



Pelletized adsorbent of pillar[5]quinone for efficient and fast adsorption of NH₃

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ABSTRACT

Developing advanced pelletized adsorbents for efficient separation of NH₃ from tail gas by pressure swing adsorption is highly desired. Herein, pillar[5]arene-based adsorbent pellets were prepared and tested for low-concentration NH₃ adsorption. The results showed that the pelletized adsorbent of 90 wt% pillar[5]quinone with the binder 10 wt% sucrose (P[5]Q-0.9@Sucrose) rapidly achieved > 50 % NH₃ capacity (6.48 mmol/g) within 29 s and reached 83 % of full capacity (12.82 mmol/g) in the subsequent 153 s at 298.2 K and 100 KPa. Meanwhile, P[5]Q-0.9@Sucrose obviously excluded the adsorption of competitive gases N₂ and H₂, resulting in high ideal selectivities for NH₃/N₂ (5040) and NH₃/H₂ (638). Column breakthrough tests further verified the excellent separate performance of P[5]Q-0.9@Sucrose in efficiently adsorbing 3 % NH₃ in NH₃/N₂/H₂ mixture. P[5]Q-0.9@Sucrose pellets also exhibited good reusability and mechanical stability during recycle and wear tests, making it a great potential application in pressure swing adsorption NH₃ separation process.

1. Introduction

Ammonia (NH₃) is an important industrial feedstock with extensive applications in both the industrial and agricultural sectors. [1–3] However, NH₃ waste gases from various chemical production processes (e.g., synthetic ammonia, urea, and melamine production) are a major environmental concern. [4,5] These emissions pose severe threats to the environment and human health due to their high toxicity and potential to form secondary pollutants such as particulate matter and ozone when released into the atmosphere. [6–8] The separation and purification of NH₃ from waste gases are critical for mitigating these adverse effects. Up to now, several methods have been employed for NH₃ separation, including liquid-phase absorption, cryogenic separation, and pressure swing adsorption (PSA) techniques. [9–11] Each of these methods has its advantages and limitations. For example, liquid-phase absorption is hard to deal with low-concentration NH₃ gas, especially when dealing with large volumes of gas mixtures. On the other hand, cryogenic

separation technologies are usually faced with high costs and high energy consumption. Conversely, PSA technology has emerged as a promising alternative due to its advantages of rapid regeneration, low energy consumption, stable process operation, and high production capacity. The efficiency of PSA depends on the performance of the adsorbent, which must be capable of rapidly and selectively absorb NH₃ to saturation within 20–180 s. [12–14] Therefore, the selection and development of appropriate adsorbent materials is crucial for the efficiency of PSA processes.

In recent years, various porous materials have been developed for NH₃ adsorption, which include metal–organic frameworks (MOFs), zeolites, activated carbon, and other nanomaterials, etc. [15–19] On the one hand, the industrial application of PSA requires molding these materials into stable and efficient shapes, such as honeycombs, micro-pellets, or cylindrical structures. [20–22] On the other hand, traditional methods like surface coating or impregnation often suffer from limited adsorption capacity and coating durability. In contrast, the

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extrusion pelletization method, which involves mixing adsorbents with binders, offers advantages such as high mechanical strength, low solvent consumption, simple operation, and scalability. For example, Wu et al. successfully molded MOF powders into pellets via the binder-assisted pelletization method, achieved the selective separation of C_2 hydrocarbons and improved the mechanical properties of the pelleted adsorbents. [23] However, the extrusion process can significantly reduce mass transfer efficiency and further impair adsorption rates. Therefore, the successful implementation of PSA NH_3 separation process depends on the careful selection of suitable adsorbents and binders, as well as the appropriate pelletization production processes. Furthermore, it is also crucial to evaluate the ability of pelletized adsorbents to capture low-concentration NH_3 mixed gases in the fixed bed, which will help provide important evidence for their effectiveness in NH_3 PSA applications.

Pillar[n]arenes represent an emerging class of solid-phase adsorbents, characterized by their unique tunable cavity sizes and the ability to feature either electron-rich or electron-deficient interiors, which enable them to offer promising advantages in gas storage and selective separation. [24] For example, Ogoshi et al. successfully synthesized pillar[5]arene-based adsorbents with molecular-scale cavities, which showed exceptional size-selective adsorption and separation performance for various carbon–fluorine compound gases. [25] Inspired by this, electron-rich NH_3 molecules (with a kinetic diameter of ~ 3 Å) can be effectively adsorbed into the electron-deficient cavity of pillar[5]arenes (5.6 Å) due to favorable size-exclusion principles and complementary electronic interactions. Therefore, the specific properties of pillar[5]arene-based adsorbents enhance the efficiency of separating diluted NH_3 from complex gas mixtures, which makes its potential PSA applications.

Herein, the moulding of two powdered materials per-hydroxylated pillar[5]arene (OHP[5]A) and pillar[5]quinone (P[5]Q) into pelletized adsorbents was successfully carried out using three binders including hydroxyl-rich sucrose, polyvinyl butyral, and aluminum oxide with different mass ratios. Then the performance of pillar[5]arene-based powdered and pelletized adsorbents for selective adsorption of NH_3 was investigated in detail, and their diffusion time constants correlated by Fick's diffusion model were further evaluated for comparison. The thermodynamic parameters including adsorption enthalpies, Henry's law constants, and reaction equilibrium constants were also estimated by the correlation of the temperature dependence of NH_3 adsorption curve. At last, the NH_3 adsorption–desorption recycles and wear test were performed to assess the reusability and mechanical stability of pillar[5]arene-based adsorbent pellets.

2. Experimental

2.1. Materials

1,4-Dimethoxybenzene (99 %), boron trifluoride diethyl etherate (98 %), aluminum oxide (Al_2O_3 , 99 %), polyvinyl butyral (PVB, M.W. 90000–120000) and hydrochloric acid (HCl, 36 %) were purchased from the Shanghai Macklin Biochemical Co., Ltd. Paraformaldehyde (95 %) and boron tribromide (BBr_3 , 99 %) were provided by the Shanghai Titan Scientific Co., Ltd. 1,2-Dichloroethane (99 %), dichloromethane (99 %), chloroform (99 %), petroleum ether (99 %), ethanol (99 %) and sucrose (99 %) were obtained from the Tianjin Fuchen Chemical Reagent Co., Ltd. Nitrogen (N_2 , 99.999 v/v%), ammonia (NH_3 , 99.999 v/v%) and hydrogen (H_2 , 99.999 v/v%) were purchased from Jiangxi Huahong Special Gas Co., Ltd. The other chemicals were used without additional purification.

