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Characterisation of CPO-27Ni Metal Organic Framework Material for Water Adsorption

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Abstract

Metal Organic Framework materials are new adsorbent materials that have high surface area and adsorption uptake, leading to be used in many applications like cooling, gas separation and energy storage. Although many MOF materials have been developed in the literature, only few MOFs are commercially available and in large quantities. CPO-27Ni is an MOF material that has been reported to offer potential in water adsorption. This paper presents experimental characterization of CPO-27Ni MOF material for water adsorption. The characterisation includes measuring the particle size using laser diffraction and the material chemical composition using X Ray Diffraction (XRD). Water adsorption isotherms and kinetics at temperature ranging from 25 °C to 55 °C and partial pressure ranging from 1% to 90% were measured using Dynamic Vapour Sorption (DVS) test facility. The isotherms were found to approach 0.47 kg/kgads over wide range of partial pressures. The measured isotherms and kinetics were then used to model a double bed adsorption system for energy storage application and compared to silica gel. The CPO-27Ni was found to outperform silica gel for half cycle time larger than 1 hour.

Keywords adsorption; energy storage; metal organic frame works; characterization

1 Introduction

Adsorption research is focused to develop compact and efficient adsorption systems for heat pumping and energy storage. The objectives of this effort could be realized by using properly design heat exchangers [1], cycle operating strategies (mass recovery, heat recovery, cascading...etc) [2] and developing adsorbent materials with high cyclic uptake [3]. The selection of adsorbent material is a key factor in the design and manufacturing of the adsorption system [3-5]. Metal organic materials are recently applied for wide range of applications including gas storage, such as methane storage [6] and hydrogen storage [7].

Adsorption of water on MOF materials has been reported by Henninger and co-authors [8] using MIL-101. Additionally, they investigated different structured materials including classical zeolite, metal organic framework (copper (II) benzene-1, 3, 5-tricarboxylate, Cu-BTC) and aluminophosphates (AIPO-18). Henninger and co-authors showed that water adsorption capacities of MIL-100 and MIL-101 types surpass those of any conventional adsorbent materials. However, these high performance MIL-100 and MIL-101 compounds are synthesized by different authors on a lab scale, difficult to obtain in a large scale.

CPO-27Ni is an MOF material that was reported to have potential for water adsorption application. This MOF material is synthesised and produced in large scale by Johnson Matthey Ltd. This paper presents experimental characterization of CPO-27Ni MOF material in terms of particle size distribution, pore volume, material composition and water adsorption isotherms and kinetics at temperature range between 25 °C to 55 °C and partial pressure step 1% to 90%. The work also investigated the energy storage performance of a single bed adsorption system using Simulink dynamic modelling.

2 CPO-27Ni characterisation

The powder X-ray diffraction (PXRD) patterns of the CPO-27Ni powder was collected using Siemens DIFFRACplus 5000 powder diffractometer with Cu $K\alpha$ radiation (1.54056 \AA). The tube voltage and amperage were set at 40 kV and 40 mA, respectively. The divergence slit and anti-scattering slit settings were variable for illumination on the 20 mm area on the sample. Each sample was scanned from 5 to $80^\circ 2\theta$, with a step size of 0.02° at 2 step/sec. The sample stage was spun at 30 rpm. The instrument was pre-calibrated using a silicon standard. Analyses showed that CPO-27Ni contains of mixtures of Leadhillite ($\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$), Strontium titanate (SrTiO_3) and aluminium oxychloride ($\text{Al}_2\text{O}_3\text{Cl}_2$).

The particle size of adsorbent was found to be between 125 micron to 355 micron defined by vibrating sieving facility. Laser diffraction technique was used to define the particle size distribution as shown in Figure 1(b). Laser diffraction analysis of CPO-27Ni showed that bimodal size distribution which could be divided into two populations. This suggests that after mechanical sieving, the CPO-27Ni sample still contains a portion of fine particles. The sample showed a VMD (D10% – D90%) of $205.0 \pm 62.2 \text{ }\mu\text{m}$ ($1.1 \pm 0.0 \text{ }\mu\text{m} - 633.8 \pm 207.7 \text{ }\mu\text{m}$) that fell between the nominal sieve size ranges, i.e., 125 – 355 μm , suggesting that the applied sieving process was satisfactorily efficient.

Using Pelsorb test facility, table 1 Show the specification of surface area using Brunauer-Emmett-Teller (BET) method. Micropore (MP) methods were used to calculate the pore size distribution. Before the analysis, samples of about 50-100 mg were degassed at vacuum (about $5 \mu\text{m Hg}$) and at $T=353 \text{ K}$ for 2 hours. It is observed from Figure 2 that the peak volume distribution appears at less than 1 nm, this means the material has micropore structure.

