

DARE2X

Decentralised Ammonia production from Renewable Energy utilising novel sorption-enhanced plasma-catalytic Power-to-X technology

D3.1 - Summary of experiments WP3

Lead beneficiary: Hulteberg Chemistry and Engineering AB

Author(s): Bianca Rolim, Josephine Digné, Christian Hulteberg

DATE: 16/09/2024

Abstract: This report summarizes the experimental work performed in the development of stable sorption materials for the separation of NH_3 to enable sorption-enhanced plasma-catalytic reactors. The adsorption capacity, kinetic behaviour, and cycle capacity of different zeolite materials were evaluated. The best performing zeolite, Zeolite 5, showed the highest adsorption capacity and the easiest regeneration behaviour, and was used in experiments to collect data for the upscaling of the adsorption unit. It was also prepared in larger scale in the desired shape and size to be used in the pilot adsorber unit.



This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101083905.



Part of this project has also received funding from UK Research and Innovation.

PROJECT DATA	
Project Acronym	DARE2X
Project Title	Decentralised Ammonia production from Renewable Energy utilising novel sorption-enhanced plasma-catalytic Power-to-X technology
Project number	101083905
Call identifier	HORIZON-CL5-2021-D3-03
Topic identifier	HORIZON-CL5-2021-D3-03-02 Next generation of renewable energy technologies
Type of action	Research and Innovation Actions
Project Duration	36 months (From 1 st October 2022)
Coordinator	Teknologisk Institut (DTI), Denmark - Christoffer Mølleskov Pedersen chm@teknologisk.dk
Website	www.dare2x.eu
DELIVERABLE DOCUMENT SHEET	
Deliverable No.	3.1
Deliverable title	Summary of experiments WP3
Description	Summary of experimental work for WP3 (Development of sorption materials)
WP No.	WP2
Related task	T3.1 – Find optimal zeolite for NH ₃ adsorption
Lead Beneficiary	HB – Hulteberg Chemistry and Engineering
Author(s)	Bianca Rolim Josephine Digné Christian Hulteberg
Contributor(s)	/
Type ¹	R
Dissemination Level ²	Public
Language	English – GB

¹ R: Document, report; DEM: Demonstrator, pilot, prototype; DEC: Website, video etc., DATA: Data sets; DMP: Data management plan; ETHICS; SECURITY; Other: Software, technical diagram, algorithms, models etc.

² PU: Public, fully open; SEN: Sensitive.

Due date	30/09/2024	Submission date	18/09/2024
DOCUMENT HISTORY			
DATE	VERSION	AUTHOR	COMMENT
05/09/2024	V 1.0	HB – Bianca Rolim	Final

Acknowledgement



Funded by
the European Union

This project has received funding from the European Union’s Horizon Europe research and innovation programme under grant agreement No 101083905.



UK Research
and Innovation

Part of this project has also received funding from UK Research and Innovation.

Disclaimer

Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

All intellectual property rights are owned by DARE2X consortium members and are protected by the applicable laws. Reproduction is not authorised without prior written agreement.

The commercial use of any information contained in this document may require a license from the owner of that information.

For citation purposes: *“Name of the authors, title of the report, DARE2X Project number 101083905, year of publication, page number, Name of the Beneficiary institution”.*



Funded by
the European Union

This project has received funding from the European Union’s Horizon Europe research and innovation programme under grant agreement No 101083905.



UK Research
and Innovation

Part of this project has also received funding from UK Research and Innovation.

ABBREVIATIONS AND ACRONYMS

HB	Hulteberg Chemistry and Engineering	DTI	Danish Technological Institute
UoL	University of Liverpool	BET	Brunauer-Emmett-Teller
PSA	Pressure Swing Adsorption	BJH	Barrett-Joyner-Halenda
TPD	Temperature programmed desorption	KPI	Key Performance Indicator
TSA	Temperature Swing Adsorption		



This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101083905.



Part of this project has also received funding from UK Research and Innovation.

TABLE OF CONTENTS

ABBREVIATIONS AND ACRONYMS	4
1. Introduction	6
2. Experimental.....	7
2.1 NH ₃ chemisorption	7
2.2 Temperature programmed desorption - TPD	7
2.3 NH ₃ physisorption.....	7
2.4 Dynamic adsorption.....	7
3. Results and Discussion	10
3.1 NH ₃ chemisorption	10
3.2 Temperature programmed desorption – TPD.....	12
3.3 NH ₃ physisorption.....	13
3.4 Dynamic adsorption.....	13
3.5 Adsorbent upscaling	19
4. Conclusions	21
5. References.....	22

LIST OF TABLES

TABLE 1: TEST PARAMETERS FOR DYNAMIC ADSORPTION EXPERIMENTS.....	9
TABLE 2: AMOUNT OF NH ₃ PHYSISORBED AND CHEMISORBED BY EACH ADSORBENT.....	11
TABLE 3: TEXTURAL PROPERTIES OF ZEOLITE 1 AND ZEOLITE 2 ADSORBENTS.....	13
TABLE 4: ADSORPTION CAPACITIES BASED ON DYNAMIC ADSORPTION EXPERIMENTS.....	16
TABLE 5: COMPARISON OF KP15 AND BEST PERFORMING ADSORBENT.....	18

LIST OF FIGURES

FIGURE 1. EXPERIMENTAL SET-UP FOR THE DYNAMIC ADSORPTION TESTS.....	8
FIGURE 2. ISOTHERM PLOTS FOR EACH ADSORBENT.	12
FIGURE 3. SPECTRA FROM NH ₃ -TPD ANALYSIS OF ALL ADSORBENTS.....	12
FIGURE 4. DYNAMIC ADSORPTION CURVES.	16
FIGURE 5. COMPARISON OF ADSORPTION CAPACITY FOR THE DYNAMIC EXPERIMENTS	18
FIGURE 6. EXTRUDER AT HB PRODUCTION WITH CAPACITY FOR 3KG/BATCH.....	19
FIGURE 7. EXTRUDATE SIMPLES AT 1.6 MM (LEFT) AND 3 MM (RIGHT).....	19

1. Introduction

Ammonia, NH_3 , is the second most produced chemical globally and accounts for 1.8% of global CO_2 emissions [1]. The majority of ammonia is currently produced through the Haber-Bosch process using fossil fuels as feedstock in centralised facilities. The decarbonisation of ammonia production requires the use of renewable energy sources, which due to their intermittent nature and general geographic isolation require a decentralised, small-scale and agile process. Because of the high temperature and pressure requirements for the Haber-Bosch process, down-scaling increases energy losses and the cost of ammonia production. Thus, there is a need for operation in milder conditions to allow for intermittent operation and lower capital expenditures. [2] [3]

Non-thermal plasma is a promising technology for ammonia synthesis as it allows for operations at low temperatures and pressures. However, the use of milder pressures requires the replacement of the condensation step currently used in the Haber-Bosch process for ammonia separation. An alternative is the use of adsorption for removal of ammonia from the reactor effluent. Therefore, a new Power-to-X technology for decentralized ammonia production based on sorption-enhanced plasma catalysis is being investigated in the DARE2X project.