2.2. Synthesis of OHP[5]A and P[5]Q

The precursor dimethoxypillar[5]arene (DMP[5]) was firstly prepared following a procedure described in the literatures. [26,27] Subsequently, 0.59 g of DMP[5]A was dissolved in a 100 mL flask with 30

mL of chloroform. Next, 5.01 g of BBr_3 was added to the mixture under an ice-water bath with continuous stirring for 0.5 h. The reaction mixture was then maintained at room temperature with stirring for an additional 72 h. After the reaction was completed, water was added to the flask to remove unreacted BBr_3 , and the crude white precipitate was obtained. The precipitate was separated by filtration and washed successively with chloroform and 0.5 mol/L HCl solution. Finally, the obtained white solid was vacuum dried at 40 °C for 24 h to give white OHP[5]A powder. In addition, another precursor reddish-brown power P[5]Q was obtained by gradual oxidation of OHP[5]A in air. The structures of the adsorbents OHP[5]A and P[5]Q are shown in Fig. 1, which were confirmed by ^1H NMR and ^{13}C NMR (Figs. S1–S6).

2.3. Preparation of pillar[5]arene-based pelletized adsorbents

Scheme 1 shows the pelletization procedure of OHP[5]A or P[5]Q with various binders to form pillar[5]arene-based adsorbent pellets. Sucrose, Al_2O_3 , and PVB were used as the binder. The typical steps are as follows: First, sucrose was prepared into 10 wt% sucrose solution. Then, 0.9 g of powdered OHP[5]A and 1.0 g of sucrose solution were placed in a mortar, and ground repeatedly until a paste mixture was formed. Next, the paste mixture was prepared into the micro-pellets with diameter range of 2–2.1 mm using a roll plate and dried under vacuum at 60 °C for 12 h. Then the white micro-pellets OHP[5]A-0.9@Sucrose were successfully obtained, in which 0.9 denotes the mass fraction of OHP[5]A in the micro-pellets. Similarly, the other micro-pellets P[5]Q-0.9@Sucrose, P[5]Q-0.95@Sucrose, P[5]Q-0.85@Sucrose, P[5]Q-0.9@ Al_2O_3 , and P[5]Q-0.9@PVB were also prepared according to the case of OHP[5]A-0.9@Sucrose.

2.4. Characterizations

The molecular structures of DMP[5], OHP[5]A, and P[5]Q were characterized by ^1H NMR and ^{13}C NMR using a 400 MHz Bruker Avance III spectrometer. The N_2 adsorption–desorption isotherms of the samples were measured at 77 K using a Micromeritics Tristar II 3020 instrument, and the data obtained were analyzed using the NLDFT method to plot the pore size distribution curves. The Fourier transform infrared (FT-IR) spectra of the adsorbents were recorded using a Nicolet 6700 spectrometer. The microstructures of the samples were observed using a Hitachi S-3400 scanning electron microscope (SEM). The thermal stability of the adsorbents was tested using a PerkinElmer Diamond thermogravimetric analyzer (TG/DTA) under the N_2 atmosphere at a temperature rate of 10 K/min over the temperature ranges of 298–973 K.

2.5. Adsorption experiments

A self-designed dual-chamber volumetric apparatus (Scheme S1) was employed to measure the adsorption capacities and rates of NH_3 by the adsorbents. [28,29] The detailed procedure of NH_3 adsorption is listed in the Supporting Information. In order to guarantee the precision of the adsorption results, the adsorbents were degassed at 353 K and 0.1 kPa before the adsorption tests. For the dynamic breakthrough experiments (Scheme S2), the adsorbents were packed into an adsorption column and then purged with He gas at 353 K for 2 h to remove any residual moisture. Next, the breakthrough experiments were carried out at 303.2 K and the mixed gas ($NH_3/N_2/H_2 = 3\%/24.25\%/72.75\%$, 100 kPa) was injected into the device using a mass flow controller at a flow rate of 15–25 mL/min. Meanwhile, the composition and concentration of the effluent gases were analyzed using a mass spectrometer to determine whether the adsorption capacities of the adsorbents had been saturated. Additionally, the adsorbents were regenerated by continuous purging with He at 353 K for 2 h and then used directly in the next cycle of NH_3 adsorption experiments.

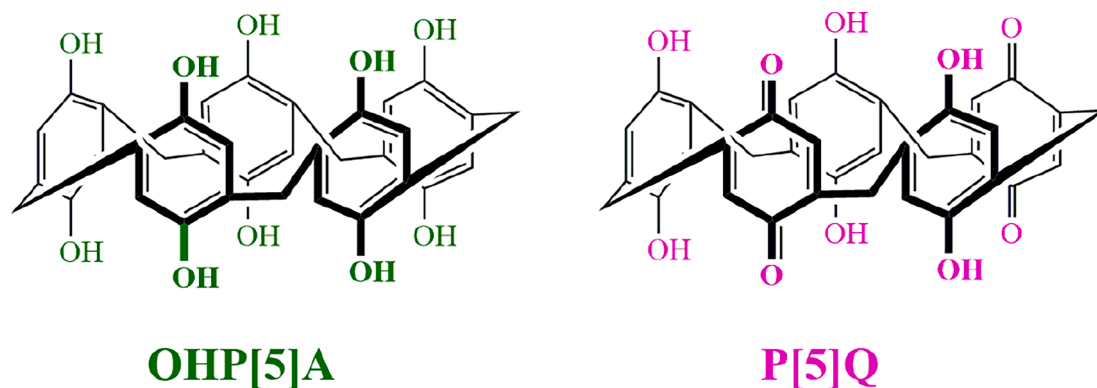
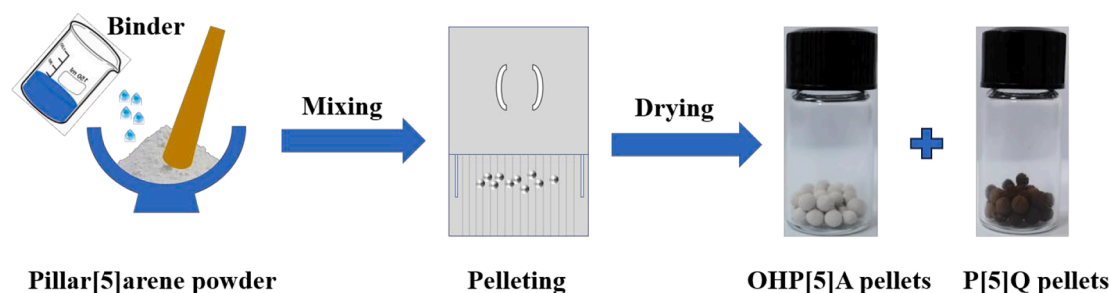


Fig. 1. Structures of the precursors OHP[5]A and P[5]Q.



