

Article

Selective Adsorption of Ammonia from Nitrogen and Hydrogen Using Zeolite 13X: Isotherm and Breakthrough Studies

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Abstract

The separation of synthesised ammonia from unreacted nitrogen and hydrogen is a crucial step in producing high-purity ammonia and enabling the efficient recycling of unreacted gases in the ammonia synthesis process. The separation of ammonia from nitrogen and hydrogen was studied using zeolite 13X. Experiments were performed using a custom-designed experimental apparatus developed specifically for this study. Adsorption isotherm data for ammonia, hydrogen, and nitrogen were obtained over a temperature range of 293–313 K and pressures up to 5 bar. The results show that the adsorption capacity of zeolite 13X for ammonia is significantly higher than for nitrogen and hydrogen. This indicates a substantially stronger affinity toward ammonia molecules, enabling highly selective adsorption. The experimental isotherm data were successfully fitted using the Sips model, which accurately described the adsorption behaviour of the gases and showed good agreement with the measured data. The adsorption performance of zeolite 13X was further evaluated through a series of dynamic breakthrough experiments under varying pressures and gas compositions. The results confirmed the high selectivity of zeolite 13X for ammonia, with negligible adsorption of nitrogen and hydrogen. Ammonia breakthrough time was found to increase with system pressure, reflecting enhanced adsorption capacity. These findings highlight zeolite 13X as an effective and reusable adsorbent for selective ammonia separation in multi-component gas streams, with promising potential for industrial applications.

Keywords: adsorption; zeolite 13X; ammonia; hydrogen; nitrogen; isotherm; breakthrough curve



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1. Introduction

Ammonia is one of the most important chemicals and is essential for numerous industrial applications, particularly in agriculture for fertiliser production. Ammonia is typically produced through the Haber–Bosch process, a method that has been finely tuned over the last century to maximise efficiency [1]. This catalytic process involves the combustion of fossil fuels with air and water to produce a mixture of hydrogen, nitrogen, and carbon dioxide. The hydrogen and nitrogen are then reacted under high pressure and temperature to synthesise ammonia [2]. However, the dependence on fossil fuels in this process raises concerns regarding its environmental impact, particularly in terms of carbon emissions [3]. In this process, the synthesis of ammonia occurs at high temperatures (400–500 °C) and pressures (150–300 atm) over a catalyst. The reaction mixture consists of ammonia along with unreacted nitrogen and hydrogen. The mixture is cooled down,

and since ammonia has a much higher boiling point ($-33\text{ }^{\circ}\text{C}$) compared to nitrogen ($-196\text{ }^{\circ}\text{C}$) and hydrogen ($-253\text{ }^{\circ}\text{C}$), it condenses into a liquid at higher temperatures [4,5]. Separating ammonia from the gas stream via condensation is challenging, and operating at low pressures (below 50 bar) is not practical due to ammonia's high vapour pressure at ambient conditions, which is 8.5 bar at $20\text{ }^{\circ}\text{C}$ [4,6].

In a conventional ammonia production plant, ammonia is separated by phase-change condensation at high pressure (300 bar) and low temperature ($25\text{ }^{\circ}\text{C}$) using water cooling. For lower-pressure manufacturing (150 bar), a refrigeration system is required to achieve the lower temperatures necessary for ammonia condensation [7]. Since gas compression and refrigeration are the primary contributors to the overall energy consumption in ammonia production, there is a critical need to design separation processes that minimise energy use and improve efficiency [7,8].

Adsorption of ammonia from unreacted nitrogen and hydrogen using adsorbents is a suitable method. The efficiency of this method depends on the sorbent capacity and affinity to bind ammonia as well as the sorption kinetics [9,10]. In this method, selective adsorbent materials, such as zeolites or metal-organic frameworks (MOFs), are used to capture ammonia due to their high affinity for it. These porous materials adsorb ammonia molecules from the gas mixture while allowing nitrogen and hydrogen to pass through. The adsorbed ammonia can later be released by adjusting temperature or pressure conditions, allowing it to be recovered in a controlled manner. This adsorption-based separation is energy-efficient compared to condensation, especially at lower pressures, making it an attractive alternative for enhancing process sustainability. If the ammonia concentration is low, the condensation temperature becomes too low to effectively separate the ammonia.

Ammonia–gas separation through adsorption and recovery for reuse is a well-established process, though it has not been widely implemented. In this method, the ammonia can be effectively desorbed and recovered through conventional regeneration strategies such as temperature swing adsorption (TSA), pressure swing adsorption (PSA), or a combination of both. The desorbed ammonia stream can then be condensed to obtain high-purity ammonia as the final product.

The challenges for ammonia adsorption are related to the selectivity, capacity, and regeneration of the adsorbents used. Regeneration is particularly important for industrial applications, as ammonia tends to bind strongly to many sorbents, making the process less efficient. Most applications focus on separating ammonia from gas streams in ammonia production, where sorbents like zeolites, alumina, silica gel, and activated carbon are commonly used [11,12]. Zeolites, with their tuneable pore structures, exhibit high selectivity and capacity for ammonia, though regeneration remains challenging due to strong adsorption. Activated carbon has been studied for its lower cost and moderate ammonia uptake, while alumina and silica gel show varying levels of adsorption efficiency [11,12].

The literature shows that various adsorbents have been investigated for ammonia separation, including activated carbons, alumina-based materials, silica gel, and zeolites. Studies by Rodrigues et al. [13], Zeng et al. [14], and Cárdenas et al. [15] on activated carbon systems reported moderate ammonia adsorption capacities but generally limited selectivity and stability under cyclic operation. Helminen et al. [11] demonstrated that zeolite-based materials, particularly zeolite 13X, exhibit significantly higher ammonia adsorption capacity compared to alumina, silica gel, and natural zeolites due to the strong interaction between ammonia and cationic sites. Ouyang et al. [16] further showed that zeolite composition (Si/Al ratio) strongly influences adsorption performance and selectivity, particularly at very low ammonia concentrations. However, most of these studies are limited to equilibrium measurements and do not provide detailed insight into dynamic adsorption behaviour or regeneration stability under practical operating conditions.

Saha et al. [17] studied the adsorption performance of ammonia on activated alumina. They systemically carried out ammonia adsorption using the synthesised porous. Vo et al. [18] reported the adsorption of ammonia gas on the synthesised mesoporous alumina.

In addition, Zheng et al. [19] reported ammonia isotherms on zeolite 13X and activated carbon, but only at atmospheric pressure, while San et al. [20] investigated adsorption–desorption behaviour in composite materials without exploring high-pressure or multi-component gas effects. Overall, the literature indicates that although ammonia adsorption behaviour is relatively well studied at low pressure, there remains a lack of systematic data on adsorption performance, selectivity in ammonia/nitrogen/hydrogen mixtures, regeneration behaviour, and dynamic breakthrough characteristics under elevated pressure conditions.

Isotherm studies offer valuable insights into the equilibrium behaviour of ammonia in various materials. However, breakthrough curve measurements, which more closely simulate real industrial conditions, have been explored to a much lesser extent.

The lack of data on how ammonia interacts with hydrogen and nitrogen in a flowing system highlights the need for further experimental studies to optimise separation processes under dynamic conditions. This information is crucial for designing efficient adsorption-based separation technologies in ammonia production.

This research aims to measure the isotherm data for ammonia and to investigate the adsorption of ammonia from a hydrogen and nitrogen gas mixture, using zeolite 13X as the adsorbent. Zeolite 13X is chosen for its well-known properties, including high surface area, uniform pore structure, and strong affinity for polar molecules like ammonia [21].

Zeolite materials have strong interactions with ammonia and good shape-selectivity [22]. The capacity of zeolite adsorbent with a lower Si/Al ratio generally leads to higher ammonia adsorption due to an increased number of available acidic sites for ammonia molecules [23,24]. The Si/Al ratio of zeolite 13X is around 1.15–1.3 [25], which makes it a suitable candidate for separating ammonia from gas mixtures. Its selective adsorption potential, especially in the presence of non-polar gases like hydrogen and nitrogen, is expected to enhance the efficiency of the separation process. By exploring the performance of zeolite 13X in this application, the study seeks to optimise ammonia recovery and contribute to the development of more energy-efficient separation technologies in ammonia production [16].

