present in our daily lives and are widely used as absorbents, ion exchangers in detergents, or catalysts in industrial processes, which are as diverse as oil refining or petrochemicals, chemicals, and fine chemicals [4, 5]. The three-dimensional crystalline structure of zeolites is considered an excellent material for ion exchange because of its high selectivity for NH_4^+ due to its microscopic structure. Natural zeolite has a polar surface, which can quickly and effectively attract ammonium ions. With a maximum adsorption capacity (mg/g) of about (13.73 mg/g), ammonia was removed from water using natural and synthetic zeolite [6].

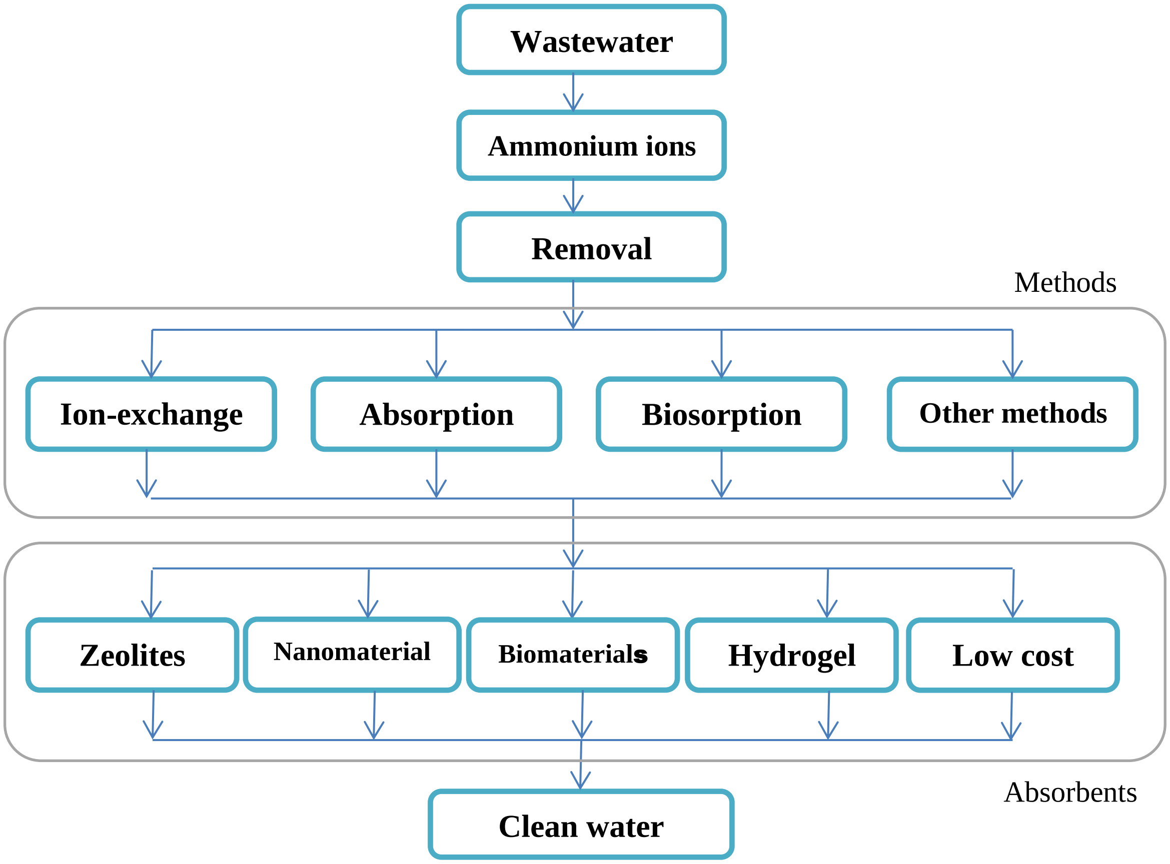

Figure (1): Flowchart of ammonium ions removal from wastewater [3].

This investigation explores the application of NZ (Sapo-11nano zeolite powder4A) for removing ammonium ions from simulated water, specifically targeting the wastewater generated by the state Company of Fertilizers in Basra. The ammonium ion concentration in the company's effluent is approximately 271 parts per million, surpassing the permissible limit set by the River Protection and Maintenance Law No. 25 of 1967 in Iraq, which is 1 ppm for industrial water. Batch adsorption studies and adsorption isotherm analysis are conducted to assess NZ's efficacy, leveraging its regular micro-pore structure and extensive surface area, which typically result in enhanced adsorption capacity.

