

REUSE OF NaA ZEOLITE FOR CO₂ ADSORPTION

J. G. Meneguim¹; L. H. de Oliveira¹; E. da Silva²; M.A.S.D. de Barros¹; P. A. Arroyo¹; J. F. Nascimento³; W. M. Grava³

1-Departamento de Engenharia Química – Universidade Estadual de Maringá,
Av. Colombo, 5790 – CEP: 87020-900 – Maringá – PR – Brasil

Telefone: (44) 3011-4758 – Email: arroyo@deq.uem.br

2- Curso de Engenharia Química – Universidade Estadual do Oeste do Paraná

Rua da Faculdade, 645 – CEP: 85903-000 – Toledo – PR – Brasil

Telefone: (45) 3379-7039 – Email: edsondeq@hotmail.com

3- TPAP/PDP/CENPES/PETROBRAS

Ilha do Fundão, Qd 07 – Rio de Janeiro – RJ – Brasil

Telefone: (21) 2162-4179 – Fax: (21) 2162-4537 – Email: jfer@petrobras.com.br.

ABSTRACT: NaA zeolite was used to study CO₂ batch cyclic adsorption at 30 °C with three different desorption steps. Desorption 1 was carried out at 30 °C and 1 bar; Desorption 2, 30 °C and 0.1 bar; and Desorption 3 was conducted at 150 °C and 0.1 bar. Results showed that even after five cycles, no significant differences were seen for each desorption procedure. Nevertheless, the working capacity of Desorption 3, was the highest one, 3.73 mol.kg⁻¹.

KEYWORDS: NaA zeolite; CO₂ adsorption; reuse.

1. INTRODUCTION

CO₂ is present in several gas mixtures and is widely used for industrial applications. It is a component of natural gas, flue gas and landfill gas. Removal of CO₂ from binary mixtures of CO₂ + CH₄ is important to improve natural gas quality. CO₂ can reduce the heating value and leads to pipeline corrosion in the presence of water. The commonly used techniques for CO₂ separation from flue gases include ammonium absorption process, dual-alkali absorption, membrane separation process, and adsorption on solid adsorbents. Adsorption and storage of CO₂ in various adsorbents have gained increasing interests recently. Zeolites, metal organic frameworks, activated carbons, molecular sieves and clays have attracted attention as adsorbents to separate such gas mixtures (Saha et al., 2010; Li et al., 2013).

An important characteristic of adsorbents for industrial application is their reuse capacity when submitted to cyclic adsorption/desorption processes. Zeolites are well-known adsorbents with high reuse capacity. Specifically, A type zeolites, also named as Linde Type A, have been largely applied in methane and natural gas purification.

The main procedures to regenerate an adsorbent are: pressure swing adsorption (PSA), temperature swing adsorption (TSA), and hybrid process where both processes are mixed.

In PSA, the gas is contacted with the material sample at elevated pressure and room temperature up to adsorption equilibrium (Meisen e Shuai, 1997). The sample is then regenerated by reducing the pressure and elutriating the adsorbed constituents with a less selective gas.

In TSA desorption is performed by increasing the temperature. As TSA requires heat transfer, it is costlier than PSA that needs pressure changes (Meisen e Shuai, 1997). The hybrid process with changes in temperature and pressure is named PTSA.

In this work the influence of temperature and pressure in the adsorption/desorption of CO₂ in NaA in batch cycles was investigated in PSA and PTSA processes.

2. EXPERIMENTAL

2.1. Materials

Fine powder of NaA zeolite (ADVERA™) from Zeolyst International was used as adsorbent.

CO₂ 99.99% pure was obtained from Linde Gas Ltda.

2.2. Methods

A weighted NaA sample was inserted in the sample container's basket of a Rubotherm magnetic suspension balance (MSB) - accuracy $\pm 1 \times 10^{-6}$ g.

All adsorption/desorption cycles started after the activation step. It consisted of heating the system with a 5 °C/min rate up to 150 °C. Then, temperature was maintained constant for 10 h, under absolute pressure of 0.1 bar. After that, the mass of adsorbent was determined in the MSB equipment.

Such temperature was previously chosen as the most adequate one for the activation step taking account adsorption capacity and loss of cristalinity and umidity (Meneguín et al., 2013).