In this research, the adsorption performance of ammonia on zeolite 13X was systematically investigated under both static equilibrium and dynamic breakthrough conditions over a wide range of operating pressures and temperatures. The novelty of this work lies in reporting both static adsorption isotherm data and dynamic breakthrough adsorption data for ammonia/nitrogen/hydrogen gas mixtures at pressures above atmospheric conditions, where experimental adsorption data for ammonia on zeolite 13X remain scarce in the literature. Ammonia adsorption equilibrium measurements were conducted at pressures up to 5 bar, providing valuable adsorption data in a pressure range that has rarely been experimentally reported. In addition, the relationship between equilibrium and dynamic adsorption capacities was analysed. The regeneration and cyclic stability of the adsorbent were also evaluated to assess its practical applicability for repeated operation. The findings of this work provide useful insight into ammonia adsorption behaviour and contribute to the development of efficient ammonia recovery and purification systems for clean energy and industrial applications.

2. Materials and Methods

2.1. Materials

Zeolite 13X was purchased from DESICCO Company, Chatswood, NSW, Australia. The particle size of zeolite was in the range of 3–5 mm, and the bulk density was 0.62 g/mL. Ammonia with a purity of 99.9% as well as hydrogen and nitrogen gas, grade 5, were purchased from Coregas Company, Yennora, NSW, Australia. The list of chemicals and the properties of zeolite 13X are reported in Tables 1 and 2.

Table 1. List of chemicals used in this research and their specifications.

Component	Supplier	CAS Number	Mass Fraction Purity	Molecular Weight (g/mole)	Analysis Method
Ammonia	Coregas, Australia	7664-41-7	0.9999	17.07	Micro-GC
Hydrogen	Coregas, Australia	1333-74-0	≥0.9995	2.016	Micro-GC
Nitrogen	Coregas, Australia	7727-37-9	≥0.99995	28.014	None

Table 2. Properties of zeolite 13X.

CAS No.	1318-02-1
Pellet size	3–5 mm
Pore size	10 Å
Analysis method	BET
Bulk density	>620 kg/m ³
$\frac{SiO_2}{Al_2O_3}$	2–3

2.2. Apparatus and Sample Preparation

Zeolite 13X was calcined in a furnace by heating up to 873 K at a rate of 2.5 K/min for 6 h to remove moisture and increase adsorption capacity [26]. The Brunauer-Emmett-Teller (BET) analysis test based on nitrogen adsorption/desorption was used for zeolite 13X for determining the surface areas and microporosity of the samples using 3Flex high performance gas adsorption (Malvern, London, UK).

To measure the adsorption isotherms of ammonia, nitrogen and hydrogen, a static volumetric adsorption instrument was used. The details of the apparatus and the measurement procedure were described in our previous studies [26–28]. The setup includes temperature and pressure sensors for both the gas storage cylinder and the reactor, with a precision of 0.01% FS and 0.1 K, respectively. The injected gas volume is controlled using a high-precision mass flow controller (MFC; Bronkhorst Company, Veenendaal, The Netherlands). The amount of gas adsorbed at each equilibrium stage is determined by monitoring the pressure in the reactor, which is maintained at a constant temperature and has a known volume. Based on these measurements, the equilibrium adsorption amount is calculated for various pressures, and the corresponding adsorption isotherm curves are generated.

The experimental setup for measurement of the breakthrough curve was designed and manufactured as shown in Figure 1. The gas mixture, consisting of ammonia, hydrogen, and nitrogen, was prepared by mixing precise amounts of pure gases from their respective cylinders using mass flow controllers (MFCs, Bronkhorst Company, The Netherlands). For safety reasons, three non-return valves (NRVs) were installed before each MFC. The flow rate of the gas mixture was measured with a mass flow meter (MFM) with an accuracy of 1%. Online transmitters were used to measure temperature and pressure, with accuracies

of 1 mbar for pressure and 0.1 K for temperature. A control panel was used to record temperature, pressure, and flow rate. Due to the exothermic adsorption of ammonia on zeolite 13X, an increase of temperature (less than 1 °C) was observed in the gas effluent at the top of the adsorption column.

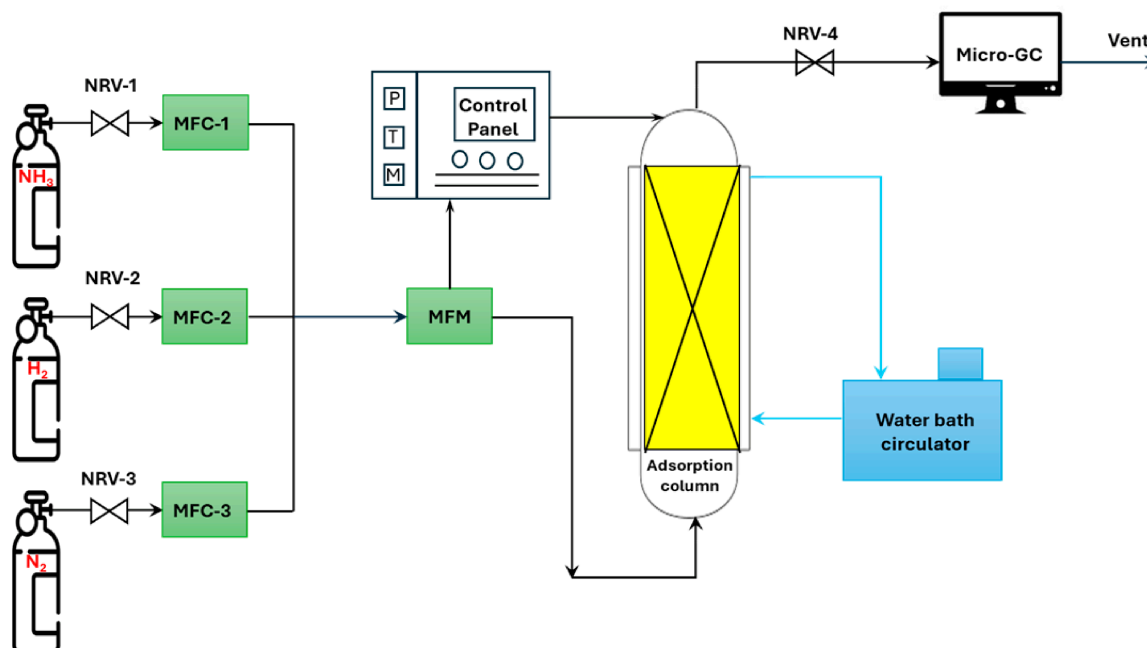


Figure 1. Schematic diagram of the experimental setup with control panel for measurement of pressure (P), temperature (T) and flow rate (M).

The gas mixture was fed into a 40 cm long, 2.5 cm diameter adsorption column equipped with a temperature-controlled cooling/heating jacket. The column was filled with 25 g zeolite 13X for isotherm measurement and 50 or 100 g zeolite 13X for breakthrough experiments. The temperature of the column was controlled by a water bath circulator, maintaining accuracy within 0.1 K. The gas mixture entered from the bottom of the column, initiating the adsorption process. The effluent gas exited from the top of the column and was analysed using an online micro-GC (990 Micro-GC, TCD detector, Agilent, Mulgrave, Australia) calibrated for rapid analysis of ammonia and hydrogen. The micro-GC can analyse the gas mixtures every minute.

The adsorption process was finished when ammonia was detected in the effluent gas, and the adsorption capacity was calculated based on the following equation:

$$q = \frac{n_g}{m_{ads}} \quad (1)$$

where n_g is the number of moles of the gas that were adsorbed by zeolite 13X and m_{ads} is the mass of zeolite 13X in kg.

The regeneration of the adsorbent was then initiated by closing the input gas valve, reducing the pressure, and raising the column temperature to 353 K. As the temperature increased and the pressure decreased, the adsorbed gases were released from the adsorbent and analysed by the micro-GC. The adsorption column was evacuated using a vacuum pump and remained for 3 h under this temperature. The effluent gas under this condition was analysed continuously until no ammonia gas was detected. After this regeneration process, a new run was started.

2.3. Adsorption Equilibrium Model

The adsorption data of ammonia, nitrogen and hydrogen on zeolite 13X were fitted with the Langmuir-Freundlich (LF) model. Langmuir and Freundlich models are the simple models for adsorption isotherm modelling because they contain only two parameters. The Langmuir model is written as

$$q = q_s \frac{bP}{1 + bP} \quad (2)$$

where q is the equilibrium adsorption capacity (mol/Kg), q_s is the monolayer adsorption capacity, b (bar⁻¹) is the affinity parameter, and P (bar) is the pressure. This model is widely used for adsorption equilibria [29]. The Freundlich equation is expressed as follows:

$$q = k.P^n \quad (3)$$

where k is the Freundlich constant and n is the constant that expresses the heterogeneity of the adsorbent surface. A well-known equation is the LF model, which is the combination of both models. The model is known as the Sips model. This model is represented by the following nonlinear equation [30]:

$$q = q_s \frac{(bP)^n}{1 + (bP)^n} \quad (4)$$

The Sips model contains three parameters and can describe most of the experimental data better than two-parameter models like the Langmuir and Freundlich models.