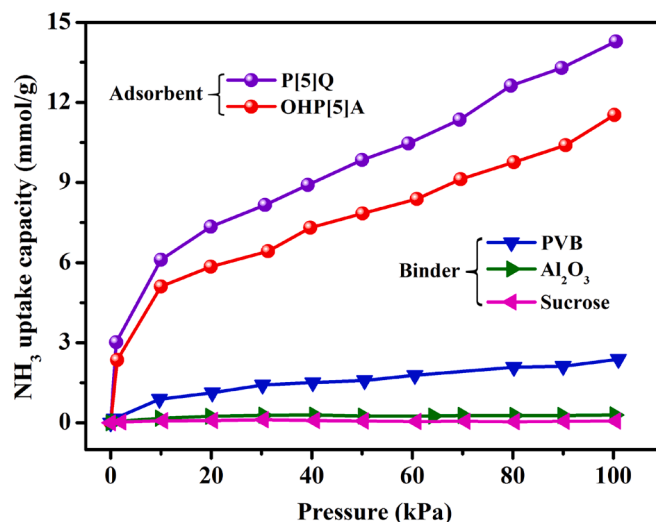
Scheme 1. The pelletization procedure of OHP[5]A or P[5]Q with various binders.

3. Results and discussion

The molding of powdered materials is the key to facilitate their practical application for low-concentration NH_3 separation and recovery in the PSA processes. Typically, the binder is used to bind with the particles of powdered materials through the strong intermolecular and/or electrostatic forces, which forms the cylindrical or spherical adsorbents. It is also seen from previous literatures [30] that tuning the particle sizes of pelletized adsorbents in the ranges of 1–5 mm can smoothly maintain both high adsorption efficiency and good mechanical properties. Thus, sucrose, PVB, and Al_2O_3 were selected as binders to cohere with powdered OHP[5]A and P[5]Q, respectively. The pillar[5]arene-based adsorbent pellets with particle sizes of about 2 mm were then successfully obtained using the extrusion-spheronization method.

3.1. NH_3 adsorption performance

The NH_3 adsorption capacities and uptake rates of precursors and binders were evaluated, and the results are plotted in Fig. 2. The results show that the adsorbents P[5]Q, OHP[5]A exhibit notable advantages in NH_3 adsorption, characterized by rapid uptake at low pressures and high capacity at atmospheric pressure. The NH_3 adsorption capacity of the precursor P[5]Q reached 50 % of the maximum capacity (14.29 mmol/g) at 298.2 K and 20 kPa, which means that P[5]Q has the potential to separate low-concentration NH_3 . Moreover, FT-IR was used to compare the changes in the characteristic peaks of P[5]Q-0.9@Sucrose adsorbent before and after NH_3 adsorption, and the results are plotted in Fig. S7. It can be observed that the characteristic absorption peaks corresponding to the in-plane stretching vibration of the C=O bonds (1649 cm^{-1}) undergo red-shift to 1631 cm^{-1} after NH_3 adsorption. The results indicate that the occurrence of a chemical interaction between the NH_3 molecules and P[5]Q-0.9@Sucrose adsorbent, rather than mere physical adsorption. Notably, the binder should minimize its impact on the pelletized adsorbent properties and the NH_3 adsorption capacity of the expected binder would be as low as possible. Compared with the binders

Fig. 2. NH_3 adsorption isotherms of P[5]Q, OHP[5]A, P[5]Q and three binders at 298.2 K.

PVB and Al_2O_3 , the NH_3 adsorption ability of sucrose was very weak and hence negligible. Meanwhile, sucrose offers economic advantages due to its low cost and wide availability. Based on the above considerations, sucrose can be selected as the appropriate binder for pelletization of P[5]Q and OHP[5]A.

The effect of binder dosages on the adsorption of NH_3 by pelletized adsorbents were evaluated, and the results are listed in Table 1 and Table S1 (Supporting Information). Obviously, the NH_3 adsorption capacities of the micro-pellets adsorbents slightly decrease as the binder dosage increases (Table 1, entries 1–4). Combined with the analysis of previous work, it is plausible that higher sucrose binder dosages lead to greater diffusion resistance and a reduction in accessible active sites.

Table 1

NH₃ adsorption capacities of powdered P[5]Q and pelleted P[5]Q-based adsorbents at 298.2 K.

Entry	State	Sample	NH ₃ adsorption capacity (mmol/g)		
			1 kPa	10 kPa	100 kPa
1	Powder	P[5]Q	3.02	6.11	14.29
2	Micro-pellet	P[5]Q-0.95@Sucrose	2.65	5.93	13.30
3	Micro-pellet	P[5]Q-0.9@Sucrose	2.21	5.60	12.90
4	Micro-pellet	P[5]Q-0.85@Sucrose	1.19	4.94	10.68
5	Micro-pellet	P[5]Q-0.9@Al ₂ O ₃	1.45	3.69	8.77
6	Micro-pellet	P[5]Q-0.9@PVB	0.71	3.25	8.52

[30–32] Moreover, sucrose binder with a dosage of 10 wt% has a limited negative effect on NH₃ uptake capacity. For example, the NH₃ capacity of P[5]Q-0.9@Sucrose reached 12.90 mmol/g (Table 1, entry 3), as well as OHP[5]A-0.9@Sucrose induced the capacity of 11.43 mmol/g (Table S1, entry 3). In contrast, the alkyl side chain structure of polymer PVB causes the steric hindrance effect that reduces the effective adsorption sites in the pelleted adsorbents, which can weaken their overall adsorption capacity (Table 1, entry 6). In addition, Al₂O₃ increases the porosity of the pelleted adsorbents and promotes the physical adsorption of NH₃ molecules, which may be the reason for moderate performance (Table 1, entry 5). Additionally, the strength tests show that the pelleted adsorbents containing the binder of 5 wt% sucrose were prone to pulverization, whereas those containing the binder of 15 wt% sucrose negatively affected NH₃ adsorption performance. Besides, the hydroxyl groups in sucrose facilitate the formation of hydrogen bonds with the quinone groups present in P[5]Q, thereby enhancing the mechanical strength of the pelleted adsorbent. At the same time, the inclusion of 10 wt% sucrose only contributes to a negligible theoretical NH₃ adsorption capacity of 0.01 mmol/g. As a result, 10 wt% sucrose was identified as the best suitable binder dosage, effectively balancing mechanical strength and NH₃ adsorption capacity.

3.2. Characterization of pelleted adsorbents

The morphological features of untreated pillar[5]arene precursors and pelleted adsorbents containing the binder sucrose were observed using SEM, as shown in Fig. 3. Clearly, it can be seen that the powdered OHP[5]A and P[5]Q precursors exhibit elongated rod-shaped particles with diameters of about 5–15 μ m, which are randomly scattered (Fig. 3a and 3c). The SEM images of pelleted adsorbents showed that the precursor particles were transformed into block structures under the action of the binder sucrose (Fig. 3b and 3d). In addition, the N₂ adsorption–desorption tests (Fig. S8) indicate that P[5]Q-0.95@Sucrose and OHP[5]A-0.95@Sucrose pelleted adsorbents exhibit very low specific surface areas, which have significantly reduced compared with the powdered precursors (Table S2). Furthermore, the FT-IR spectrum of P[5]Q-0.9@Sucrose exhibited characteristic absorption peaks at 1649 cm⁻¹ (in-plane stretching vibration of C=O) and 1128 cm⁻¹ (stretching vibration of C-O), which correspond to P[5]Q and sucrose, respectively. Therefore, these findings are consistent with the results of SEM, which suggests effective integration between the powdered pillar[5]arene precursors and the binder sucrose.