Zeolites are categorized as aluminosilicates having a distinct crystalline structure. Al, Si, and O are their three primary components. For a given framework, it is possible to tailor the properties of the zeolite for a desired application, by varying the Si/Al ratio and the counterion. [4] Zeolite materials are excellent adsorbents due to selectivity with respect to specific components in a gas mixture. They exert strong interactions with NH_3 species and good shape-selectivity. [5] [6]

Work Package 3 of the DARE2X project is led by HB and involves the development of stable NH_3 sorption materials for collection of NH_3 and enabling sorption-enhanced reactors. This report summarizes the experimental work related to the sorption materials, their adsorption capacity, kinetic behaviour, and cycle capacity.

2. Experimental

Na-zeolite 2 was prepared through incipient wetness method with NaOH (74.2g NaOH for 500.1g Zeolite 2) and calcined at 400°C for 4 hrs. The other zeolite samples were used as received.

2.1 NH₃ chemisorption

The total acidity of the adsorbents was determined with chemisorption using NH₃ as probing sorbent. The evaluation was performed in a 3Flex instrument (Micromeritics®, Norcross, GA). Samples between 0.1-0.5 g were analysed at 35 °C.

2.2 Temperature programmed desorption - TPD

The strength of adsorption was evaluated using TPD. The evaluation was done with NH₃ and performed in a 3Flex instrument (Micromeritics®, Norcross, GA). Samples between 0.1-0.25g were analysed from 50 °C to 700 °C (ramp 10 °C/min). The samples dosed with NH₃ for 15 min at 50 °C, after which helium was used as gas (10 mL/min) during heating.

2.3 NH₃ physisorption

The textural properties of the adsorbents were evaluated (approx. 0.25 g) by determination of the N₂ adsorption-desorption isotherms using a 3Flex instrument (Micromeritics®, Norcross, GA, U.S). The specific surface area was determined using the Brunauer-Emmett-Teller (BET) equation, and the pore characteristics (size and volume) were determined using the Barrett-Joyner-Halenda (BJH) method [7] [8]. The samples were degassed under vacuum conditions at 90 °C for 30 min and subsequently at 250 °C for 220 min (ramp 10 °C/min) prior to the N₂ physisorption analysis.

2.4 Dynamic adsorption

For the dynamic adsorption tests, the system used is depicted in **Figure 1**. The gas flows are controlled by controlled by a Bronkhorst mass flow controller and the pressure is regulated by a Bronkhorst pressure controller. The filling of the reactor bed is specified for each experiment. The temperature is measured in the reactor bed. The system is placed inside a furnace and heated to the desired temperature. After the reactor, the gas is led to analysis, which is performed by online measurements with a Bacharach ammonia gas monitor equipment.

The gases used were: N₂ from Strandmöllen and 5 mol% NH₃ in N₂ from Nippon Gases.

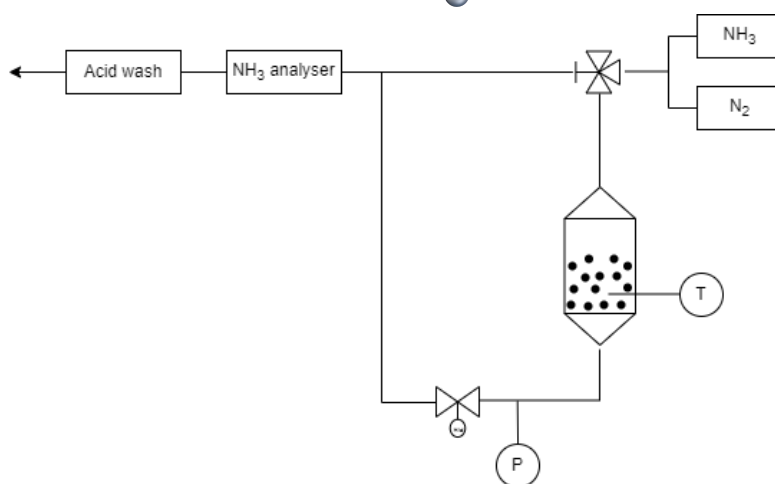


Figure 1. Experimental set-up for the dynamic adsorption tests.

The samples for the dynamic adsorption tests were prepared by mixing the zeolites with 20% wt alumina dispersion (Nyacol® AL20), calcined at 500°C, milled and sieved to the particle size of 10-20 mesh (0.85-2.0 mm).

Test parameters for each experiment are detailed in **Table 1**. The adsorbent was loaded in the reactor and then dried for at least 2hr at 120°C under N₂ flow of 5nL/h for removal of adsorbed water. Then the system's temperature and pressure were adjusted, under N₂ flow, as determined by initial parameters for each experiment. Once the correct temperature and pressure were reached, gas flow with NH₃ and logging of its concentration after the reactor were started. The measurements were performed continuously to observe the breakthrough, i.e. the first NH₃ measurements above the baseline. Once the maximum capacity of the analyser, 1000 ppm, was reached, the adsorption cycle was considered finished, whether the adsorbent was saturated or not, and the NH₃ flow was stopped. The system parameters, such as N₂ flow, temperature and pressure were adjusted for the desorption cycle. Logging of NH₃ concentration was not possible when it exceeded 1000 ppm, but once it reached 0 ppm the desorption cycle was considered finished. For each adsorbent and reactor loading, the amount of adsorption/desorption cycle run is specified. Once the experiment was finished, logging was stopped, and temperature and pressure set back to atmospheric. The used adsorbent was removed from the reactor and a new test started.