The Toth model [30] is another adsorption isotherm model commonly used for interpreting equilibrium adsorption data. It is a three-parameter equation that represents an extended and more generalized form of the Langmuir model. The Toth model equation is shown below:

$$q = q_m \frac{b P}{\left(1 + (bP)^t\right)^{1/t}} \quad (5)$$

where q_m is the monolayer adsorption capacity, b (bar⁻¹) is the affinity parameter, and t is the Toth heterogeneity parameter.

The root mean square deviation (RMSD) is defined based on the following equation:

$$RMSD\% = 100 \sqrt{\frac{\sum_{i=1}^N \left[\frac{q_i^{\text{exp}} - q_i^{\text{mod.}}}{q_i^{\text{exp}}} \right]^2}{N}} \quad (6)$$

where q is the adsorption capacity and N is the number of experimental adsorption data points. The superscripts exp and mod denote the experimental and modelling data points.

Equilibrium selectivity provides a useful tool for the initial screening and ranking of adsorbents. At a given temperature, the equilibrium selectivity can be expressed as follows:

$$S_{N,M} = \frac{K_N}{K_M} \quad (7)$$

where K_N and K_M are the Henry constant of N and M component, respectively. For this reason, equilibrium selectivity is also called the Henry selectivity [31].

To calculate the Henry constant from a Sips isotherm, the low-pressure limit of the Sips equation must be used. Henry's law at low pressure is expressed as follows:

$$\lim_{P \rightarrow 0} \frac{q}{P} = K_H \quad (8)$$

3. Results and Discussion

3.1. Characterisation of Zeolite 13X

Nitrogen adsorption–desorption isotherms at 77 K were used as the experimental technique for zeolite 13X, while the specific surface area was calculated using the Brunauer–Emmett–Teller (BET) model. Furthermore, the method used to estimate the micropore volume was the t-plot method. The surface area was calculated as 515 m²/g with a micropore volume of 0.16 cm³/g. The adsorption/desorption isotherm of nitrogen at 77 K is shown in Figure 2. The isotherm is type I according to IUPAC classification [32]. The sharp increase in nitrogen adsorption at low relative pressures (P/P_0) < 0.1 is attributed to the micropore filling in the zeolite structure. In the intermediate relative pressure range (approximately 0.1–0.9), the isotherm shows a gradual increase in adsorption capacity. This region corresponds to a combination of monolayer formation, multilayer adsorption on external surfaces, and progressive filling of accessible pore surfaces. This behaviour is typical of microporous solids with additional external surface contribution and possible minor textural porosity.

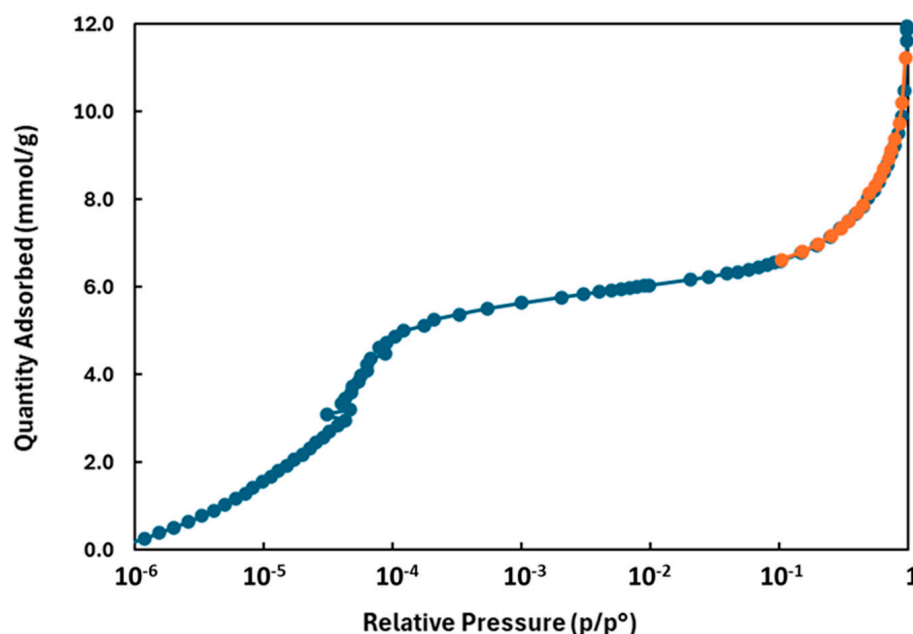


Figure 2. Nitrogen adsorption/desorption isotherm at 77 K for zeolite 13X (●: adsorption; ●: desorption).

At high relative pressures ($P/P_0 > 0.9$), the steep rise in adsorption is mainly associated with capillary condensation in interparticle voids and particle packing (textural porosity) rather than mesopore filling. This indicates that the high-pressure uptake is governed predominantly by external void spaces between agglomerated particles rather than internal pore structure.

Figure 3 shows the pore-size distribution represented by the measured pore radius using the N₂ adsorption–desorption data. The pore size distribution was calculated using the Horvath–Kawazoe (HK) method. The obtained micropore diameter is slightly smaller than the nominal pore diameter commonly reported for zeolite 13X (~7.4 Å) [33], such deviation is acceptable considering the limitations and assumptions associated with the HK method and N₂ adsorption measurements at 77 K.

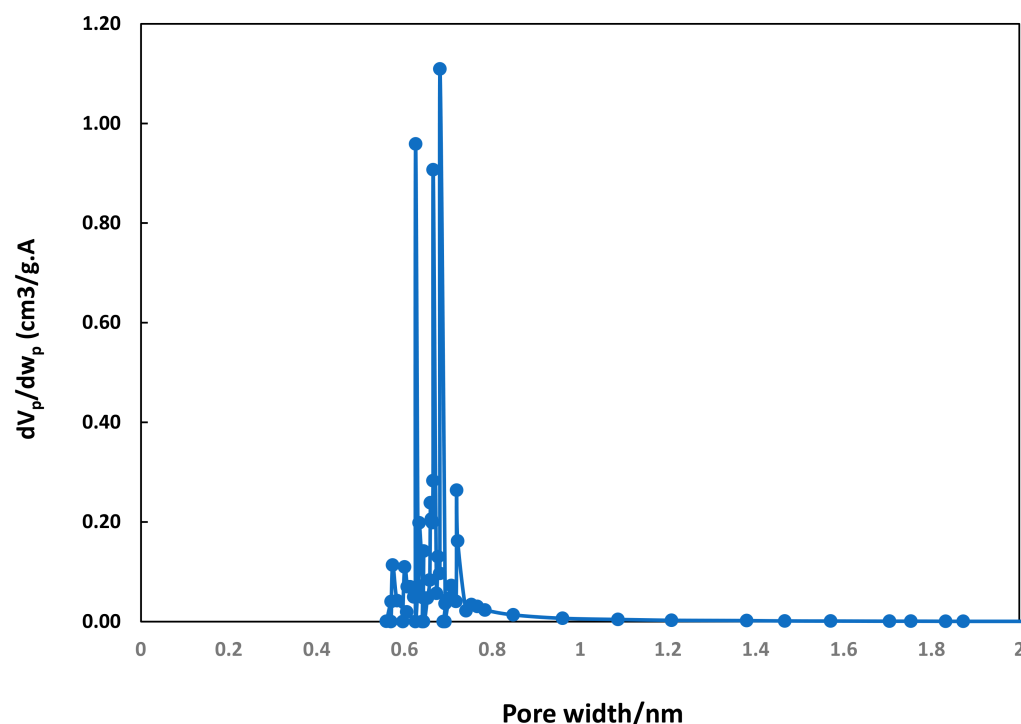


Figure 3. Pore size distribution for zeolite 13X.

3.2. Isotherm Experimental Results

The adsorption isotherms of ammonia, nitrogen, and hydrogen were measured at the three temperatures 293, 303, and 313 K and at pressures up to 5 bar. These measurements were conducted using the adsorbent saturation method. The adsorption capacity (q), expressed in moles of adsorbate per kg of adsorbent (mole/kg), is reported as a function of absolute pressure at constant temperature. The adsorption isotherms for ammonia were measured twice, and the mean values were reported. The adsorption isotherms for ammonia, hydrogen and nitrogen are presented in Figures 4–7 and compared with the Sips model [30]. As Figure 4 shows, at pressures below 2 bar, the equilibrium data are well described by the Sips isotherm model.