It is seen from Fig. S9 that the FT-IR spectra of precursors and pelleted adsorbents are very similar, implying that the adsorbed sites from pillar[5]arene are well retained for NH₃ adsorption. Furthermore, the TGA results indicate that the decomposition curves of the pelleted adsorbents are approximately the same as those of the precursor, suggesting that a small amount of binder does not have a large impact on the thermal stability of the pelleted adsorbents (see Fig. S10). It is worth noting that the decomposition temperature ($T_D > 450$ K) of the pelleted adsorbents, which shows their good stability under high-temperature desorption conditions.

3.3. NH₃ adsorption selectivity

The impact of temperatures and pressures on the NH₃ adsorption performance of the pelleted adsorbents were further investigated. The

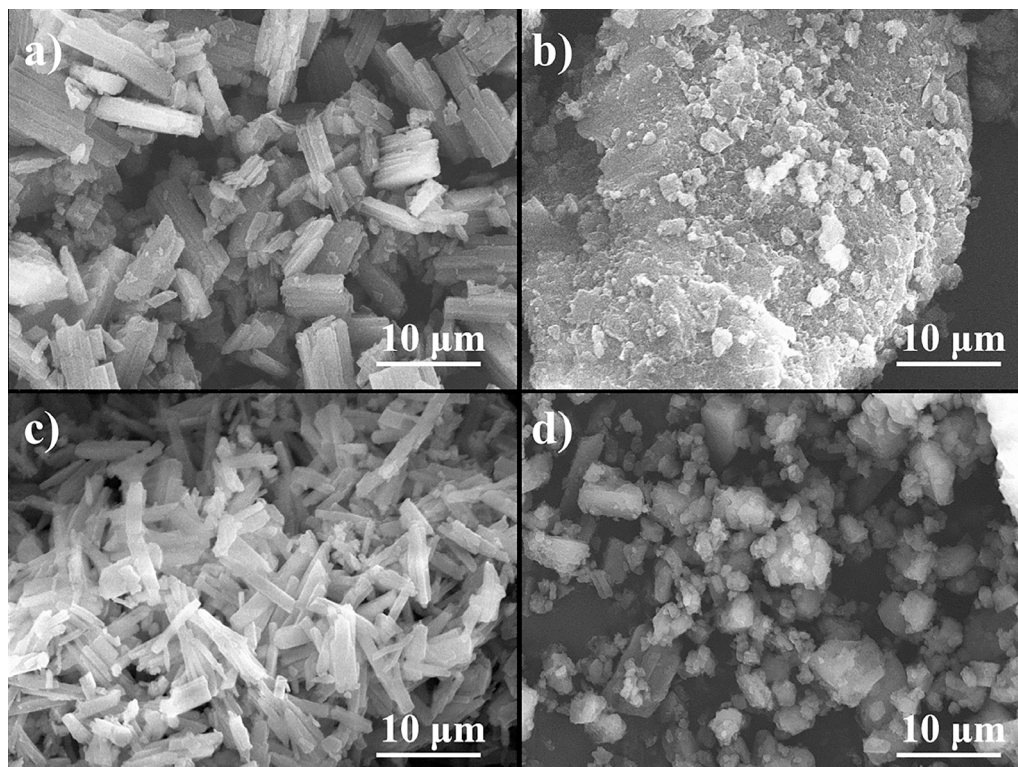


Fig. 3. SEM images of (a) OHP[5]A, (b) OHP[5]A-0.9@Sucrose, (c) P[5]Q, and (d) P[5]Q-0.9@Sucrose.

NH_3 adsorption isotherms fitted using the Langmuir model (see Fig. 4a and 4b). The results show the adsorption capacities of P[5]Q-0.9@Sucrose increases rapidly at 0–15 kPa, showing its good application for the adsorption of diluted NH_3 gas. In addition, the NH_3 adsorption capacities of P[5]Q-0.9@Sucrose and OHP[5]A-0.9@Sucrose decrease with increasing temperature, confirming the exothermic nature of NH_3 adsorption process. Furthermore, the increase in the partial pressure of NH_3 has the positive effect on their NH_3 adsorption capacities. The NH_3 adsorption performance of P[5]Q-0.9@Sucrose at 100 kPa is better than that of OHP[5]A-0.9@Sucrose, highlighting its excellent potential for NH_3 adsorption and separation.

In industrial waste gases, the presence of various gases (e.g., H_2 , N_2) coexisting with NH_3 often leads to competitive adsorption, which reduces the separation selectivity of adsorbents [28,29]. Then, the H_2 and N_2 adsorption capacities of pillar[5]arene-based pelletized adsorbents were measured to assess their NH_3 selective adsorption performance at 298.2 K and 100 kPa (Fig. 4c and 4d). The ideal selectivity of NH_3/H_2 and NH_3/N_2 for OHP[5]A-0.9@Sucrose and P[5]Q-0.9@Sucrose were calculated using ideal adsorbed solution theory (IAST) method [30–32], and the results are listed in Table S3 in the Supporting Information. It is found that the IAST selectivities of NH_3/N_2 and NH_3/H_2 for P[5]Q-0.9@Sucrose are 5040 and 638, respectively. This suggests that the pelletized adsorbent P[5]Q-0.9@Sucrose shows a very poor affinity with the competitive gases N_2 and H_2 , demonstrating its good NH_3 selective adsorption capability in the mixture of $\text{NH}_3/\text{N}_2/\text{H}_2$.

3.4. NH_3 adsorption rate

The adsorption rate is a critical parameter that influences the efficiency of PSA process. In industrial PSA applications, the contact times

between the adsorbents and the gases must be usually in the range of 20–180 s [13,14,33]. Hence, the NH_3 adsorption rates of powdered precursors and pelletized adsorbents were measured and the results are shown in Fig. 5. It can be observed that both P[5]Q-0.9@Sucrose and OHP[5]A-0.9@Sucrose achieved NH_3 -saturated adsorption within 5 min, which are slightly inferior to that of the powdered precursors P[5]Q and OHP[5]A. This shows that the pellets adsorbents have a relatively

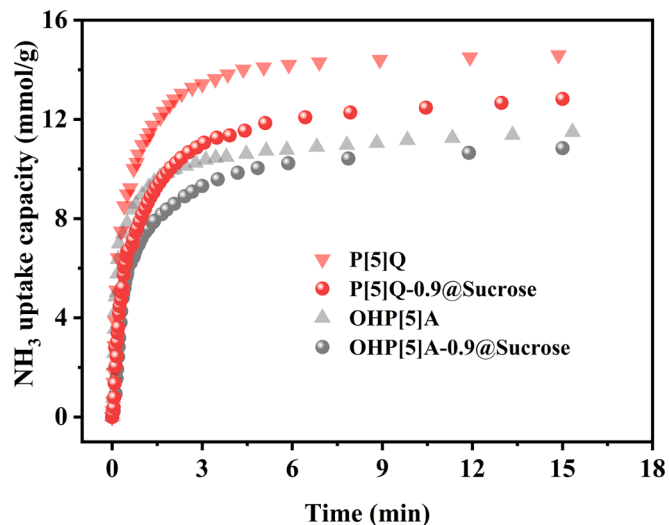


Fig. 5. NH_3 adsorption rate curves of powdered precursors and pelletized adsorbents at 298.2 K and 100 kPa.