2. Materials and Method

2.1. Materials

NZ(Sapo-11nano zeolite powder4A) samples used in this study were taken from commercial sources with the chemical composition (SiO_2 content 6%, Al_2O_3 content 48%, NaO content $\geq 0.2\%$) with Pro Volume $\geq 0.16 cm^3$, specific surface area (SSA=$<180 m^2/g$) and Particle Size$\leq$100nm, and it can be reused after generation. The other chemicals used in the experiments in this study had a high degree of purity and were from commercial sources as a guaranteed grade, and they were used as received without further treatment

2.2. Method

2.2.1. Reagent Preparation

Chemical reactions are used in the Nessler method to determine the quality of ammonia and an ammonium compound. Mixing 2g of potassium iodide with 5 mL of water to form Nessler's Reagent. To make a 20ml solution, mix this mixture with 3g of mercury (II) iodide. The last 40g of potassium hydroxide (30%) is added to make the base alkaline [7].

2.3. Experimental Work

2.3.1. Batch Adsorption Experiments

Batch mode adsorption studies for NH_4^+ have been carried out to investigate the effect of different parameters, such as adsorbent dosage (2.5) g, initial NH_4^+ concentration (100) ppm, and contact time (4) hours. The stock solution of NH_4^+ (1000) ppm was prepared by dissolving appropriate amounts of anhydrous NH_4Cl in deionized water as simulated water waste. Batch adsorption experiments were performed. Five conical flasks of 100mL containing 50 ml of ammonium ion solution (100) ppm and different weights (0.5, 0.75, 1.5, 2, 2.5) g of NZ (adsorbent) at pH 8 and temperature 25° C, shaking at a speed of 300 rpm at different periods, at the end of the experiment; the remaining adsorbent was removed from the suspension by centrifuging at 8000 rpm for 30 min. The solutions containing NH_4^+ were filtered, and the concentration of NH_4^+ was determined using the Nessler method, the most common spectrophotometric method, to measure the concentration of NH_4^+. The removal efficiency (R %) was calculated using the following equation (1), and the amount of adsorbed per mass of adsorbent was by equation (2).

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (1)$$

$$q = \frac{x}{m} = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

Where R% removal percent, C_o and C_e intial and equilibrium concentration mg/l, V sample volume L and m mass of NZ g.

2.3.2. Equilibrium Isotherm Experiment (NZ Dosage Experiments)

In this experiment was taken five conical flasks were taken with 50 ml of NH_4^+ solution at a concentration of 100 mg/l prepared from the stock solution of NH_4^+ (1000) ppm at (pH = 8) and room temperature (25° C). Contacting with different adsorbent dosages NZ (0.5, 0.75, 1.5, 2, 2.5) g and agitated in the shaker at speed 300 rpm for 4 hours as shown in Figure (2), then left to settle for 24 hours, filtered after removed from suspension by centrifuging. The remaining ammonium ion concentration is measured using a spectrophotometer.

Figure (2): The adsorbent and the adsorbate during the batch adsorption analysis in the shaker.

2.3.3. Initial Concentration Experiments

In this experiment, prepared different initial concentrations of NH_4^+ solution (20, 50, 100, 200, and 300) ppm from the stock solution of ammonium chloride as NH_4^+ (1000) ppm ; other variables were kept constant (pH=8, Temp =25 ± 5^o C). Depending on the previous experiment's results, 2.5g of NZ was added and shaken at 300 rpm for (4) hours. Removed from suspension by centrifuging, filtering the sample, and preparing this sample for measurement.

2.3.4. Kinetic Experiments (Contact Time Experiments)

Experiments were conducted to study the effectiveness of contact time in the material's adsorption on the New Zealand surface. Five samples of ammonium solution (50 ml) were taken at a concentration of (100) ppm. They were brought into contact with (2.5 g) of adsorbent (nano zeolite type 4A) at a pH of 8 and a temperature of 25°C and shaken at a speed of 300 rpm, with different periods (15, 30, 60, 90, 120, and 240) minutes. Samples were analyzed to determine the amount of adsorbent (qt) and concentration (Ct) at time (t).