Table 1. Test parameters for dynamic adsorption experiments.

Exp number	Type of test	Adsorbent	Weight adsorbent (g)	Reaction (Number of cycles)	[NH ₃] (ppm)	Total gas flow (nL/h)	T (°C)	P (bar)
1	PSA	Zeolite 1	2.31	Ads (3)	10,000	20.9	30	5
				Des (3)	0	20.9	30	1
2	PSA	Zeolite 2	2.32	Ads (3)	10,000	20.9	30	5
				Des (3)	0	20.9	30	1
3	PSA	Zeolite 1	2.32	Ads (2)	10,000	20.9	100	5
				Des (2)	0	20.9	100	1
4	PSA	Zeolite 2	2.32	Ads (3)	10,000	20.9	100	5
				Des (3)	0	20.9	100	1
5	TSA	Zeolite 2	2.32	Ads (3)	10,000	20.9	30	1
				Des (3)	0	20.9	200	1
6	TSA	Zeolite 1	2.32	Ads (3)	10,000	20.9	30	1
				Des (3)	0	20.9	600	1
7	PSA	Zeolite 1	2.32	Ads (2)	1000	20.9	30	5
				Des (2)	0	20.9	30	1
8	TSA	Zeolite 1	2.32	Ads (2)	1000	20.9	30	1
				Des (2)	0	20.9	600	1
9	PSA	Zeolite 1	2.32	Ads (2)	1000	20.9	30	5
				Des (2)	0	20.9	30	1
10	PSA	Zeolite 5	3.32	Ads (3)	1000	20.9	30	5
				Des (3)	0	20.9	30	1
11	PSA	Zeolite 5	3.33	Ads (3)	1000	20.9	100	5
				Des (3)	0	20.9	100	1
12	Flow swing	Zeolite 5	3.33	Ads (3)	1000	20.9	30	1
				Des (3)	0	20.9	30	1
13	TSA	Zeolite 5	3.32	Ads (3)	1000	20.9	30	1
				Des (3)	0	20.9	300	1

3. Results and Discussion

3.1 NH₃ chemisorption

The total acidity of the adsorbents was determined using NH₃ as the probing sorbent, **Table 2** and **Figure 2**. The results of the experiments are given as the total ammonia adsorption capacity, which is the sum of the physisorption and chemisorption.

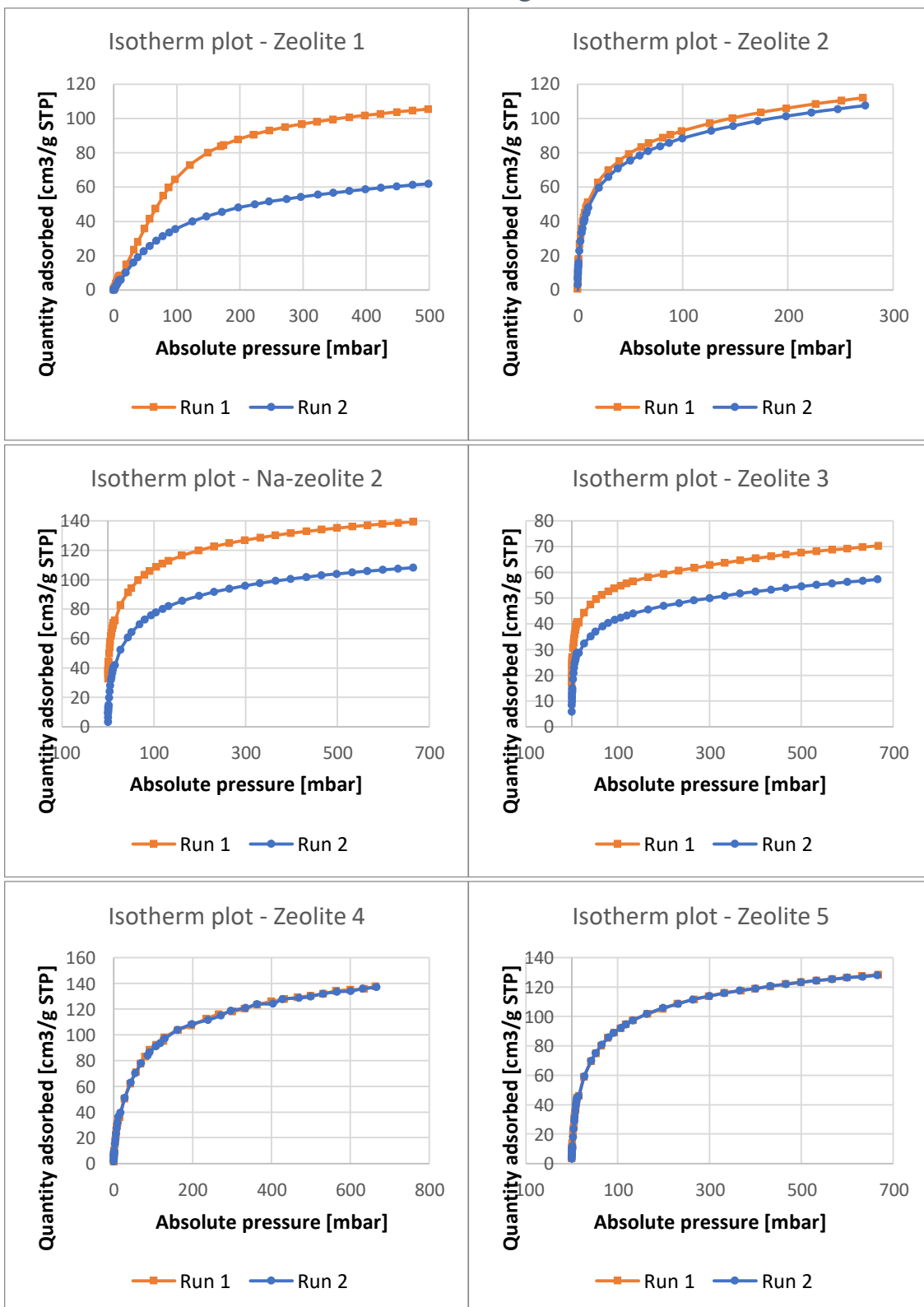
Physisorption involves the physical bonding of gas molecules with the solid surface and the forces involved are intermolecular forces (van der Waals forces). Chemisorption, on the other hand, involves a chemical reaction between the adsorbate and adsorbent. [9]