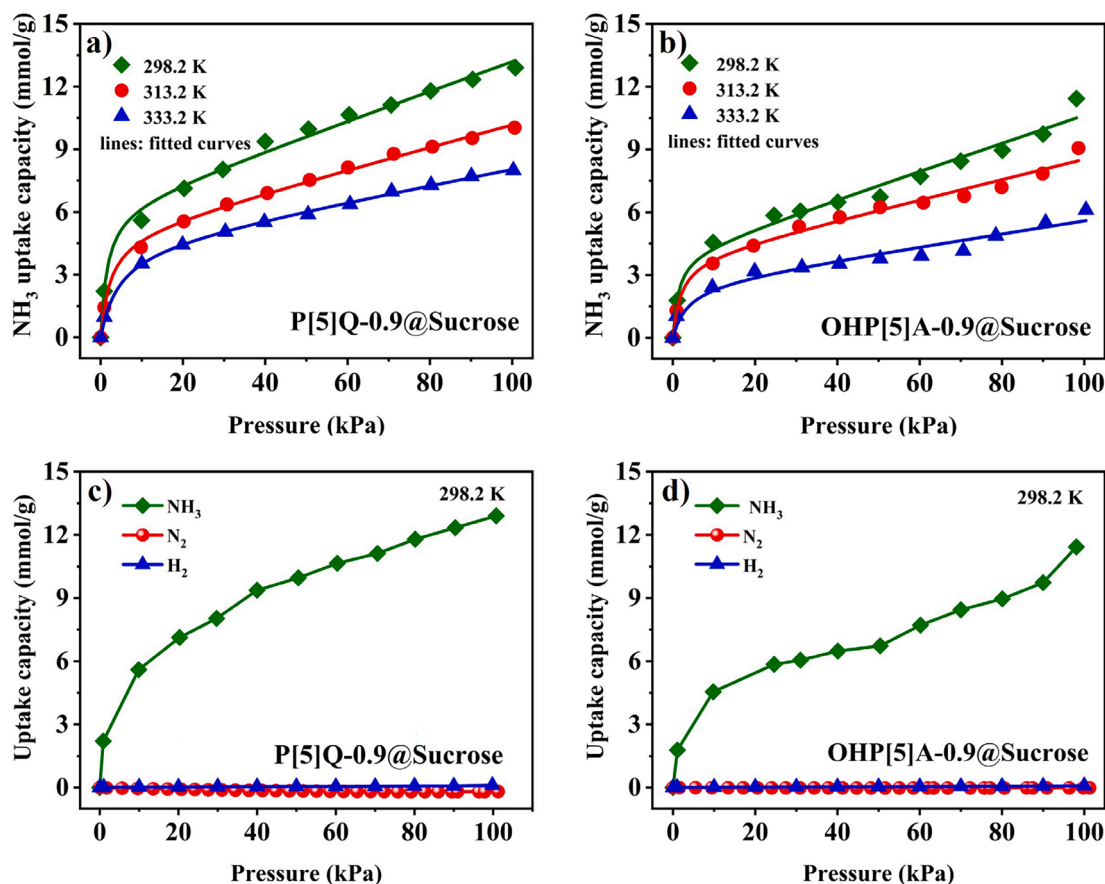


Fig. 4. The NH_3 adsorption isotherms of (a) P[5]Q-0.9@Sucrose and (b) OHP[5]A-0.9@Sucrose at 100 kPa, NH_3 , N_2 , and H_2 adsorption isotherms of (c) P[5]Q-0.9@Sucrose and (d) OHP[5]A-0.9@Sucrose at 298.2 K and 100 kPa.

high mass transfer resistance compared with the powder adsorbents. To investigate the changes in diffusion resistance of adsorbents before and after pelletization, the Fick diffusion model (Eq. (1)) [33–35] was further used to fit the 70 %–100 % NH_3 saturated adsorption data for powdered P[5]Q, OHP[5]A, and pelleted P[5]Q-0.9@Sucrose and OHP[5]A-0.9@Sucrose. The results indicate that the experimental data fit well with the Fick diffusion model (Fig. 6). The diffusion time constants of the pelleted adsorbents are found to decrease compared with the precursors, and all of the fitting R^2 are more than 0.93 (Table 2). This can be attributed to the denser packing within the pelleted adsorbents, which creates a little higher diffusion resistance than the powdered precursors. Nonetheless, the pelletized adsorbent P[5]Q-0.9@Sucrose could still achieve 50 % saturated NH_3 capacity (6.48 mmol/g) within 29 s at 298.2 K and 100 Kpa. This means that the pelleted adsorbents P[5]Q-0.9@Sucrose could rapidly capture NH_3 and have a good potential for NH_3 PSA process.

$$1 - \frac{m_t}{m_{\max}} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_e t}{\tau_c^2}\right) \quad (1)$$

3.5. NH_3 adsorption breakthrough performance

To further assess the NH_3 dynamic adsorption performance of the pelleted adsorbents, breakthrough curves of $\text{NH}_3/\text{N}_2/\text{H}_2$ (3 %/24.25 %/72.75 %) gas mixtures were measured via column breakthrough experiments. The breakthrough performance of NH_3 adsorption for P[5]Q-0.9@Sucrose and OHP[5]A-0.9@sucrose is shown in Fig. 7 and Fig. S11.

Table 2

The fitting diffusion time constants of precursors and adsorbents based on the 70% saturation NH_3 adsorption capacities.

Entry	State	Sample	Diffusion time (min^{-1})	R^2
1	Powder	OHP[5]A	0.1269	0.9369
2	Micro-pellet	OHP[5]A-0.9@Sucrose	0.0766	0.9903
3	Powder	P[5]Q	0.0962	0.9885
4	Micro-pellet	P[5]Q-0.9@Sucrose	0.0709	0.9962

It was observed that P[5]Q-0.9@Sucrose showed excellent retention time (up to 5108 $\text{s} \cdot \text{g}^{-1}$ at 15 mL min^{-1}) at 303.2 K with a flow rate range of 15–25 mL min^{-1} . The results suggest the suitability of P[5]Q-0.9@Sucrose the separation of dilute NH_3 under various dynamic conditions, which highlights its potential for practical applications. However, the breakthrough retention time of pelleted adsorbent OHP[5]A-0.9@sucrose is not satisfied. Additionally, it is seen from Fig. 7 that the H_2 and N_2 breakthrough occurs almost instantaneously, confirming the good selectivity of NH_3/H_2 and NH_3/N_2 for P[5]Q-0.9@Sucrose. These results demonstrate that the pelleted P[5]Q-0.9@Sucrose adsorbent can selectively adsorb and separate NH_3 from the gas mixture of NH_3 , H_2 , and N_2 .