2.3.5. Analysis Method

The efficiency of the process was evaluated by quantifying ammonium ions NH_4^+ using a spectrophotometer (UV-1800 Spectrophotometer) with the Nessler method. Samples were taken periodically after each experiment and filtered using Centrifuge to remove suspended particles before analysis; 2 mL of Nestler's Reagent was placed on the samples. Then, samples were analyzed using a spectrophotometer, and the wavelength was fixed at 425 nm [8-9].

3. Results and Discussion

3.1. Effect of Adsorbent Dosage (Nano-zeolite) on the Removal of Ammonium Ions and the Equilibrium Adsorption Capacities

Adsorbent dosage represents an important parameter due to its strong effect on the adsorbent capacity at a given initial concentration of the adsorbate. The work was done at room temperature, and pH 8 was chosen to change the weight of the Nano-zeolite type (4A) to know the effect of weight on the removal of ammonium ions. Table (1) represents the values we obtained through the laboratory experiment. It was observed that the ammonium ion removal developed gradually from the lowest dose of zeolite to the highest dose, where the removal percentage reached (98%) at the highest dose of 2.5g, as shown in Figure (3). The ammonium adsorption capacity decreased from 11.0 to 1.96 mg/g.

In comparison, the NZ dose increased from 0.25 to 2.5 g, as shown in Figure (4), given that the initial ammonium concentration remains constant despite changes in the dose of zeolite. It is only natural that the gradient of ammonium concentration per unit mass of zeolite decreases as the dose increases. Thus, the driving force of ammonium adsorption generated by the higher concentration gradient inevitably decreases under this condition [10-12].

Table (1): Effect of Zeolite Dosage on the removal of ammonium ions and the equilibrium adsorption capacities.

zeolite weight g	C_o ppm	C_e ppm	x/m= q mg/g	C_e/q	Ln C_e	Ln q	Removal%
0.25	100	45	11.0	4.09	3.80	2.39	55
0.75	100	20	5.33	3.75	2.99	1.67	80
1.5	100	5.4	3.15	1.71	1.68	1.14	94.6
2.0	100	4.5	2.38	1.89	1.50	0.86	95.5
2.5	100	1.6	1.96	0.81	0.47	0.67	98.4