In order to achieve bulk gas separation by adsorption, the adsorbent must be used repeatedly, i.e. regenerated between the adsorption cycles. The desorption step takes a rather long time if thermal desorption is employed due to poor thermal conduction in the adsorbent packed bed. A solution is to employ low pressure desorption where the time constant of desorption is of the same order of magnitude as that of adsorption or even smaller. Thus, the separation is achieved by repeating adsorption at higher pressure and desorption at lower pressure, a type of operation called PSA (Pressure Swing Adsorption). [10]

Due to weaker interaction energy involved, physisorption is an easily reversible process and therefore more appropriate choice for an adsorption unit that needs to be regenerated several times. This regeneration can be achieved through the faster pressure swing method, instead of using thermal desorption, which would be necessary for the chemisorption. The most promising materials were, therefore, the ones which showed highest adsorption capacity, particularly if due to physisorption.

Table 2. Amount of NH₃ physisorbed and chemisorbed by each adsorbent.

Adsorbent	Quantity adsorbed (ml/g)			Total adsorption capacity (mg NH ₃ ·g ⁻¹ sorb)
	Physisorption	Chemisorption	Total	
Zeolite 1	38.7	37.1	75.8	56.8
Zeolite 2	89.2	4.6	93.8	70.3
Na-Zeolite 2	84.4	30.8	115.2	86.4
Zeolite 3	43.6	12.4	56.0	42.0
Zeolite 4	100.7	0.6	101.3	76.0
Zeolite 5	100.4	0.0	100.4	75.3
Zeolite 6	74.2	18.0	92.2	69.1
Zeolite 7	105.9	7.2	113.1	84.8



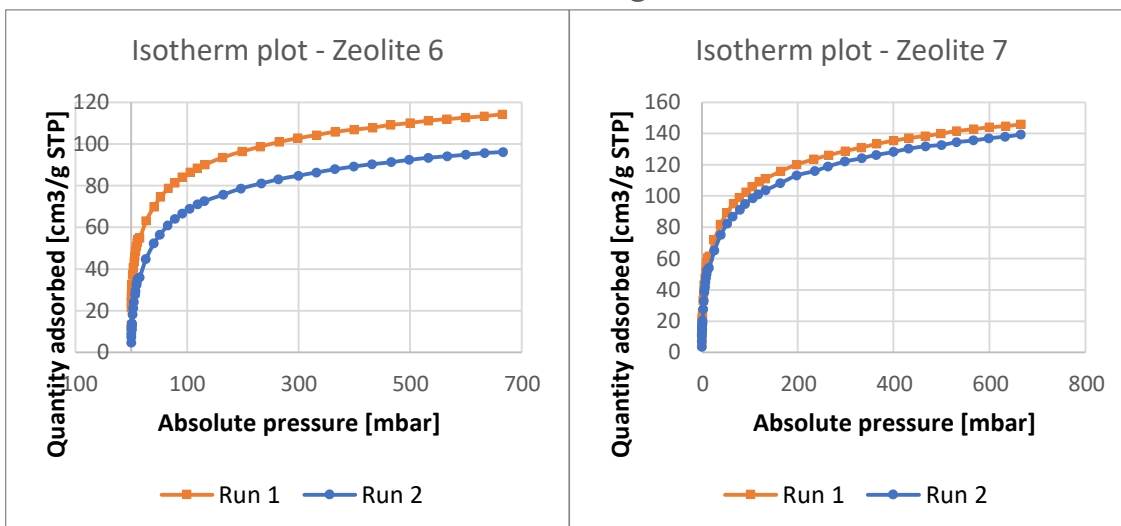


Figure 2. Isotherm plots for each adsorbent.

3.2 Temperature programmed desorption – TPD

The strength of adsorption of the zeolite materials was evaluated by TPD, **Figure 3**. It shows the temperature needed for the desorption of ammonia from the material. If thermal desorption were to be used as a way to regenerate the adsorbent, the lower temperature observed for the peak in the curve, the lower temperature would be needed in the desorption step. Most materials evaluated show a peak around 200°C, with the exception being Zeolite 1, at around 600°C.

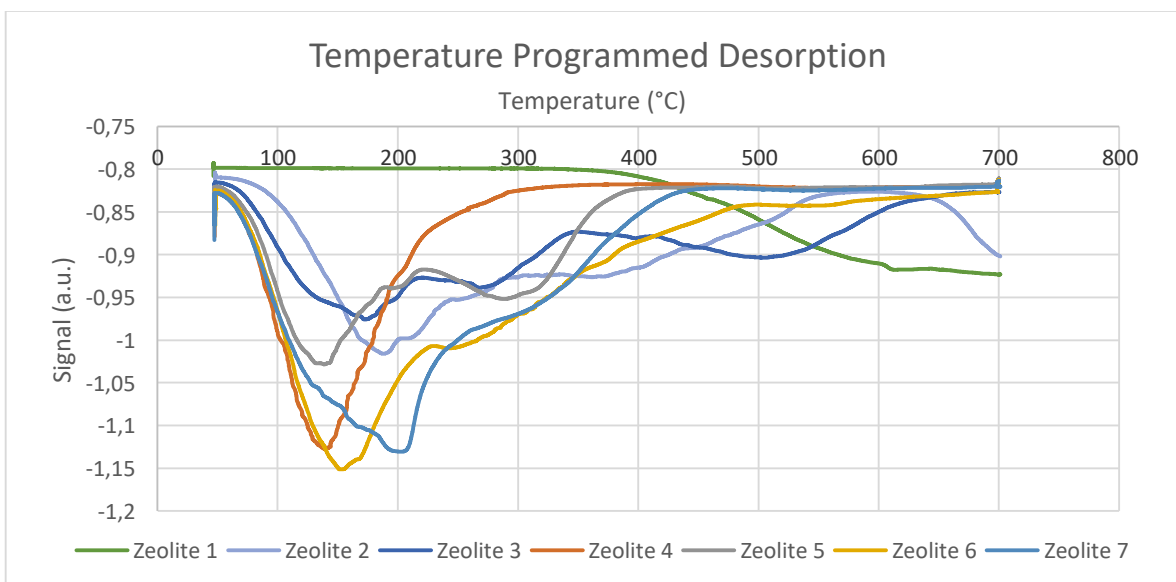


Figure 3. Spectra from NH₃-TPD analysis of all adsorbents.