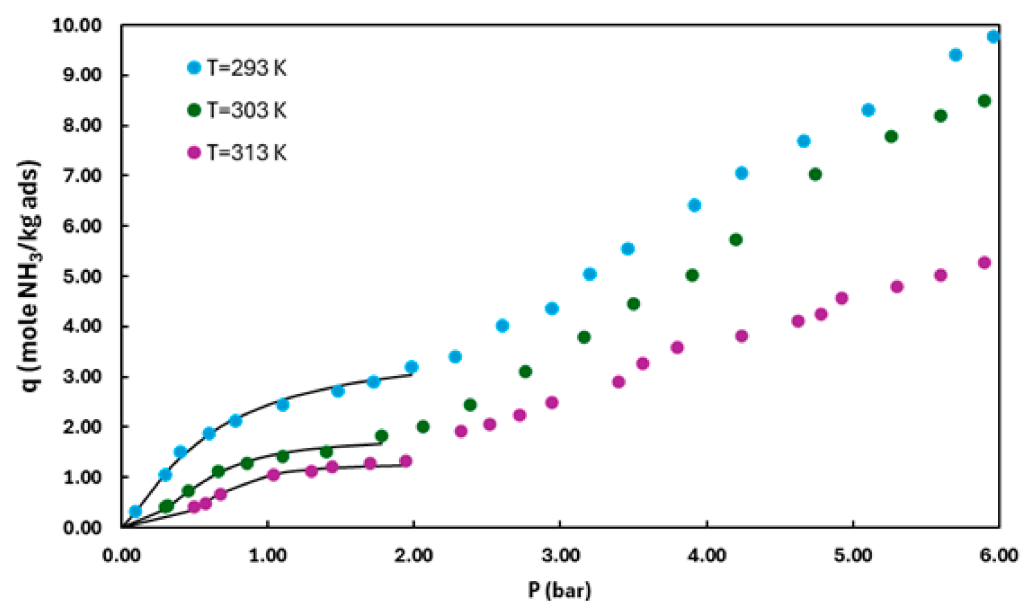


Figure 4. Adsorption isotherm experimental data for ammonia adsorption on zeolite 13X at different temperatures.

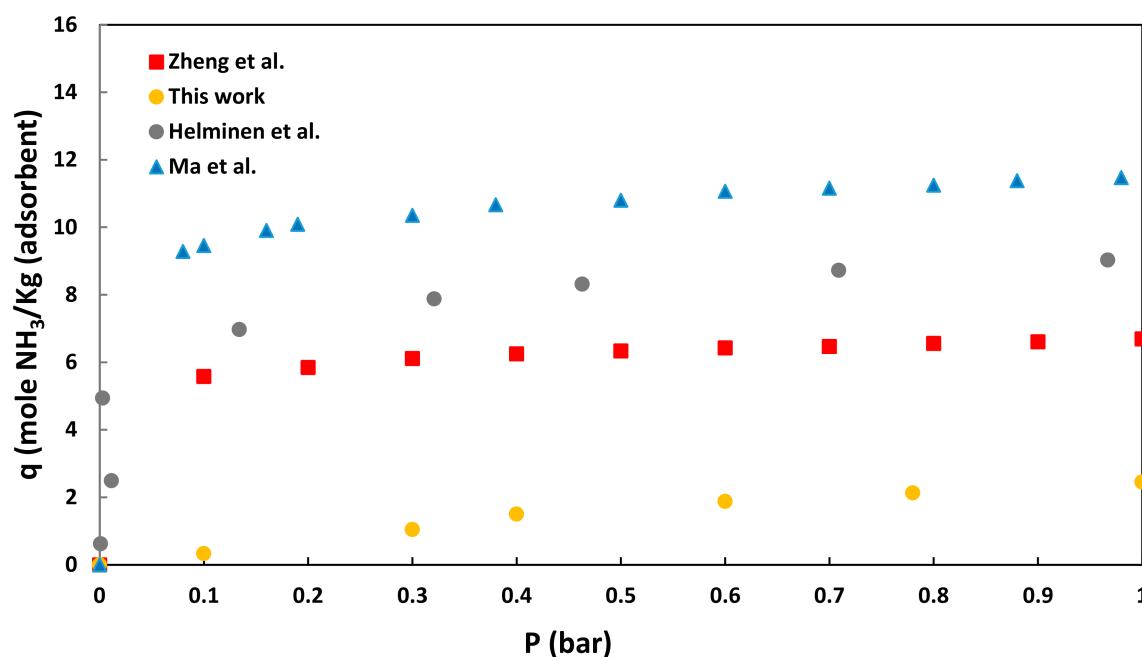


Figure 5. Comparison the adsorption isotherm experimental data for ammonia adsorption on zeolite 13X with the literature data: Zheng et al. [19] at 293 K, Helminen et al. [12] at 293 K, Ma et al. [34] at 298 K and this work at 293 K.

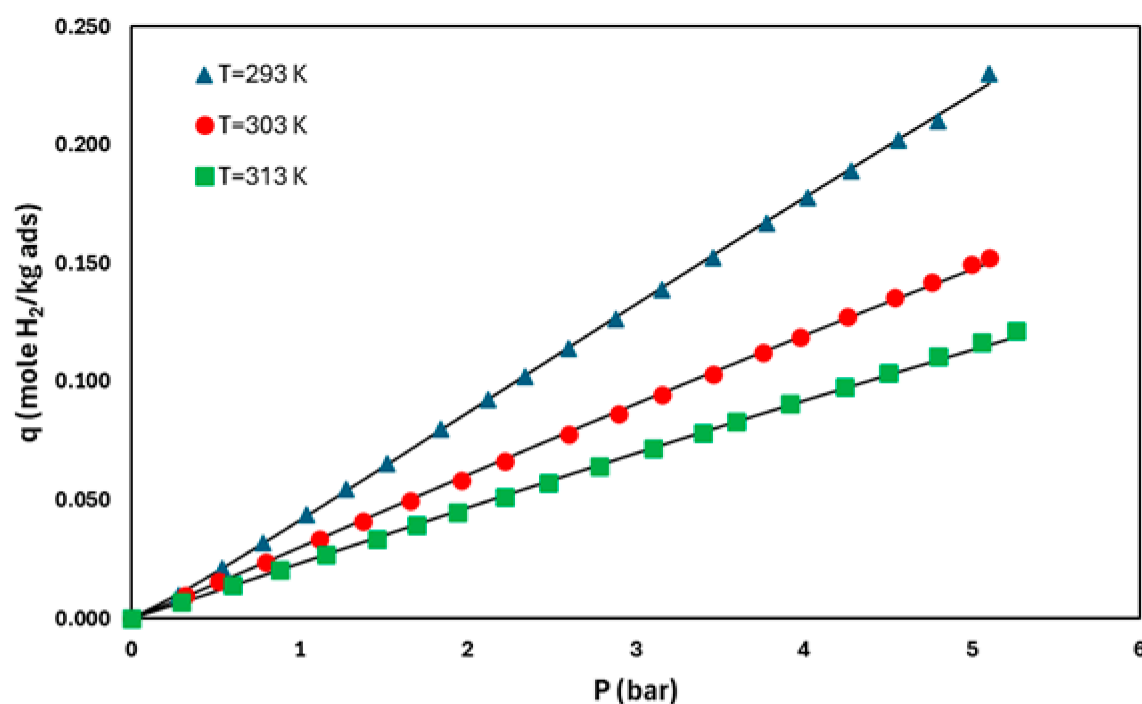


Figure 6. Adsorption isotherm experimental data for hydrogen on zeolite 13X at different temperatures; the solid line indicates Sips modelling.

This behaviour is attributed to a site-limited adsorption mechanism followed by a transition to secondary adsorption within the micropores. At low pressures, ammonia is strongly adsorbed on the high-energy cationic sites (Na^+) through strong electrostatic interactions. As pressure increases, these primary adsorption sites gradually become saturated. Around ~2 bar, a transition occurs where adsorption shifts from primarily site-specific binding to additional adsorption in the micropore volume (secondary filling). This change in adsorption regime appears as an inflection in the isotherm.