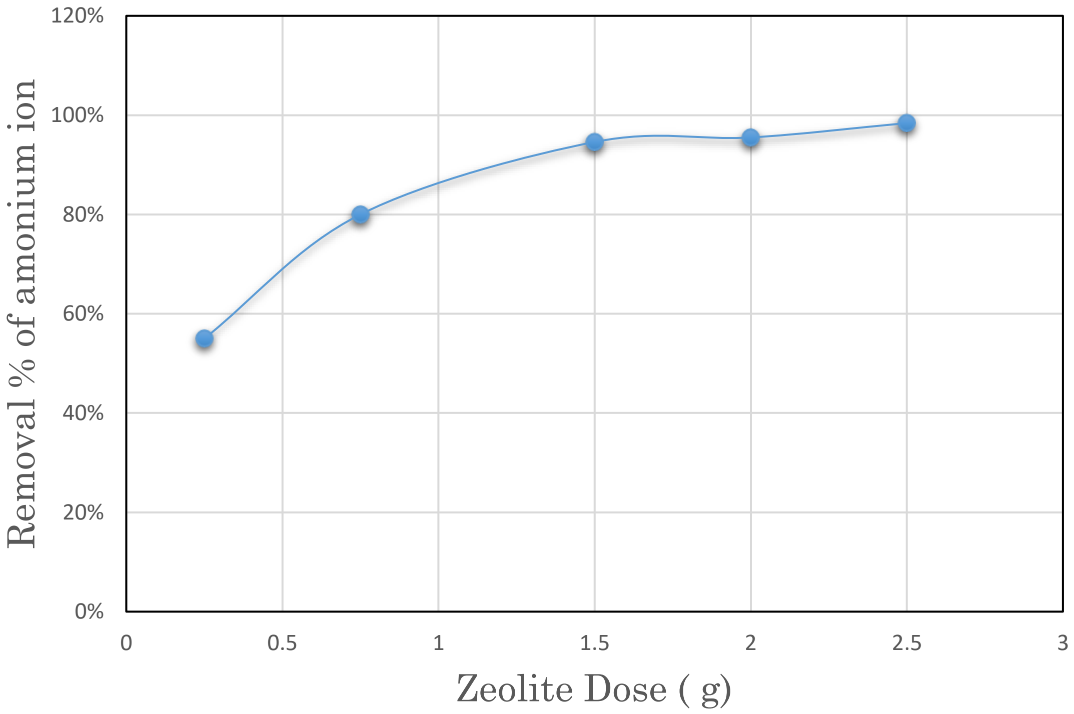

Figure (3): Effect of Zeolite Dosage on the removal of ammonium ions

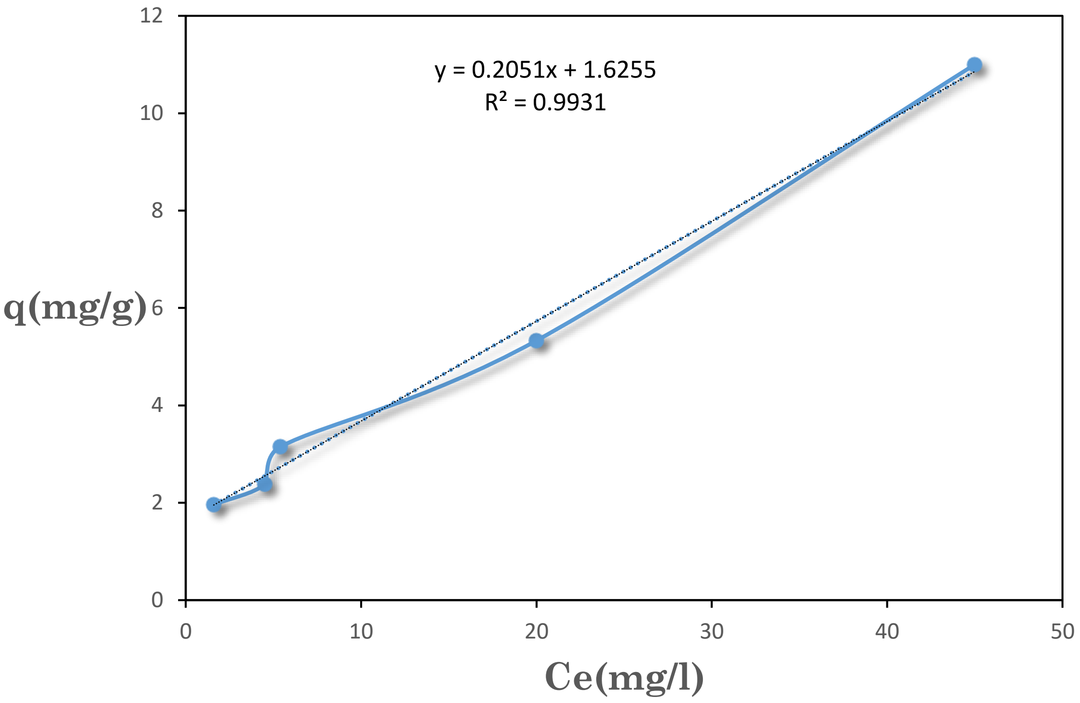

Figure (4): Equilibrium isothermal curve of ammonium adsorption at different NZ dosages.

3.2. Effect of Initial Ammonium Concentration on the Removal of Ammonium Ions on the Equilibrium Adsorption Capacities

Experiments were carried out to study the efficiency of removing ammonium ions with different initial Concentrations of NH_4^+ solution (20, 50,100, 200, and 300) ppm and the effect of Initial NH_4^+ concentration on the equilibrium adsorption capacities. NZ dosage (2.5) g, the inherent pH was recorded as 8, temperature = 25ºC. The results of removal efficiency by changing the concentrations are shown in Table (2); it can be noticed that the experimental data indicate that the removal percentage of ammonium ion decreased with increasing the initial ammonium ion concentration. The removal percentage of ammonium ions decreased from 99 % when the concentration was 20 ppm to 91.6 % when the concentration was 300 ppm; this could be attributed to the weak binding between ion exchanger material (NZ) and NH_4^+. The adsorption data indicated that the adsorption capacity of ammonium increases on the surface of nano zeolite with increasing initial ammonium concentration, which is the result of an increase in the driving force [11, 12], shown in Figure (5) and Figure (6).