3.3 NH₃ physisorption

The textural properties of two adsorbent materials were evaluated, **Table 3**. Key parameters, such as the specific surface area, the pore volume and the pore diameters are listed. As expected, the surface areas are high, with the zeolite 2 coming in at the highest value. Please keep in mind that these are values with 20% alumina binder in the material. The pore volumes and diameters also reflect the high surface area.

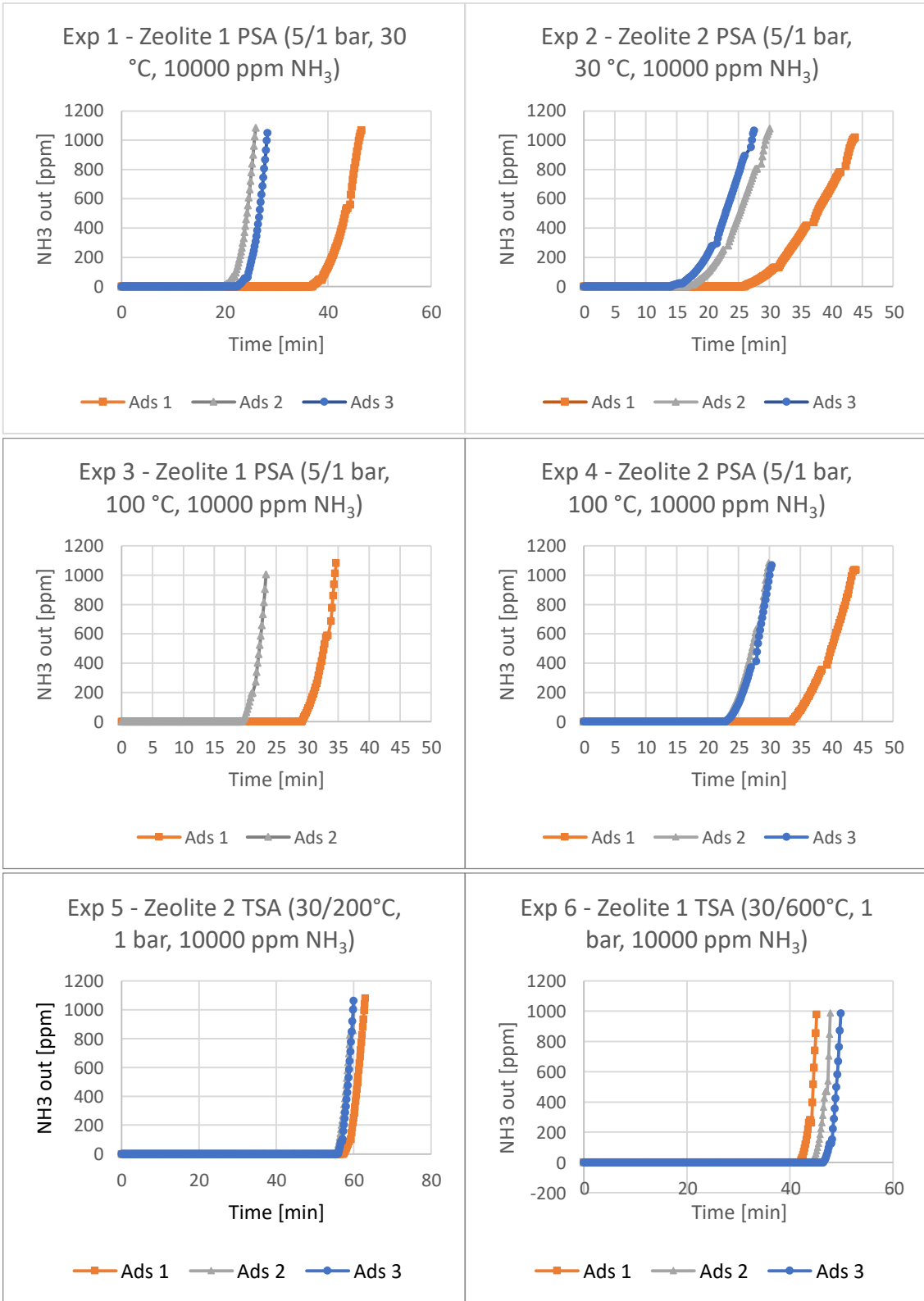
Table 3. Textural properties of Zeolite 1 and Zeolite 2 adsorbents.