3.6. Thermodynamic analysis

To gain more information about the NH_3 adsorption behavior of

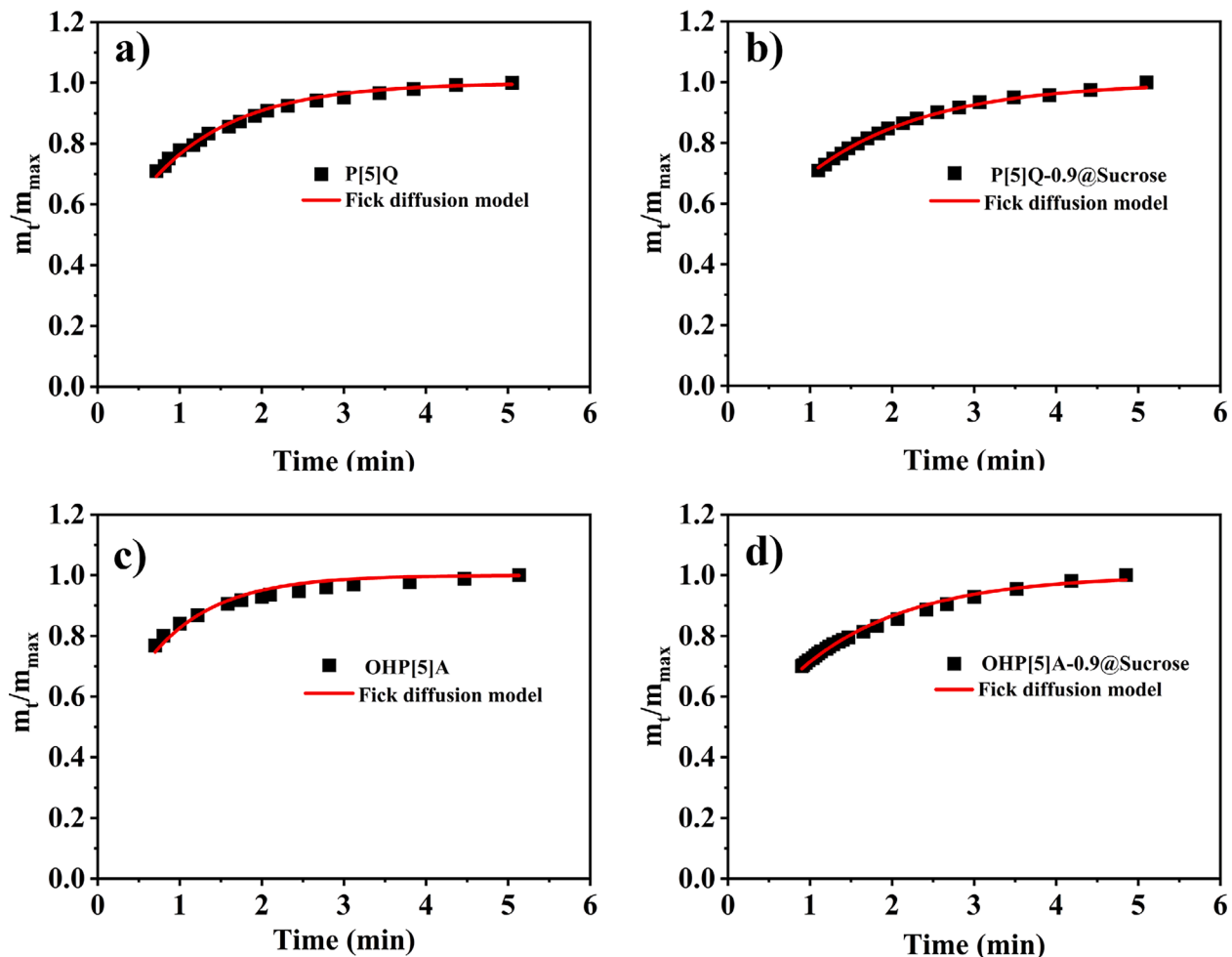


Fig. 6. Fitted curves of powdered precursors and pelletized adsorbents at 298.2 K and 100 kPa based on Fick diffusion model.

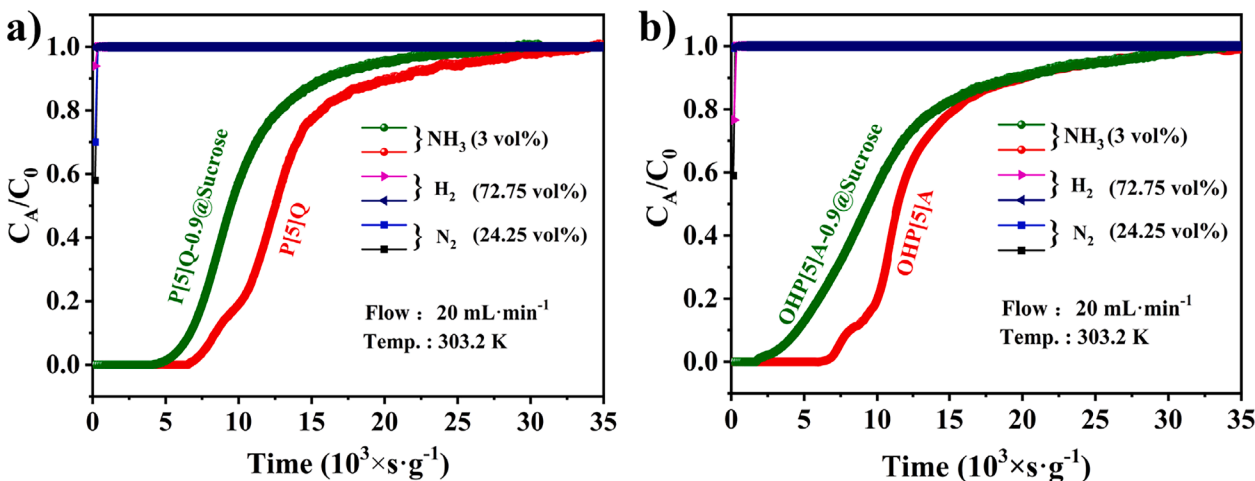


Fig. 7. Breakthrough curves for $\text{NH}_3/\text{N}_2/\text{H}_2$ (3 %/24.25 %/72.75 %) separation on (a) P[5]Q, P[5]Q-0.9@Sucrose and (b) OHP[5]A, OHP[5]A-0.9@sucrose at 303.2 K.

pelletized adsorbents P[5]Q-0.9@Sucrose and OHP[5]A-0.9@sucrose, their adsorption data were fitted and correlated with the empirical equations (Supporting Information, Eqs. S2-S4), which can clarify the contributions of physical and chemical adsorption to the NH_3 adsorption capacity [36,37]. The results are shown in Fig. 8 and the related thermodynamic parameters are also listed in Table 3. It can be observed that the NH_3 adsorption capacities increase significantly at 0–10 kPa and show nonlinear trends, which are attributed to the dominance of the chemical adsorption. As the NH_3 partial pressure continues to increase, the active sites gradually approach saturation, which means that the NH_3 adsorption process is tuned to be controlled by physical adsorption in the high-pressure range (10–100 kPa). Combined with the above FI-IR analysis, the chemical adsorption of the pelleted adsorbents is dominated by the quinone groups and electron deficient cavities, whereas physical adsorption occurs via Van der Waals interactions. Also, it can be seen from Table 3 that the equilibrium constants K for P[5]Q-0.9@Sucrose and OHP[5]A-0.9@sucrose decrease significantly with increasing temperature.