Table (2): Effect of Initial Ammonium Concentration on removing ammonium ions and the equilibrium adsorption capacities.

Initial Conc. C_o ppm	C_e ppm	x/m= q mg/g	Removal%
20	0.2	0.39	99.0
50	0.4	0.99	99.2
100	1.8	1.96	98.2
200	14.5	3.71	92.7
300	25.0	5.50	91 .6

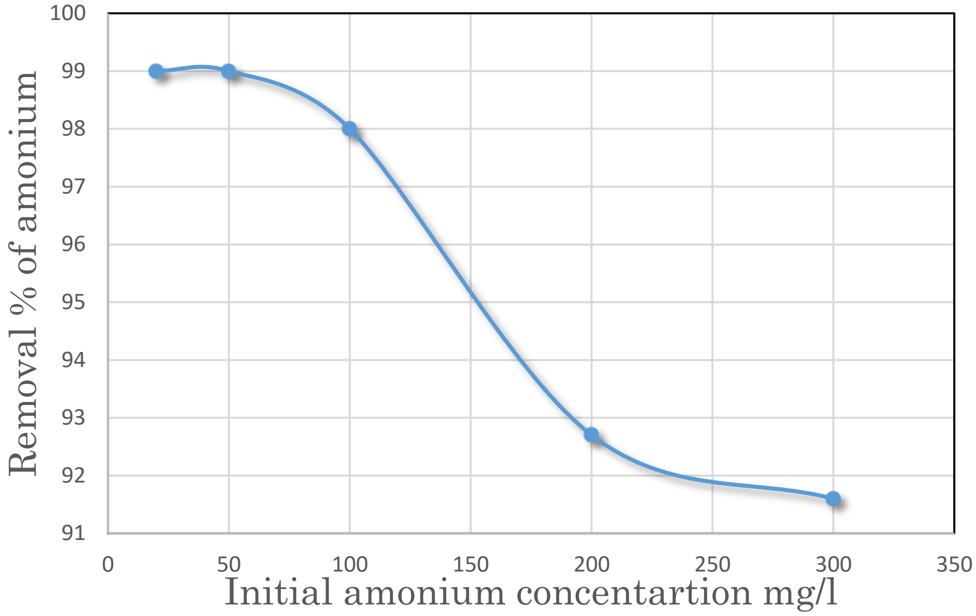

Figure (5): Effect of Initial Ammonium Concentration on the removal of ammonium ions.

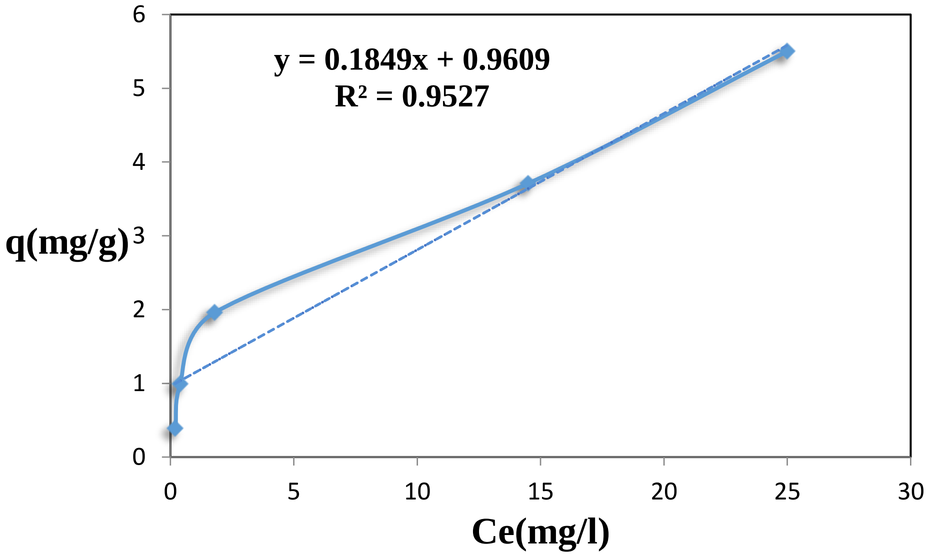

Figure (6): Equilibrium isothermal curve at different Initial Ammonium Concentration.