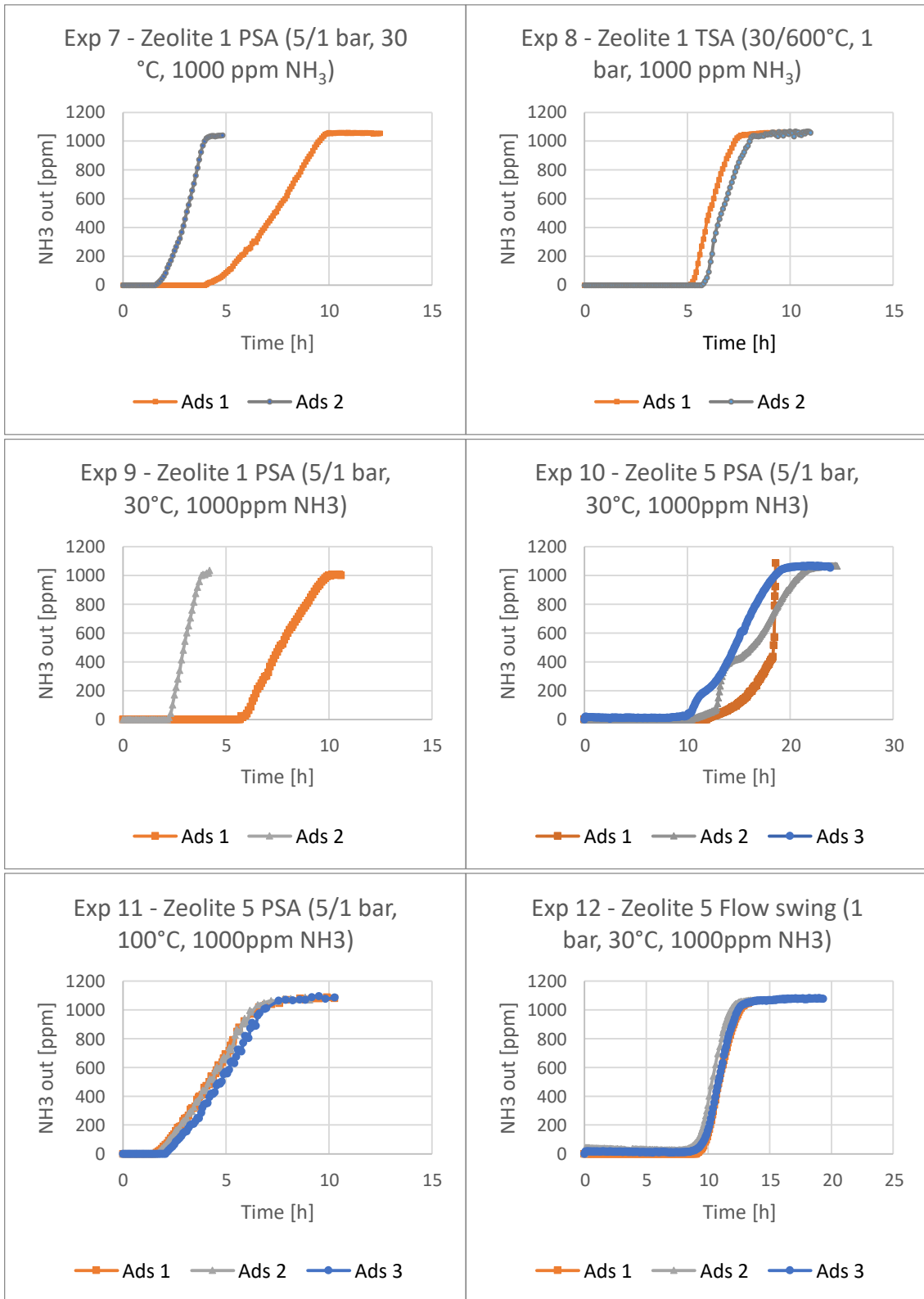
Adsorbent	BET surface area (m ² /g)	BJH desorption pore volume (ml/g)	BET pore diameter (nm)
Zeolite 1	325.1	0.23	9.35
Zeolite 2	414.7	0.19	9.04

3.4 Dynamic adsorption

The zeolites that showed highest amount physisorption and lowest desorption temperature were considered the most promising and had their kinetic adsorption behaviour in the dynamic adsorption tests, **Figure 4**. The results from these experiments show the dynamic adsorption capacity, kinetic behaviour, breakthrough time and cycle stability for the zeolite materials.

The adsorption capacity for each experiment was calculated through integration of the area below the adsorption curve until the first breakthrough of ammonia or until saturation of the adsorbent, **Table 4**. The test parameters, temperature, pressure ammonia concentration and gas flow rates, were chosen with consideration to parameters from the plasma reactor that synthesizes ammonia, physical constraints of the test rig and information needed for the upscale of the adsorption unit.





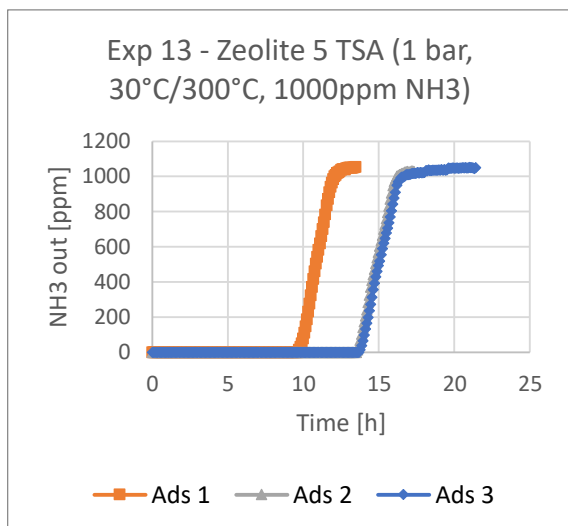


Figure 4. Dynamic adsorption curves.

Table 4. Adsorption capacities based on dynamic adsorption experiments.

Exp number	Type of test	Adsorbent	[NH ₃] (ppm)	Cycle	T (°C)	P (bar)	Adsorption capacity (mg NH ₃ /g ads)	Comments
1	PSA	Zeolite 1	10,000	Ads 1	30	5/1	39.69	Until breakthrough
				Ads 2	30	5/1	21.36	
				Ads 3	30	5/1	24.20	
2	PSA	Zeolite 2	10,000	Ads 1	30	5/1	28.12	Until breakthrough
				Ads 2	30	5/1	18.15	
				Ads 3	30	5/1	15.48	
3	PSA	Zeolite 1	10,000	Ads 1	100	5/1	31.14	Until breakthrough
				Ads 2	100	5/1	21.00	
4	PSA	Zeolite 2	10,000	Ads 2	100	5/1	36.13	Until breakthrough
				Ads 3	100	5/1	24.56	
5	TSA	Zeolite 2	10,000	Ads 1	30/200	1	61.40	Until breakthrough
				Ads 2	30/200	1	59.26	
				Ads 3	30/200	1	59.98	
6	TSA	Zeolite 1	10,000	Ads 1	30/600	1	44.85	Until breakthrough
				Ads 2	30/600	1	47.52	
				Ads 3	30/600	1	49.83	
7	PSA	Zeolite 1	1000	Ads 1	30	5/1	30.35	Until saturation
				Ads 2	30	5/1	11.96	
8	TSA	Zeolite 1	1000	Ads 1	30/600	1	30.66	Until saturation
				Ads 2	30/600	1	34.67	
9	PSA	Zeolite 1	1000	Ads 1	30	5/1	33.68	Until saturation
				Ads 2	30	5/1	12.72	
10	PSA	Zeolite 5	1000	Ads 1	30	5/1	79.39	Until saturation
				Ads 2	30	5/1	48.43	
				Ads 3	30	5/1	43.76	
11	PSA	Zeolite 5	1000	Ads 1	100	5/1	4.80	Until saturation
				Ads 2	100	5/1	4.40	
				Ads 3	100	5/1	10.11	
12	Flow swing	Zeolite 5	1000	Ads 1	30	1	40.81	Until saturation
				Ads 2	30	1	35.44	
				Ads 3	30	1	39.29	
13	TSA	Zeolite 5	1000	Ads 1	30/300	1	42.44	Until saturation
				Ads 2	30/300	1	59.34	
				Ads 3	30/300	1	59.08	