Furthermore, the chemisorption enthalpy (ΔH_{chem}), physisorption enthalpy (ΔH_{phy}), and other thermodynamic parameters of the pelleted adsorbents were calculated using classical thermodynamic equations (Supporting Information, Eqs. S5-S7). The results are summarized in Table S4. Notably, the Gibbs free energy (ΔG) of NH_3 adsorption is slightly greater than 0 for both pelleted adsorbents, suggesting that a

Table 3

The related thermodynamic parameters by fitting the adsorption isotherm of P[5]Q-0.9@Sucrose and OHP[5]A-0.9@Sucrose.

Sample	T (K)	q_m (mmol/g)	K (kPa ⁻¹)	H (kPa·g/mmole)	R^2
OHP[5]A-0.9@Sucrose	298.2	4.04	0.766	15.06	0.982
	313.2	3.83	0.522	20.95	0.989
	333.2	2.65	0.279	33.06	0.961
P[5]Q-0.9@Sucrose	298.2	6.29	0.641	14.29	0.994
	313.2	5.00	0.437	18.95	0.998
	333.2	4.51	0.226	26.91	0.999

weak thermodynamic driving force for the adsorption process. However, the efficient NH_3 adsorption tests suggest that chemisorption interactions between NH_3 molecules and the electron-deficient internal cavities of the pelletized adsorbents can overcome this theoretical limitation, and lead to effective adsorption. As shown in Fig. 9, linear fits of $\ln K$ versus $1/T$ and $\ln H$ versus $1/T$ were performed to determine the ΔH_{chem} and ΔH_{phy} values for P[5]Q-0.9@Sucrose and OHP[5]A-0.9@sucrose, respectively. The $\Delta H_{\text{(chem/phy)}}$ values were found to range from −14.95 kJ/mol to −24.76 kJ/mol, where P[5]Q-0.9@Sucrose compared to OHP[5]A-0.9@sucrose has a slightly higher ΔH_{chem} value. This provides evidence for the higher adsorption rate and

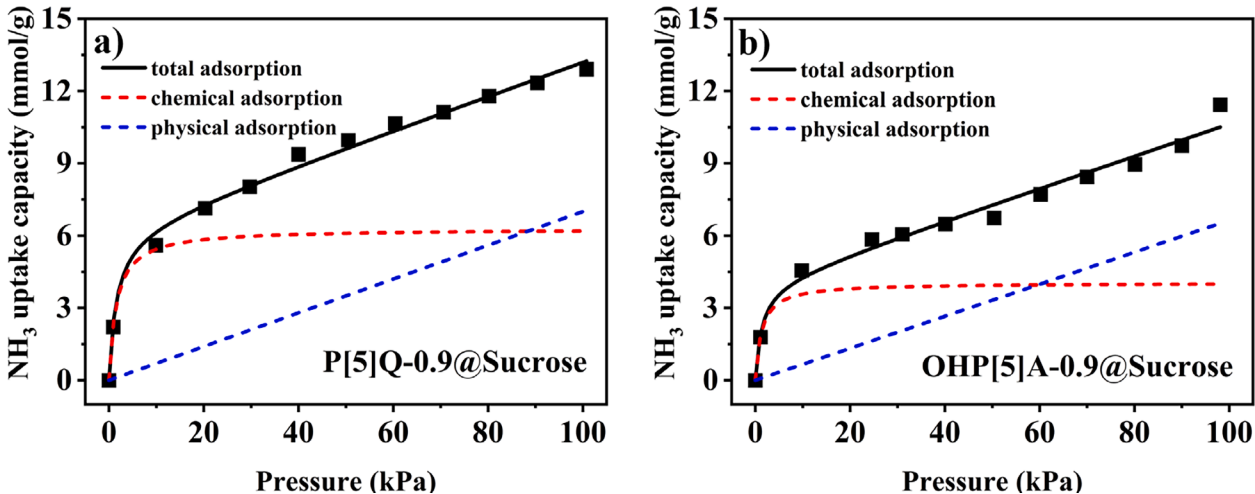


Fig. 8. The fitted total, chemical and physical adsorption curves of NH_3 on (a) P[5]Q-0.9@Sucrose and (b) OHP[5]A-0.9@sucrose at 298.2 K and 100 kPa.