3.3. Effect of Contact Time on the Removal of Ammonium Ions on Equilibrium Adsorption Capacities

Contact time is one of the most effective factors in batch adsorption. The experimental values for ammonium ion removal and adsorption capacity are shown in Table (3). Figure (7) shows that the experimental data indicate that the percentage of ammonium ion removal increases in the first 15 minutes. They gradually equalize and finally reach equilibrium after 240 minutes. Then, the rate of removal of ammonium ions decreases. Changes in NH_4^+ result from the many free active adsorbent sites [12-16]. The experimental adsorption capacity (***q_t***) was estimated at an interval time (***t***) by using Eq. (2); the graph of (***q_t*** vs. ***t***) is shown in Figure (8).

Table (3): Effect of Contact time on the removal of ammonium ions and the equilibrium adsorption capacities.

Contact time min	C_o ppm	C_t ppm	x/m= q_t mg/g	Removal%
15	100	16.5	1.67	83.5
60	100	10.5	1.79	89.5
90	100	8.2	1.83	91.8
120	100	6.5	1.87	93.5
240	100	2.0	1.96	98.0

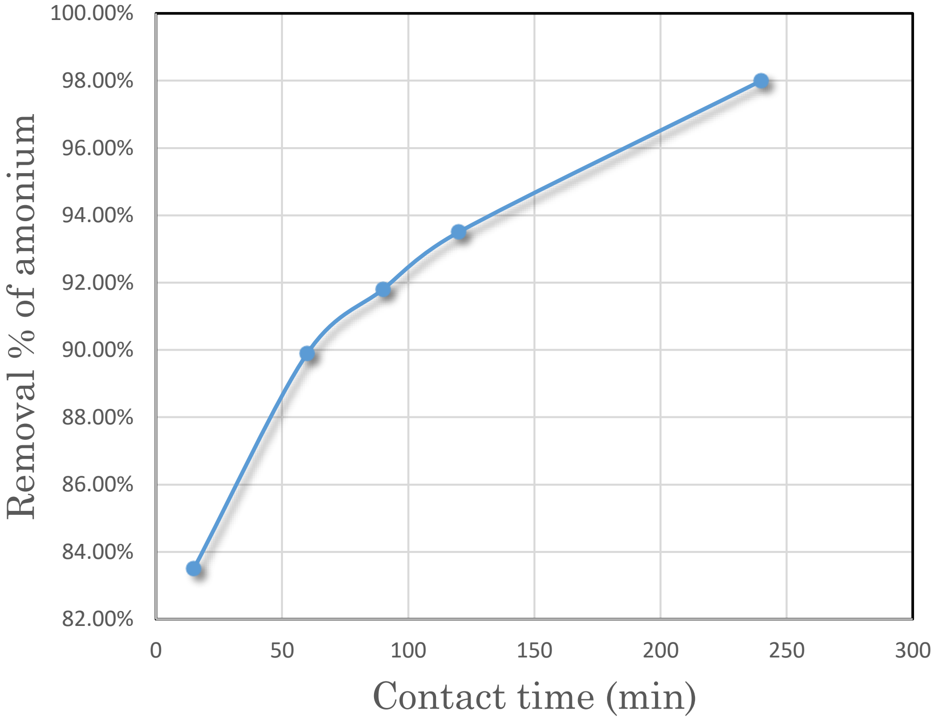

Figure (7): Effect of Contact time on the removal of ammonium ions.