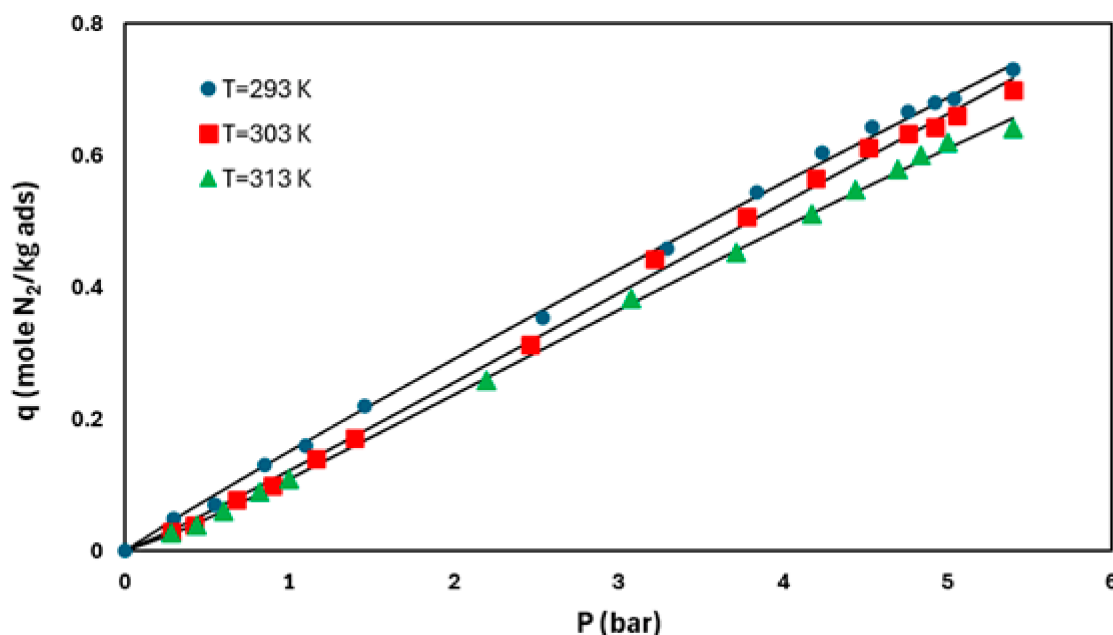


Figure 7. Adsorption isotherm experimental data for nitrogen on zeolite 13X at different temperatures; the solid line indicates Sips modelling.

The experimental adsorption data for ammonia, hydrogen and nitrogen are reported in the Supplementary Information.

Figure 4 shows the experimental data for ammonia adsorption. The adsorption capacity decreases with increasing temperature, indicating the exothermic nature of the adsorption process. The rate of increase in the adsorption of ammonia is different at $P < 2$ bar. The results show that the ammonia adsorption isotherms on zeolite 13X display a Langmuir-type (Type I) behaviour, characteristic of monolayer adsorption on microporous materials. However, at $P > 2$ bar, the adsorption capacity increases, suggesting multilayer adsorption or the involvement of additional adsorption mechanisms beyond the initial monolayer saturation.

The experimental data for the ammonia adsorption isotherm in this study were compared with the literature values for ammonia adsorption on zeolite 13X in Figure 5. It should be noted that experimental data for ammonia adsorption at pressures higher than one bar is scarce; we found just three sets of isotherm data for ammonia adsorption on zeolite 13X at pressures less than one bar. However, large discrepancies between the experimental data were observed. All sets of experimental data identified in the literature reported higher maximum adsorption capacities than those observed in this work [12,19]. Helminen et al. [12] reported a maximum adsorption capacity of 9 mole/kg at 96.7 kPa and 298 K, while Zheng et al. [19] observed a capacity of 6.7 mole/kg at 1 bar and 293 K. Ma et al. [34] reported the maximum adsorption capacity of 11.5 mole/Kg at 1 bar and 298 K. All these values exceed the maximum adsorption capacity obtained in this study, which was approximately 2 mole/kg at 1 bar and 293 K. However, the adsorption capacity of 9 mole/kg was observed at a higher pressure than 5 bar. This discrepancy may be attributed to differences in the type or quality of zeolite 13X used. For pressure levels more than one bar, the adsorption of ammonia on zeolite 13X is increased with pressure and tends to approach a saturation plateau. The continued increase in ammonia uptake above 1 bar suggests that adsorption is not limited to monolayer coverage but involves cooperative interactions and pore-filling effects at higher pressures.

Figure 6 presents the experimental adsorption isotherm data for hydrogen on zeolite 13X. The results indicate that hydrogen adsorption is negligible at pressures below 1 bar,

suggesting limited interaction between hydrogen molecules and the zeolite surface under low-pressure conditions. As the pressure increases beyond 1 bar, the adsorption capacity rises, reflecting enhanced occupation of available micropores by hydrogen molecules. However, this adsorption behaviour is notably affected by temperature. As the temperature increases, the adsorption capacity decreases, which is consistent with the exothermic nature of physical adsorption. Higher temperatures lead to increased kinetic energy of hydrogen molecules, reducing their tendency to remain adsorbed on the zeolite surface.

Figure 7 illustrates the experimental adsorption isotherm data for nitrogen on zeolite 13X. The results show that the adsorption capacity of nitrogen is significantly lower than that of ammonia, reflecting weaker interactions between nitrogen molecules and the zeolite surface. However, nitrogen adsorption is higher than that of hydrogen, indicating that nitrogen has a moderate affinity for zeolite 13X. This suggests that the nitrogen adsorption on zeolite 13X is not negligible and is influenced by molecular size and polarizability. The intermediate adsorption behaviour of nitrogen, compared to ammonia and hydrogen, highlights the selective adsorption characteristics of zeolite 13X for different gases based on their physical and chemical properties.

The isotherm data show that ammonia exhibits a significantly higher adsorption capacity compared to hydrogen and nitrogen, both of which display minimal adsorption on the zeolite surface. This difference in adsorption behaviour implies that zeolite 13X has a much stronger affinity for ammonia molecules, enabling selective adsorption. Consequently, ammonia can be efficiently separated from the mixture through adsorption-based processes, while hydrogen and nitrogen remain largely desorbed.

The kinetic diameter of ammonia (0.29 nm) [35] is smaller than nitrogen (0.36 nm) [36], allowing ammonia molecules to more easily access the pore structure of zeolite 13X. This size advantage facilitates faster diffusion and enhances the adsorption rate of ammonia within the porous zeolite. Additionally, ammonia possesses a higher polarizability and a significantly larger dipole moment compared to nitrogen, which strengthens its interaction with the polar sites of the zeolite surface. These physicochemical properties contribute to the higher adsorption affinity of ammonia on zeolite 13X.

In contrast, hydrogen exhibits the smallest kinetic diameter (0.289 nm) [37], but due to its non-polar nature and extremely low polarizability, it interacts only weakly with the zeolite surface. As a result, hydrogen shows the lowest adsorption strength among the three gases and is not significantly retained by zeolite 13X. On the other hand, ammonia demonstrates the highest adsorption strength, driven by both size compatibility and strong electrostatic interactions with the zeolite framework [38].

3.3. Isotherm Modelling and Selectivity

The experimental adsorption data were fitted using the Sips and Toth models to describe the adsorption behaviour of gases on zeolite 13X. The Sips model was identified as the most appropriate model due to its ability to describe adsorption on energetically heterogeneous surfaces while accounting for finite adsorption capacity. This makes it particularly suitable for zeolite 13X, where ammonia adsorption occurs on a distribution of cationic sites with varying adsorption energies.

The Sips model was confirmed for the adsorption isotherm of ammonia on zeolite 13X by another researcher [19]. The Sips model parameters obtained from the fitting are summarised in Table 3. For ammonia, the Sips model fitting was specifically performed using data at pressures below 2 bar, where the adsorption behaviour closely follows a Type I isotherm, characteristic of monolayer adsorption on a microporous material. The Sips model demonstrated good agreement with the experimental data, indicating its suitability

for capturing the heterogeneous adsorption sites and non-ideal behaviour observed in real systems.

Table 3. The parameters of the Sips model for the studied gases at different temperatures.

Gas	NH ₃			N ₂			H ₂		
T (K)	293	303	313	293	303	313	293	303	313
q _s (mol/kg)	3.65	1.99	1.43	5.44	4.43	3.30	1.81	1.20	1.02
b (bar)	1.720	1.574	1.361	0.026	0.044	0.057	0.034	0.031	0.027
n	1.31	1.95	2.57	0.96	1.16	1.18	1.11	1.05	1.04
RMSD%	4.2	5.2	3.4	2.9	4.0	1.3	1.1	1.3	1.2

The Toth model parameters were also obtained from the experimental data and are reported in Table 4. As shown in this table, the RMSD obtained from the Toth model is higher than that of the Sips model.

Table 4. The parameters of the Toth model for the studied gases at different temperatures.

Gas	NH ₃			N ₂			H ₂		
T (K)	293	303	313	293	303	313	293	303	313
q _m (mol/kg)	3.16	1.75	1.33	2.52	2.78	2.65	0.85	0.81	0.79
b (bar)	1.120	0.840	0.660	0.058	0.046	0.043	0.050	0.036	0.029
t	2.35	4.88	11.15	1.83	7.92	8.14	7.31	7.60	7.82
RMSD%	5.5	8.0	7.1	5.5	6.3	10.2	5.7	2.5	0.8

The Henry constant and the selectivity based on nitrogen are reported in Table 5. For ammonia, the Henry constant was estimated from the low-pressure region (0.1–0.4 bar), yielding an average value of $\sim 3.85 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{bar}^{-1}$ at 293 K, although slight deviation from linearity indicates the onset of strong adsorption interactions even at low pressure.