The adsorption step was conducted at 30 °C using a Julabo thermostatic bath. NaA zeolite with adsorbed CO₂ in equilibrium conditions was weighted up to 40 bar.

The CO₂ isotherms were obtained through a mass balance using the MSB experimental data based on Dreisbach et al. (2002). Then,

$$m_{exp} = (m_{sc} + m_s + m_a) - \rho(V_{sc} + V_s + V_a) \quad (1)$$

where m_{exp} , m_{sc} , m_s , m_a , ρ , V_{sc} , V_s , and V_a , are the balance displayed mass, sample container mass, adsorbent mass, adsorbate mass, gas density, sample container volume, adsorbent volume impenetrable to adsorbate, and adsorbate volume, respectively. All mass values were expressed in grams whereas volume values were used in cm³ and density in g/cm³.

The desorption step was conducted in three different ways:

Desorption 1 → pressure was reduced from 40 to 1 bar and maintained at this final pressure for 2 h isothermally;

Desorption 2 → Desorption 1 with the final pressure of 0.1 bar;

Desorption 3 → Desorption 2 heated up to 150 °C using a rate of 5 °C/min rate and kept constant for 2 h.

Each adsorption/desorption cycle was repeated 5 times.

For better understanding, Figure 1 shows pressure, temperature and displayed mass (m_{exp}) variations versus time for Desorption 2. Desorption 1 and Desorption 3 had similar plots.

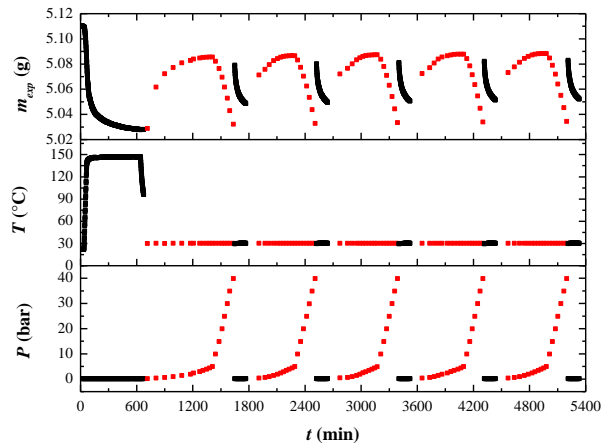


Figure 1. Pressure, temperature and displayed mass variations with experiment time for Desorption 2. Black experimental data: activation and desorption. Red experimental data: adsorption

3. RESULTS AND DISCUSSION

The five adsorption/desorption isotherm cycles for each desorption procedure are shown in Figures 2 to 4. In all cases NaA adsorbed CO₂ and successfully desorbed with PSA (Desorption 1 or 2) and PTSA (Desorption 3) cycles.

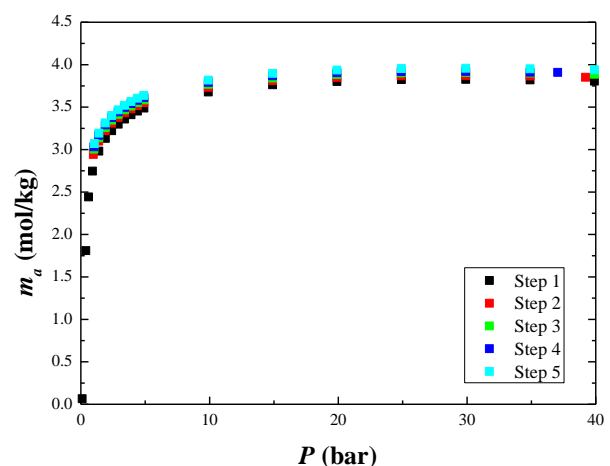


Figure 2. CO₂ adsorption/desorption cycles for Desorption 1.

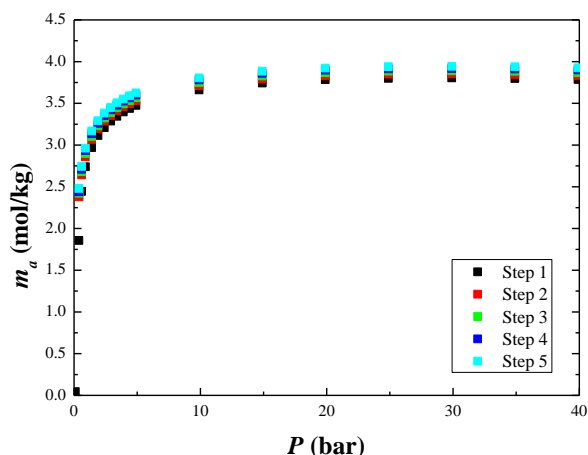


Figure 3. CO₂ adsorption/desorption cycles for Desorption 2.