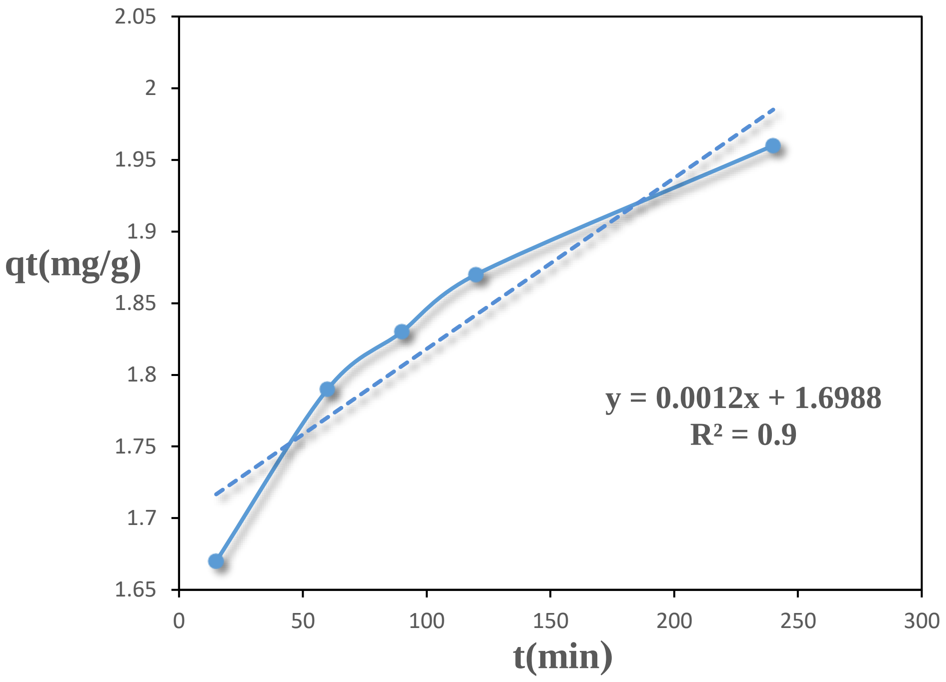

Figure (8): Equilibrium isothermal curve at different Contact times.

3.4. Isothermal Adsorption Models of Ammonium Ion

The explanation for how nanozeolite removes NH_4^+ ions is based on Langmuir and Freundlich isotherms, where the equilibriums isotherms show the correlation between the equilibrium adsorbate concentrations and the material absorption rate of the adsorbent mass units [12-19].

3.4.1. Freundlich's Isotherm

It is commonly used to characterize adsorption properties on heterogeneous surfaces. The equation expresses it:

$$\ln q = \ln k + \frac{1}{n}\ln C_e \qquad (3)$$

Where K and n are Frendlich constants, q adsorption capacity mg/g and Ce equilibrium concentration mg/l.

3.4.2. Langmuir's Isotherm

It is commonly used when only one adsorption layer develops on the adsorbent surface. The equation expresses it:

$$\frac{Ce}{q} = \frac{1}{q_{\max} b} + \frac{Ce}{q_{\max}} \qquad (4)$$

Where q adsorption capacity mg/g and Ce equilibrium concentration mg/l, b Langmuir constant and qmax theoretical maximum adsorption capacity.

Adsorption isotherms are beneficial for maximizing the usage of zeolite as an adsorbent and are necessary for describing how NH_4^+ concentration will interact with zeolite. The Freundlich isotherm curve and the Langmuir isotherm curve are plotted in Figures (9 &10).

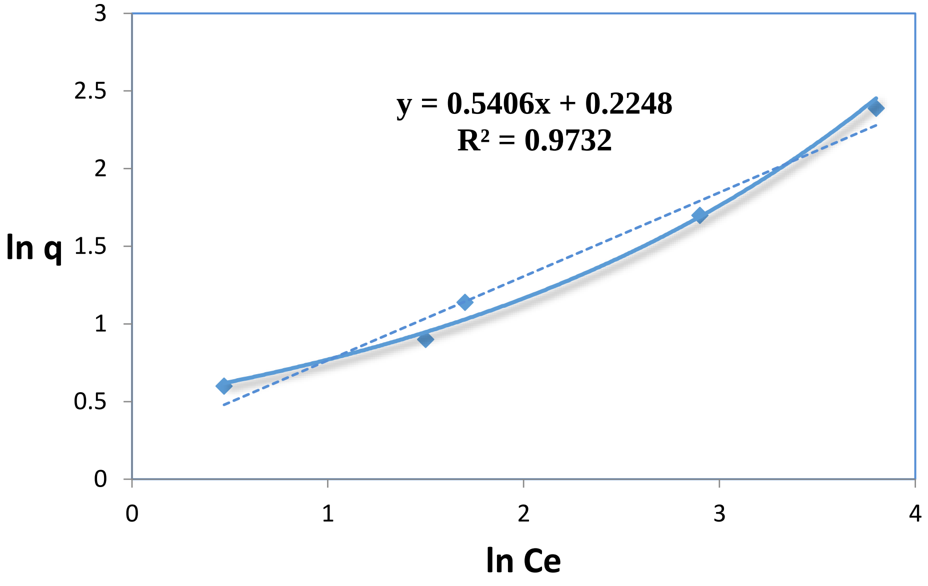

Figure (9): Freundlich isotherm diagrams for ammonium adsorption with a zeolite dose change.