Table 5. Henry's constant and selectivity values for ammonia, nitrogen and hydrogen gas.

Gas	NH ₃			N ₂			H ₂		
T (K)	293	303	313	293	303	313	293	303	313
K _H	3.85	2.13	1.50	0.14	0.19	0.18	0.06	0.04	0.03
S _{N2}	27.5	11.2	8.3	1	1	1	0.43	0.21	0.17

The Henry constants for nitrogen and hydrogen were estimated from the fitted Sips isotherm parameters. Since the heterogeneity parameter for both gases was found to be close to unity ($n \approx 1$), the Sips model reduces to a Langmuir-type linear form in the low-pressure region. Under this condition, the Henry constant can be expressed as

$$K_H = b \cdot q_m \quad (9)$$

which represents the initial slope of the adsorption isotherm.

The larger Henry constant refers to a stronger tendency of the gas toward the adsorbent surface. The Henry constant of ammonia is the highest among the studied gases. Furthermore, the selectivity of ammonia compared to nitrogen is the highest and shows the affinity of ammonia toward adsorption on zeolite 13X.

The selectivity of ammonia over nitrogen decreases with increasing temperature (27.5 at 293 K to 8.3 at 313 K), indicating that adsorption is governed by exothermic physisorption interactions. A similar decreasing trend is observed for hydrogen, while nitrogen

remains the reference component. This behaviour confirms that higher temperatures reduce the adsorption affinity of weakly and moderately interacting gases, leading to lower selectivity values.

3.4. Breakthrough Adsorption Experiments

Breakthrough adsorption experiments on zeolite 13X were conducted at various adsorption pressures, using a feed gas with a constant ammonia concentration. The gas mixture, comprising ammonia, hydrogen, and nitrogen, was passed through the adsorption column, and the effluent was continuously monitored using a micro-GC. The micro-GC measured the gas composition every minute throughout the experiment. It is worth noting that the micro-GC is equipped with two columns: one designed for hydrogen analysis and the other for measurement of ammonia and nitrogen concentrations.

The breakthrough adsorption experiments were conducted in six runs at a temperature of 293 K, as presented in Table 6. As shown in the table, the experiments were carried out in two stages. In the first stage, the breakthrough tests were performed using a mixture of ammonia and nitrogen (run Nos. 1–3). In the second stage, hydrogen was added to the mixture to study its effect on the adsorption behaviour (run Nos. 4–6).

Table 6. Composition and conditions of breakthrough adsorption experiments on zeolite 13X at 293 K.

Run No.	NH ₃ Mole %	H ₂ Mole%	N ₂ Mole%	Flowrate (mL/min)
1	20	0	80	50
2	20	0	80	50
3	10	0	90	50
4	10	10	80	50
5	10	10	80	100
6	10	10	80	100

The results of each run are reported in Table 7. In the first run, a gas mixture consisting of 20 mole% ammonia and 80 mole% nitrogen was passed through an adsorption column packed with 100 g of zeolite 13X, at a temperature of 293 K and a pressure of 1.26 bar. The concentration of the effluent gas was continuously monitored using a micro-GC. After 138 min, the first breakthrough of ammonia was detected, indicating that zeolite 13X effectively adsorbed ammonia molecules during this period.

Table 7. The results of the breakthrough adsorption experiment for zeolite 13X and adsorption capacity, Q (mole NH₃/kg adsorbent) at 293 K.

Run No.	Zeolite 13X Mass (gr)	Pressure (bar)	Adsorption Time (min)	Q (mole/kg)	Q _{static} (mole/kg)
1	50	1.26	138	1.23	0.91
2	50	0.68	85	0.76	0.50
3	50	0.70	125	0.56	0.23
4	50	1.46	98	0.44	0.51
5	100	2.70	139	0.62	0.95
6	100	2.80	110	0.49	0.98

This result demonstrates the strong affinity of zeolite 13X for ammonia, with a noticeable delay in ammonia detection in the effluent, while nitrogen, having a much lower adsorption affinity, passed through the column almost immediately. The delayed breakthrough time confirms the selective adsorption behaviour of zeolite 13X toward ammonia,

making it a promising material for ammonia separation or purification processes from nitrogen-rich gas mixtures.

In the second run, the effect of pressure on ammonia adsorption was investigated by reducing the system pressure to 0.7 bar while keeping the ammonia–nitrogen mixture composition the same as in the first run. As expected, the lower pressure led to a decrease in the adsorption capacity of the bed. This was observed by the earlier breakthrough of ammonia, with the first peak detected after 85 min. The reduced residence time of ammonia on the adsorbent surface highlights the pressure-dependent nature of the adsorption process, consistent with physical adsorption behaviour.

In the third run, the influence of ammonia concentration in the feed gas was examined. The ammonia content in the ammonia–nitrogen mixture was reduced to 10 mole%, while maintaining the same temperature conditions as in the first run. Under these conditions, the first breakthrough of ammonia occurred after 125 min. Despite the lower ammonia concentration, the delayed breakthrough compared to the second run (with reduced pressure) suggests that concentration plays a significant role in adsorption dynamics, but the total adsorption loading was inherently lower due to the reduced amount of ammonia in the feed.

These observations confirm that both pressure and ammonia concentration substantially affect the adsorption performance of zeolite 13X. Higher pressure and higher ammonia content favour greater adsorption capacity and delayed breakthrough, supporting the material's suitability for selective ammonia capture under optimised conditions.

In the second stage of the experiments, hydrogen was introduced into the gas stream at a concentration of 10 mole%. In the fourth run, the total system pressure was set to 1.46 bar, and the gas mixture comprising ammonia, nitrogen, and hydrogen was passed through the zeolite 13X adsorption column. The ammonia breakthrough was observed after 98 min. Notably, hydrogen and nitrogen showed negligible adsorption on zeolite 13X, as they were detected in the effluent almost immediately after the start of the experiment. This result confirms the weak interaction of hydrogen and nitrogen with the adsorbent and highlights the high selectivity of zeolite 13X for ammonia under these conditions.

In the fifth run, the system pressure was increased to 2.7 bar while maintaining the same gas composition. Under these conditions, the ammonia breakthrough occurred after 139 min, indicating a significant enhancement in the adsorption capacity of zeolite 13X at elevated pressure. The extended breakthrough time suggests that higher pressure promotes greater adsorption of ammonia molecules due to increased driving force and improved adsorbate–adsorbent interactions. Figures 8 and 9 shows the ammonia breakthrough curve for the fourth and fifth runs. These figures show that ammonia adsorption is increased with the pressure of the systems. These results demonstrate that while hydrogen and nitrogen have minimal interaction with zeolite 13X, the adsorption of ammonia is strongly influenced by pressure. Increasing the system pressure enhances the overall adsorption performance, making pressure optimisation a key factor in designing efficient ammonia separation systems using zeolite 13X.

To evaluate the reusability of the adsorbent, zeolite 13X was regenerated after the fifth run using the desorption procedure described in Section 2.2. Following regeneration, a sixth breakthrough adsorption experiment was carried out under the same conditions as the fifth run, with a system pressure of 2.7 bar and the same gas composition.

The results showed that ammonia breakthrough occurred after 110 min, which is slightly earlier than in the fifth run (139 min) but still indicates a relatively high adsorption capacity. This minor decrease in performance suggests that the regeneration process was largely effective and that zeolite 13X retains its adsorption properties after use.