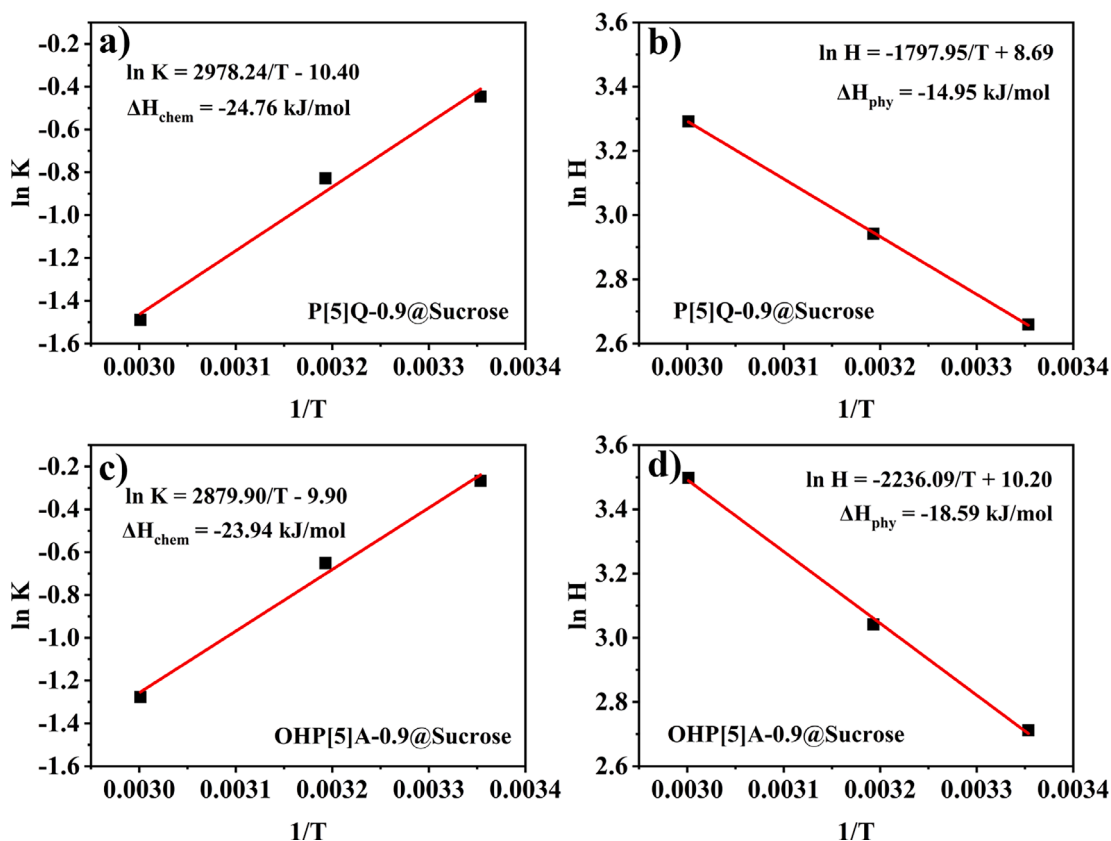


Fig. 9. Linear fit of $\ln K$ and $1/T$, $\ln H$ and $1/T$ for NH_3 adsorption in P[5]Q-0.9@Sucrose and OHP[5]A-0.9@Sucrose.

adsorption capacity of the former over the latter. Overall, the pelletized adsorbents P[5]Q-0.9@Sucrose has a great potential application in PSA NH_3 separation process.

3.7. Reusability and mechanical stability

The reusability of the pelletized adsorbent P[5]Q-0.9@Sucrose for NH_3 adsorption was tested as shown in Fig. 10a. It is found that the desorption temperature of 353.2 K only released most of captured NH_3 . Besides the residual fraction, the available NH_3 adsorption capacity of P[5]Q-0.9@Sucrose has no obvious change over the subsequent 7 cycles. Compared with the fresh P[5]Q-0.9@Sucrose, FT-IR patterns of the

reused P[5]Q-0.9@Sucrose did not change obviously (Fig. S12). These results demonstrate that the pelletized adsorbent P[5]Q-0.9@Sucrose show excellent reusability and stability for NH_3 adsorption and separation.

Furthermore, in order to gain the mechanical stability of P[5]Q-0.9@Sucrose adsorbent pellets, the wear test was examined in a planetary ball mill at 200 rpm for 2 h (Fig. 10b). The results indicate that the high-speed operation only makes the P[5]Q-0.9@Sucrose pellets have the weight loss of less than 4.20 % during 2 h. Most of the P[5]Q-0.9@Sucrose pellets remained spherical structure, demonstrating the good anti-pulverization ability of P[5]Q-0.9@Sucrose. Moreover, it was found that the mechanical strength of the pelletized adsorbents

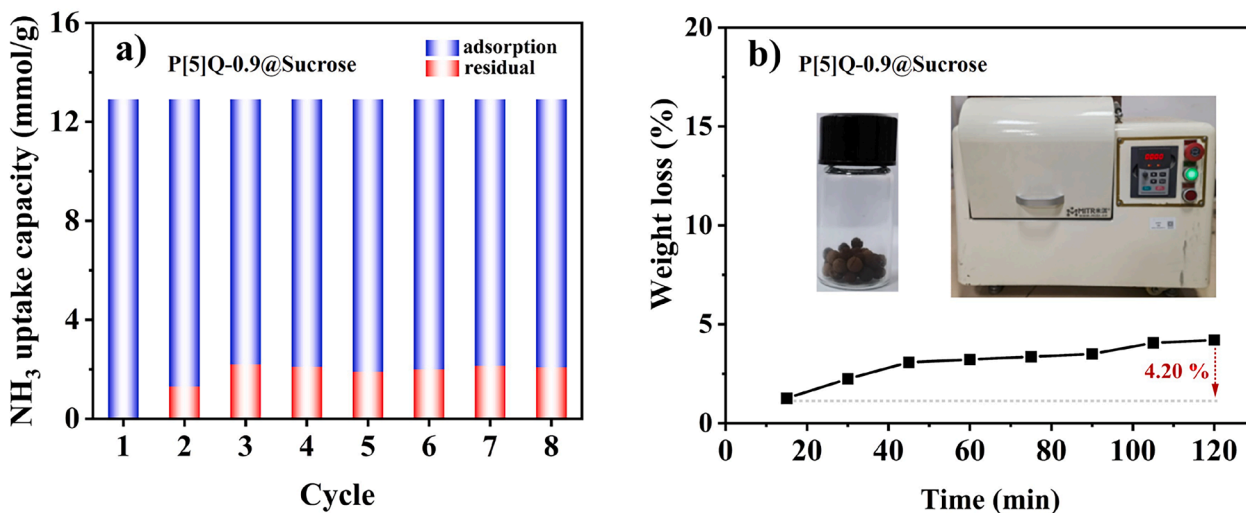


Fig. 10. (a) Recycling performance of P[5]Q-0.9@Sucrose for NH_3 adsorption. (b) The wear test for P[5]Q-0.9@Sucrose in a planetary ball mill with 200 rpm/min.

improves with the increase in the binder dosage used (Fig. S13). However, it is important to balance the binder dosage, as excessive dosages may negatively impact on porosity or NH_3 adsorption efficiency of the pelletized adsorbents. Overall, the pelletized adsorbent P[5]Q-0.9@Sucrose exhibits good reusability and high mechanical stability, highlighting its potential application in industrial NH_3 PSA process.

4. Conclusion

In summary, we have successfully demonstrated the importance of binder selection and pelletization conditions for optimizing the performance of the pelletized pillar[5]arene-based adsorbents for the adsorption and separation of low-concentration NH_3 in PSA applications. Among the tested binders, sucrose proved to be the most effective, significantly increased the mechanical strength and maintained high NH_3 adsorption capacities (12.9 mmol/g) of P[5]Q-0.9@Sucrose. Furthermore, the minimal contribution of the binder materials to the overall adsorption performance was also highlighted, as the presence of the binders in optimal weight (10 wt%) did not significantly affect NH_3 adsorption capacities. This demonstrates the feasibility of using these binder-assisted pelletized adsorbents in practical PSA processes without substantial loss in efficiency. Overall, the findings suggest that P[5]Q-0.9@Sucrose has the potential to achieve efficient and selective separation of NH_3 in industrial PSA applications.

CRediT authorship contribution statement

Wen-Qiang Gong: Investigation, Formal analysis. **Wei Hui:** Methodology, Writing – original draft, Writing – review & editing. **Yan Zhou:** Investigation. **Dan-Dan Cai:** Validation. **Ming-Shuai Sun:** Validation. **Duan-Jian Tao:** Conceptualization, Resources, Funding acquisition, Project administration. **Zheng-Hong Luo:** Investigation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2025.131648>.

Data availability

Data will be made available on request.

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