Some results for the dynamic adsorption tests are grouped for easiness of analysis, **Figure 5**. It is possible to see that the adsorption capacity during PSA experiments is higher in the first cycle but then is stable during the other cycles due to the amount of ammonia that is chemisorbed during the first cycle but is not able to be regenerated through pressure swing. Therefore, this is not observed during the TSA experiments, where the adsorption capacity actually increases after the first cycle, since not only all ammonia, both physisorbed and chemisorbed, is desorbed but also water is released from the zeolite pores, increasing the volume available for adsorption in the next cycle.

Zeolite 5 showed the highest adsorption capacity of the tested adsorbents, but it was very dependent on the temperature, being approximately 10x larger at 30°C than 100°C.

When looking at the different operating modes for the Zeolite 5 adsorbent, it can be seen that the use of a higher pressure, 5 bar, during adsorption increased its adsorption capacity, being higher than the flow swing experiment, 1 bar, which was, otherwise, performed in the same conditions.

The adsorption capacity was stable in the second and third cycles for all the different desorption modes.

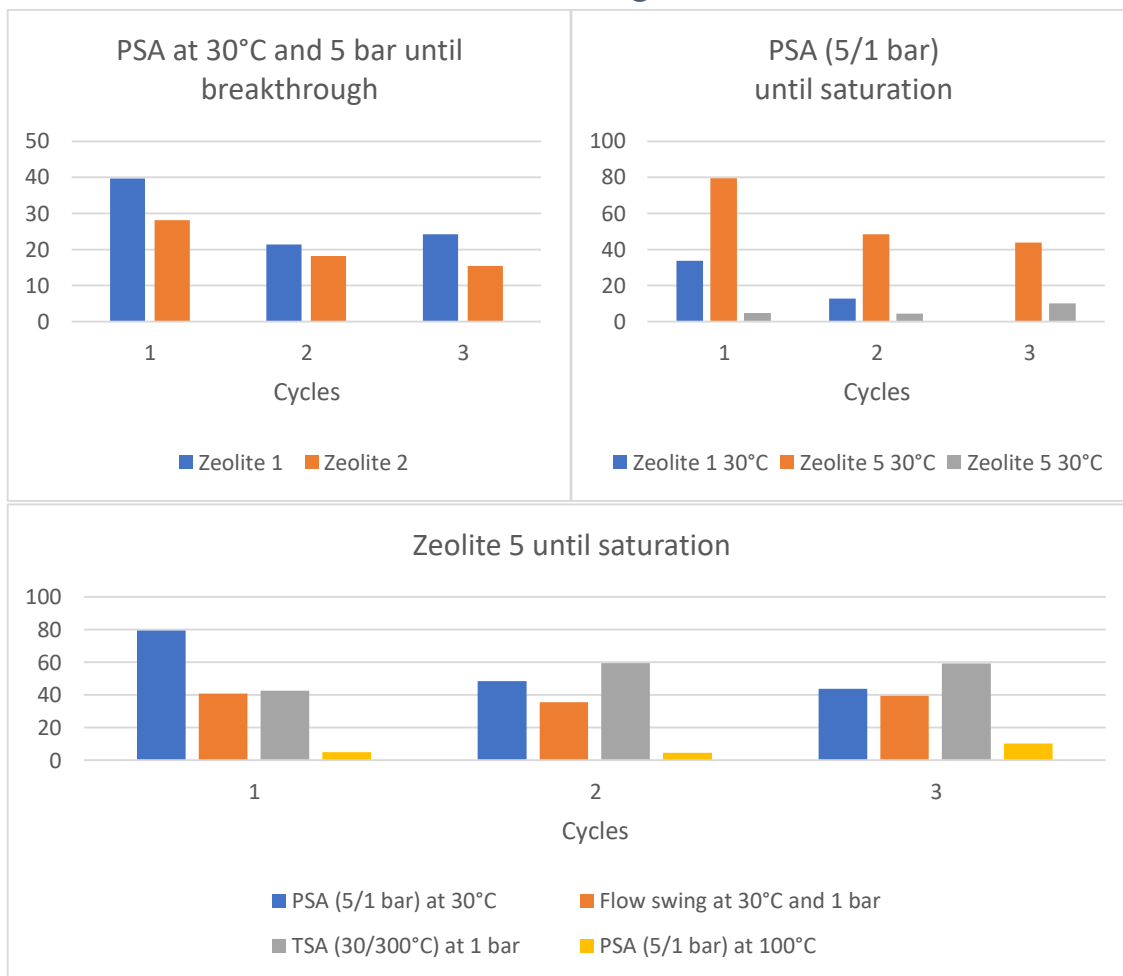


Figure 5. Comparison of adsorption capacity for the dynamic experiments.

KPI5, to find an adsorbent material capable of adsorbing more than $150 \text{ mgNH}_3 \cdot \text{g}^{-1}$ at 30°C and 1 bar and retain this capacity for 20 cycles, was not achieved, **Table 5**. It was deemed to take a disproportionate amount of time and resources to optimize the adsorption capacity and instead the need for higher adsorption capacity will be bypassed through the process design for the adsorption unit.

The pilot unit will be designed for a specific amount of time in each cycle with the current adsorption capacity and showcase a proof-of-concept. In the eventual upscale, several adsorption columns will be used in parallel in different staged of the adsorption/desorption cycle and the system will be able to function continuously without demanding much higher costs or space despite the lower adsorption capacity.

Table 5. Comparison of KPI5 and best performing adsorbent.