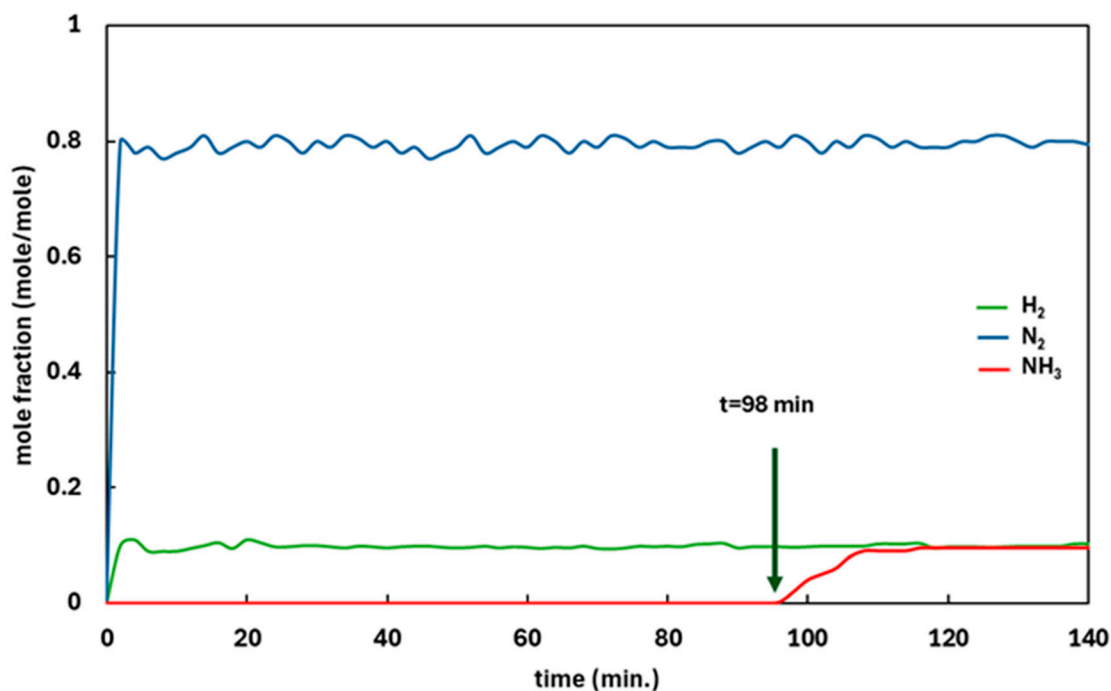


Figure 8. Experimental data for the breakthrough behaviour of zeolite 13X at 293 K, 1.46 bar pressure and a feed flow rate of 50 mL/min.

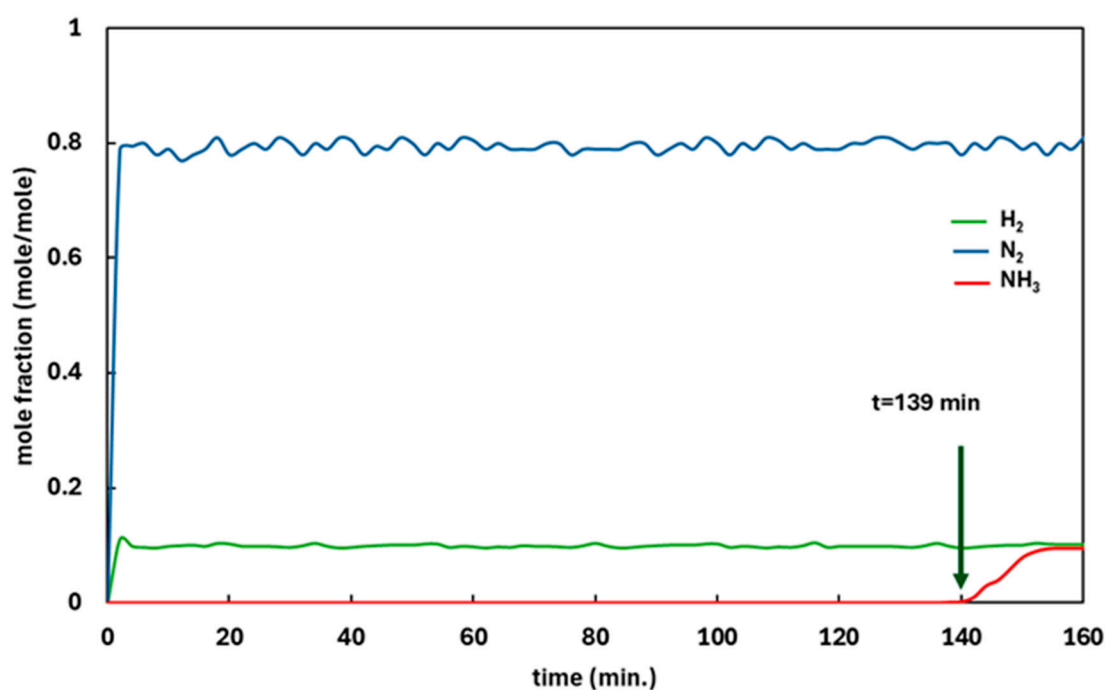


Figure 9. Experimental data for the breakthrough behaviour of zeolite 13X at 293 K, 2.7 bar pressure and a feed flow rate of 100 mL/min.

These findings imply that zeolite 13X exhibits good stability and can be reused for ammonia separation in multi-component gas streams with minimal loss in performance. This reusability enhances the economic and operational feasibility of using zeolite 13X in practical adsorption-based separation processes. Further cycles of adsorption–desorption would help to more thoroughly assess the long-term durability and regeneration efficiency of the adsorbent.

Table 6 compares the dynamic adsorption capacities obtained from breakthrough experiments with the equilibrium capacities derived from static ammonia isotherms at 293 K. The results show that both values are generally comparable, but some deviations are observed depending on operating conditions. At lower ammonia partial pressures, the dynamic capacities are slightly higher than the equilibrium values, while at higher partial pressures the equilibrium capacities become higher. These differences are mainly attributed to mass transfer zone (MTZ) effects, axial dispersion, and non-isothermal behaviour during breakthrough, as well as possible limitations in equilibrium measurements due to slow adsorption kinetics on zeolite 13X.

4. Conclusions

Zeolite 13X is a suitable adsorbent for the separation of ammonia from gas mixtures containing nitrogen and hydrogen. New experimental adsorption isotherm data were acquired for ammonia, hydrogen, and nitrogen in the temperature range of 293–313 K and at pressures up to 5 bar.

The adsorption performance of zeolite 13X for separating ammonia from gas mixtures containing nitrogen and hydrogen was systematically investigated through a series of breakthrough experiments under varying pressure and composition conditions. The results demonstrated that zeolite 13X exhibits a strong and selective affinity for ammonia, while nitrogen and hydrogen show negligible adsorption. This selectivity is attributed to the smaller kinetic diameter of ammonia, its higher polarizability, and stronger dipole moment, which enhance its interaction with the zeolite's polar surface.

The breakthrough time for ammonia was found to increase with system pressure, indicating that adsorption capacity is pressure-dependent and can be optimised for improved performance. Moreover, the presence of hydrogen in the gas stream had no significant impact on ammonia adsorption, further confirming the poor interaction of hydrogen with the adsorbent.

Importantly, zeolite 13X showed good regeneration potential, maintaining much of its adsorption capacity after thermal desorption and reuse in a subsequent run. These findings confirm that zeolite 13X is an effective and reusable adsorbent for selective ammonia capture in multi-component gas streams, making it a promising material for applications such as ammonia recovery, gas purification, and emission control in industrial processes.

However, despite these promising results, there is still much work to be done to translate these findings into practical industrial applications. Further research is needed to assess long-term stability over multiple adsorption–desorption cycles, evaluate performance under real process conditions, and optimise system design and scale-up strategies for continuous industrial use.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16115481/s1>, The isothermal experimental data are presented in the supplementary information. Tables S1: The Experimental adsorption data for pure ammonia on Zeolite 13X at different temperatures; Tables S2: The Experimental adsorption data for pure hydrogen on Zeolite 13X at different temperatures; Tables S3: The Experimental adsorption data for pure nitrogen on Zeolite 13X at different temperatures.