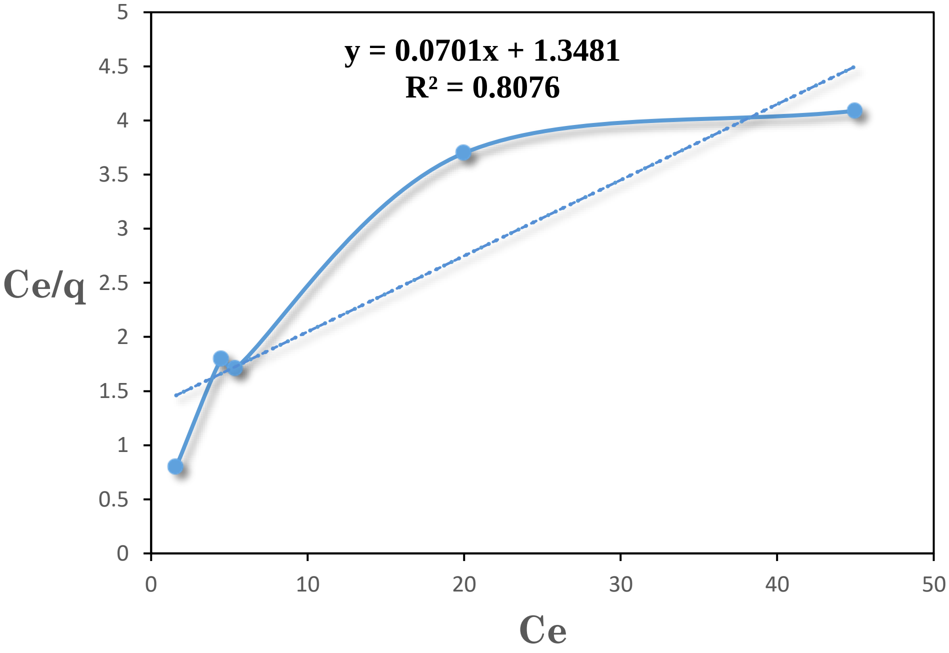

Figure (10): Langmuir isotherm diagrams for ammonium adsorption with NZ dose change.

The experimental data fit with the Freundlich equation and the Langmuir equation for ammonium ion adsorption, which were found and listed below in Table (4).

Table (4): Freundlich and Langmuir adsorption model constants for ammonium ion zeolite dose change.

Freundlich isotherm constant			Langmuir isotherm constant		
K (mg/g)	n	R^2	q_{max} mg/g	b (L/mg)	R^2
1.33	1.9	0.97	14.3	0.04	0.80

After comparing the Freundlich and Langmuir models for the ammonium adsorption process, it was discovered that the Freundlich isotherm model described the adsorption process with a high coefficient of determination (R^2=0.97), better than the Langmuir isotherm model (R^2=0.8). Allowed a higher removal rate of ammonium ions by adjusting the sorbent dose (NZ); the isotherm more accurately depicts zeolite's adsorption capacity and is more suitable for ammonium ion removal experiments. Adsorption energy on the surface of natural adsorbate leads to considering these homogeneous multilayer adsorption surfaces for an opposite charge, which resists the formation of a complete monolayer of the adsorbate [20-21].

4. Conclusions and Recommendations

The nanozeolite material was obtained from the local market with good characteristics, which led to good results in removing ammonium ions, by studying the effect of doses of zeolite. The removal percentage was reached (98%) using 2.5g for a time of 240 minutes. Experimental results describe the Freundlich and Langmuir isotherms. The correlation coefficient R^2 was equal to (0.97 and 0.80), respectively. However, Freundlich's model description of the ammonium ion removal isotherms was superior. It was concluded that the main mechanism of the ammonium absorption process is heterogeneous absorption. The adsorption capacity was high at low doses of adsorbent. And the contact time is one of the most effective factors in batch adsorption. It is possible to prepare nano zeolites in multiple ways and compare them with non-nano zeolites and studying other determinants such as pH and temperature change and knowing their effect on the ammonium ion's adsorption capacity and removal rate.It is possible to use the research's data And at the level of an applied system to remove the ammonium ion from the fertilizer company's industrial water or any industrial water with a high ammonium ion content.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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