	Adsorption capacity	Capacity retention
KPI5	>150 mgNH ₃ .g ⁻¹ sorb at 30°C and 1bar	99% after 20 cycles
Best performing adsorbent	79.39 mgNH ₃ .g ⁻¹ sorb at 30°C and 1bar	75% after 3 cycles

3.5 Adsorbent upscaling

When moving from the laboratory scale to industrial scale, the *modus operandi* of the production has to be more rational. HB has for more than a decade been actively developing methods for the production of catalysts and adsorbents in ton scale. The recipe developed in the laboratory scale, for the zeolites with binders, has been proven to be straightforward to scale. The most suitable method of production is extrusion. In extrusion, the powder and binders are mixed with water and other additives, e.g. agents to slow cracking on drying and fibres to enhance the stability of the extrudates. The mixture of powder, binder and additives has the consistency of a paste and is thoroughly mixed via kneading before extrusion. In the extruder, the paste is pushed through a die and into the desired shapes by selecting the die.

HB possesses own extruding capabilities, **Figure 6**, and has prepared extrudate samples in different sizes, **Figure 7**. Due to size limitations in the design of the adsorber pilot unit, i.e. to minimize pressure drop in the column but still guaranteeing enough adsorbent particles in the width of the column, the particle size of 1.6 mm was chosen for upscaling.

As it is required by the pilot unit, samples of Zeolite 5 adsorbent will be prepared by HB in the correct amount and size. They will also be dried for water removal and be ready to use as delivered.



Figure 6. Extruder at HB production with capacity for 3kg/batch.

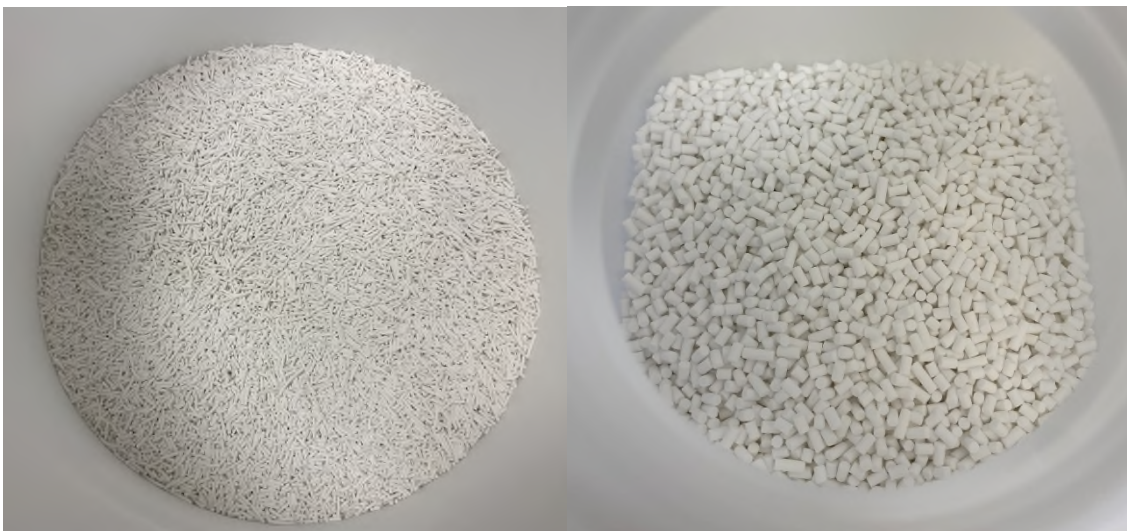


Figure 7. Extrudate simples at 1.6 mm (left) and 3 mm (right).

4. Conclusions

The zeolites that showed the highest amount of physisorption and the lowest desorption temperature were considered the most promising for the adsorption system. Since physisorption is an easily reversible process, it is more adequate for an adsorption unit that needs to be regenerated several times, and this regeneration can thus be achieved through PSA.

The kinetic adsorption behaviour of the most promising materials was evaluated in the dynamic adsorption tests. Zeolite 5 had the highest adsorption capacity after the 1st cycle of the tested adsorbents, 48 mg NH₃/g ads, at 30°C, 5/1 bar and 1000 ppm NH₃ concentration. The results from the dynamic adsorption tests were also useful to the design of the pilot unit since it determined not only the best operating conditions for the adsorbent but also the adsorber dimensions and expected cycle times.

The chosen adsorbent, Zeolite 5, was also prepared in larger scale in the desired shape and size to be used in the pilot adsorber unit.

5. References

- [1] The Royal Society, *Ammonia: zero-carbon fertiliser, fuel and energy store - Policy Briefing*, 2020.
- [2] C. Smith, A. K. Hill and L. Torrente-Murciano, "Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape," *Energy Environ. Sci.*, vol. 13, p. 331, 2020.
- [3] K. H. R. Rouwenhorst, Y. Engelmann, K. van 't Veer, R. S. Postma, A. Bogaerts and L. Lefferts, "Plasma-driven catalysis: green ammonia synthesis with intermittent electricity," *Green Chem.*, 2020.
- [4] Y. Dehmani, B. Mohammed, R. Oukhrib, A. Dehbi , T. Lamhasni , Y. Brahmi, A. El-Kordy , D. S. Franco, J. Georgin, E. C. Lima, A. A. Alrashdi, N. Tijani and S. Abouarnadasse, "Adsorption of various inorganic and organic pollutants by natural and synthetic zeolites: A critical review," *Arabian Journal of Chemistry*, vol. 17, no. 1, 2024.
- [5] A. Mosca, J. Hedlund, F. Ridha and P. Webley, "Optimization of synthesis," *Adsorption*, no. 14, p. 687, 2008.
- [6] T. Z. San, J. H. Park, M. Z. Win, L. S. D. Ugli, W. Oo and K. B. Yi.
- [7] S. Brunauer, P. H. Emmett and E. Teller, "Adsorption of Gases in Multimolecular Layers.," *J. Am. Chem. Soc.*, no. 60, pp. 309-319, 1938.
- [8] E. P. Barrett, L. G. Joyner and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous. I. Computations from Nitrogen Isotherms," *J. Am. Chem. Soc.*, no. 73, pp. 373-380, 1951.
- [9] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K. S. W. Sing, "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," *Pure Appl. Chem.*, vol. 87, no. 9, pp. 1051-1069, 2015.
- [10] M. Suzuki, *Adsorption Engineering*, Tokyo: Kodansha, 1990.