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References

1. Erisman, J.W.; Sutton, M.A.; Galloway, J.; Klimont, Z.; Winiwarter, W. How a century of ammonia synthesis changed the world. *Nat. Geosci.* **2008**, *1*, 636–639. [\[CrossRef\]](#)
2. Ertl G. Jennings, J. *Catalytic Ammonia Synthesis*; Plenum: New York, NY, USA, 1991; pp. 109–132.
3. Efficiency, E. Tracking industrial energy efficiency and CO₂ emissions. *Int. Energy Agency* **2007**, *34*, 1–12.
4. Smith, C.; Hill, A.K.; Torrente-Murciano, L. Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape. *Energy Environ. Sci.* **2020**, *13*, 331–344. [\[CrossRef\]](#)
5. Rouwenhorst, K.H.; Van der Ham, A.G.; Lefferts, L. Beyond Haber-Bosch: The renaissance of the Claude process. *Int. J. Hydrogen Energy* **2021**, *46*, 21566–21579. [\[CrossRef\]](#)
6. Rouwenhorst, K.H.; Van der Ham, A.G.; Mul, G.; Kersten, S.R. Islanded ammonia power systems: Technology review & conceptual process design. *Renew. Sustain. Energy Rev.* **2019**, *114*, 109339. [\[CrossRef\]](#)
7. Lin, B.; Wiesner, T.; Malmali, M. Performance of a small-scale Haber process: A techno-economic analysis. *ACS Sustain. Chem. Eng.* **2020**, *8*, 15517–15531. [\[CrossRef\]](#)
8. Sánchez, A.; Martín, M. Optimal renewable production of ammonia from water and air. *J. Clean. Prod.* **2018**, *178*, 325–342. [\[CrossRef\]](#)
9. Huberty, M.S.; Wagner, A.L.; McCormick, A.; Cussler, E. Ammonia absorption at haber process conditions. *AIChE J.* **2012**, *58*, 3526–3532. [\[CrossRef\]](#)
10. Lin, B.; Hsieh, I.M.; Malmali, M. Rapid pressure swing adsorption for small scale ammonia separation: A proof-of-concept. *J. Adv. Manuf. Process.* **2021**, *3*, e10077. [\[CrossRef\]](#)
11. Helminen, J.; Helenius, J.; Paatero, E.; Turunen, I. Comparison of sorbents and isotherm models for NH₃-gas separation by adsorption. *AIChE J.* **2000**, *46*, 1541–1555. [\[CrossRef\]](#)
12. Helminen, J.; Helenius, J.; Paatero, E.; Turunen, I. Adsorption equilibria of ammonia gas on inorganic and organic sorbents at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 391–399. [\[CrossRef\]](#)
13. Rodrigues, C.C.; de Moraes, D., Jr.; Da Nobrega, S.W.; Barboza, M.G. Ammonia adsorption in a fixed bed of activated carbon. *Bioresour. Technol.* **2007**, *98*, 886–891. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Zeng, T.; Huang, H.; Kobayashi, N.; Li, J. Performance of an activated carbon-ammonia adsorption refrigeration system. *Nat. Resour.* **2017**, *8*, 611–631. [\[CrossRef\]](#)
15. Cardenas, C.; Sigot, L.; Vallières, C.; Marsteau, S.; Marchal, M.; Latifi, A.M. Ammonia capture by adsorption on doped and undoped activated carbon: Isotherm and breakthrough curve measurements. *Sep. Purif. Technol.* **2023**, *313*, 123454. [\[CrossRef\]](#)
16. Ouyang, W.; Zheng, S.; Wu, C.; Hu, X.; Chen, R.; Zhuo, L.; Wang, Z. Dynamic ammonia adsorption by FAU zeolites to below 0.1 ppm for hydrogen energy applications. *Int. J. Hydrogen Energy* **2021**, *46*, 32559–32569. [\[CrossRef\]](#)
17. Saha, D.; Deng, S. Characteristics of ammonia adsorption on activated alumina. *J. Chem. Eng. Data* **2010**, *55*, 5587–5593. [\[CrossRef\]](#)
18. Vo, H.T.; Kim, J.; Kim, N.Y.; Lee, J.-K.; Joo, J.B. Effect of pore texture property of mesoporous alumina on adsorption performance of ammonia gas. *J. Ind. Eng. Chem.* **2020**, *91*, 129–138. [\[CrossRef\]](#)
19. Zheng, C.; Xie, Y.; Niu, Y.; Wang, C.; Hu, J.; Kang, K.; Song, H.; Bai, S. Modeling of multi-temperature Type I and II benzene/ammonia adsorption isotherms: Dual LF model and linearized DR model. *Sep. Purif. Technol.* **2024**, *338*, 126246. [\[CrossRef\]](#)
20. San, T.Z.; Park, J.H.; Win, M.Z.; Ugli, L.S.D.; Oo, W.; Yi, K.B. Enhanced ammonia adsorption-desorption properties of synthesized zeolite-carbon composite with the effect of Si/Al ratio. *Sep. Purif. Technol.* **2025**, *353*, 128560. [\[CrossRef\]](#)
21. Yue, B.; Liu, S.; Chai, Y.; Wu, G.; Guan, N.; Li, L. Zeolites for separation: Fundamental and application. *J. Energy Chem.* **2022**, *71*, 288–303. [\[CrossRef\]](#)
22. Cho, K.; Yoon, H.C.; Beum, H.T.; Kim, S.H.; Lee, C.H.; Kim, J.-N. Facile synthesis of carbon-based nanoporous adsorbent exhibiting high ammonia uptake under low pressure range. *Microporous Mesoporous Mater.* **2020**, *307*, 110460. [\[CrossRef\]](#)
23. White, J.C.; Dutta, P.K.; Shqau, K.; Verweij, H. Synthesis of Ultrathin Zeolite Y Membranes and their Application for Separation of Carbon Dioxide and Nitrogen Gases. *Langmuir* **2010**, *26*, 10287–10293. [\[CrossRef\]](#)
24. de Pietre, M.K.; Freitas, J.C. Fundamental studies on zeolite-adsorbate interactions: Designing a better aluminosilicate adsorbent for pollutants' removal. *Environ. Earth Sci.* **2022**, *81*, 17. [\[CrossRef\]](#)
25. Aristizabal-González, C.; Munoz-Senmache, J.C.; Prerna Siepmann, J.I.; Tsapatsis, M.; Hernandez-Maldonado, A.J. Ammonia Adsorption at High Temperature and Pressure Using Sodium Containing Aluminosilicates: Selectivity over Nitrogen and Multicycle Working Capacities. *Ind. Eng. Chem. Res.* **2025**, *64*, 4027–4039. [\[CrossRef\]](#)

26. Golipour, H.; Mokhtarani, B.; Mafi, M.; Moradi, A.; Godini, H.R. Experimental measurement for adsorption of ethylene and ethane gases on copper-exchanged zeolites 13X and 5A. *J. Chem. Eng. Data* **2020**, *65*, 3920–3932. [[CrossRef](#)]
27. Rahmani, M.; Mokhtarani, B.; Mafi, M.; Rahmanian, N. Acid gas removal by superhigh silica ZSM-5: Adsorption isotherms of hydrogen sulfide, carbon dioxide, methane, and nitrogen. *Ind. Eng. Chem. Res.* **2022**, *61*, 6600–6610. [[CrossRef](#)]
28. Rahmani, M.; Mokhtarani, B.; Rahmanian, N. High pressure adsorption of hydrogen sulfide and regeneration ability of ultra-stable Y zeolite for natural gas sweetening. *Fuel* **2023**, *343*, 127937. [[CrossRef](#)]
29. Ruthven, D.M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons: Hoboken, NJ, USA, 1984.
30. Tóth, J. *Adsorption: Theory, Modeling, and Analysis*; Marcel Dekker: New York, NY, USA, 2001.
31. Moura, P.A.S.; Bezerra, D.P.; Vilarrasa-Garcia, E.; Bastos-Neto, M.; Azevedo, D.C.S. Adsorption Equilibria of CO₂ and CH₄ in Cation-Exchanged Zeolites 13X. *Adsorption* **2016**, *22*, 71–80. [[CrossRef](#)]
32. Donohue, M.D.; Aranovich, G.L. Classification of Gibbs adsorption isotherms. *Adv. Colloid Interface Sci.* **1998**, *76*, 137–152. [[CrossRef](#)]
33. Reich, R.; Danisi, R.M.; Kluge, T.; Eiche, E.; Kolb, J. Structural and compositional variation of zeolite 13X in lithium sorption experiments using synthetic solutions and geothermal brine. *Microporous Mesoporous Mater.* **2023**, *359*, 112623. [[CrossRef](#)]
34. Ma, H.; You, Z.; Huang, Y.; Liu, W.; Zhai, X.; She, X. Innovative Design of Li Modified Zeolite 13X for Efficient and Selective Adsorption of Ammonia Applied for Hydrogen Energy. *SSRN* **2025**. [[CrossRef](#)]
35. Kanezashi, M.; Yamamoto, A.; Yoshioka, T.; Tsuru, T. Characteristics of ammonia permeation through porous silica membranes. *AIChE J.* **2010**, *56*, 1204–1212. [[CrossRef](#)]
36. Ridha, F.N.; Webley, P.A. Anomalous Henry's law behavior of nitrogen and carbon dioxide adsorption on alkali-exchanged chabazite zeolites. *Sep. Purif. Technol.* **2009**, *67*, 336–343. [[CrossRef](#)]
37. Delgado, J.A.; Águeda, V.; Uguina, M.; Sotelo, J.; Brea, P.; Grande, C.A. Adsorption and diffusion of H₂, CO, CH₄, and CO₂ in BPL activated carbon and 13X zeolite: Evaluation of performance in pressure swing adsorption hydrogen purification by simulation. *Ind. Eng. Chem. Res.* **2014**, *53*, 15414–15426. [[CrossRef](#)]
38. Kerry, F.G. *Industrial Gas Handbook: Gas Separation and Purification*; CRC Press: Boca Raton, FL, USA, 2007.

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