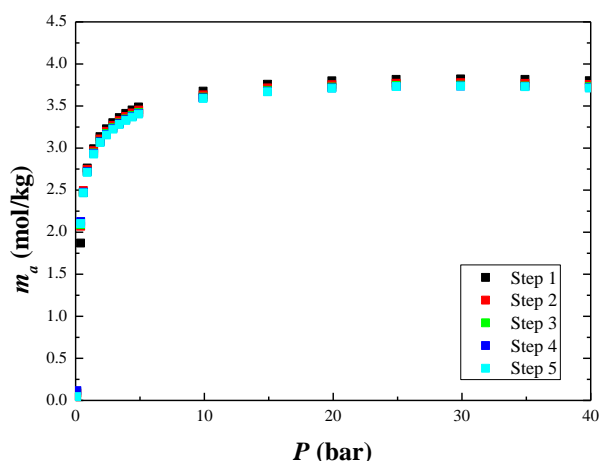


Figure 4. CO₂ adsorption/desorption cycles for Desorption 3.

Experimental results are seen in Table 1 where the quantity of CO₂ adsorbed at 40 bar ($m_{a,40}$), the residual quantity of CO₂ after the desorption process ($m_{a,res}$) and the working capacity ($m_{a,work}$), that is the difference between the adsorbed and residual amounts are presented.

In agreement with Figures 2 to 4, it is seen that the work capacity maintained constant for the five cycles of each Desorption method. It may indicate that cycles can be done for a long time without loss of adsorption efficiency.

On the other hand, huge differences are seen when the influence of pressure in the PSA processes (Desorption 1 and Desorption 2) and the PTSA process (Desorption 3) are compared.

Results related to PSA showed that a decrease in pressure from 1 to 0.1 is strongly recommended as the working capacity of Desorption 2 is close to three times higher than in Desorption 1. The average $m_{a,work}$ for Desorption 1 was 0.92 mol·kg⁻¹ while for Desorption 2 it reached 2.65 mol·kg⁻¹.

Heating to 150 C provided even better results as the working capacity of Desorption 3 provided was estimated 3.73 mol·kg⁻¹. Therefore, according to the operational results, it may be concluded that PTSA is the best method to promote the efficient reuse of NaA in the separation of CO₂ from a fluid phase.

Table 1. CO₂ adsorbed mass at 40 bar ($m_{a,40}$ / mol·kg⁻¹), the residual mass after desorption ($m_{a,res}$ / mol·kg⁻¹) and the working capacity ($m_{a,work}$ / mol·kg⁻¹).^a

Step	Desorption 1			Desorption 2			Desorption 3		
	$m_{a,40}$	$m_{a,res}$	$m_{a,work}$ ^a	$m_{a,40}$	$m_{a,res}$	$m_{a,work}$ ^a	$m_{a,40}$	$m_{a,res}$	$m_{a,work}$ ^a
1	3.81	2.88	0.93	3.79	1.11	2.68	3.80	0.02	3.78
2	3.85	2.94	0.91	3.83	1.17	2.66	3.76	0.01	3.75
3	3.89	2.96	0.93	3.87	1.22	2.65	3.73	0.02	3.71
4	3.91	3.00	0.91	3.90	1.27	2.63	3.72	0.00	3.72
5	3.94	3.03	0.91	3.92	1.31	2.61	3.71	0.00	3.71

^a $m_{a,work} = m_{a,40} - m_{a,res}$

4. CONCLUSIONS

Results presented herein made us conclude that NaA can be used in the separation of CO₂ through adsorption processes. Moreover, up to five

cycles, no significant differences were seen in the working capacity suggesting that the reuse of such zeolite can be done for many other cycles.

According to the working capacities, it was seen that lower pressures promoted better results.

Pronounced increase was also seen in the PTSA processes.

Therefore, based on technical parameters, Desorption 3, related to the PTSA cycles provided the best results for CO₂ separation in NaA zeolite.

5. ACKNOWLEDGMENTS

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