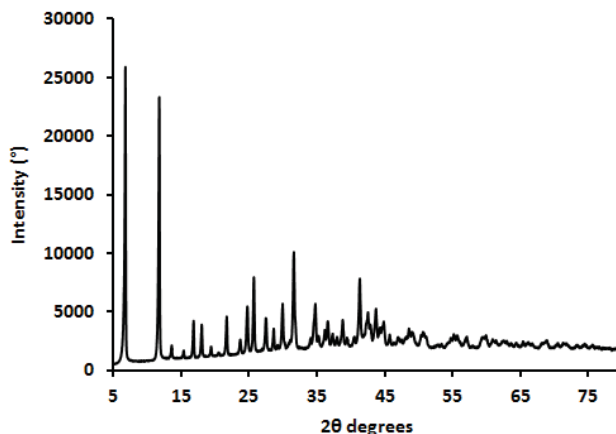


Figure 1(a): XRD analysis of CPO-27Ni

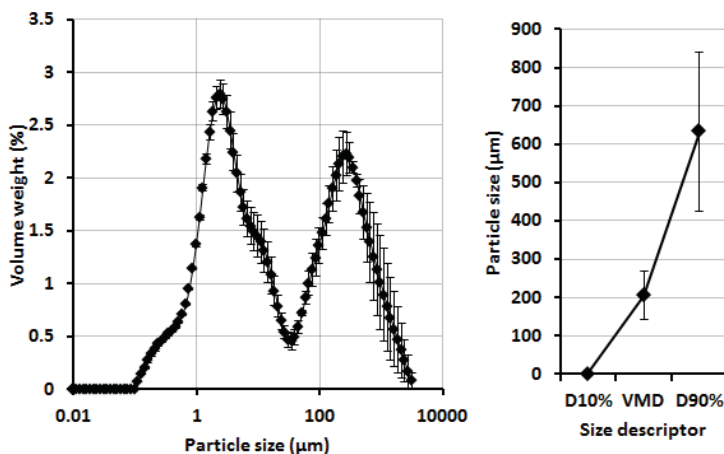
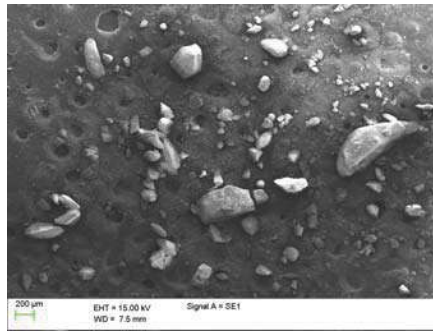
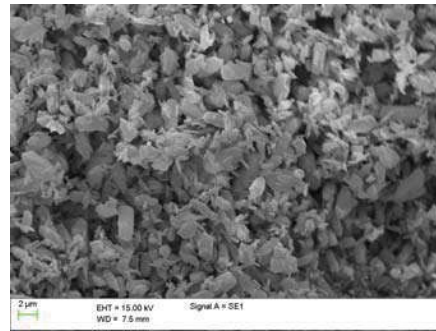


Figure 1(b): Particle size analysis distribution using laser diffraction



CPO-27Ni



Enlarged view on particle surface

Figure 1(c): SEM images of CPO-27Ni

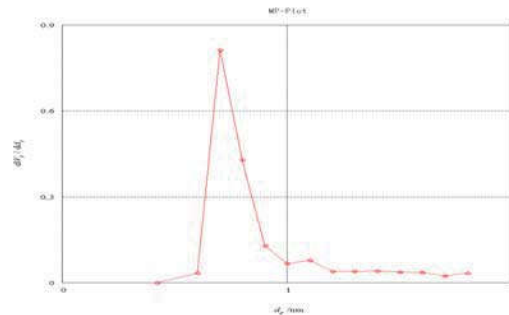


Figure 2: Pore size distribution

Table 1: Pore structure of CPO-Ni using Pelsorb facility

Surface area (m^2/g)	Total Pore volume (cm^3/kg)	Pore mean diameter (nm)
299	217	0.7

3 Adsorption isotherms

Adsorption isotherms and kinetics are required to predict the water uptake at various operating conditions. Figure 3(a) shows the adsorption isotherms of CPO-27Ni and silica gel, it is observed that dry CPO-27Ni has higher uptake especially at low pressure ratio compared to silica gel. The steep profile of CPO-27Ni is preferable especially for adsorption systems that work at low temperature ambient conditions. Figure 3(b) show the effect of isotherm temperature on the uptake capacity. The uptake changes with both bed temperature and water pressure, although the bed temperatures appears to follow single curve when relating the uptake to partial pressure ratio.

Figure 4 shows the adsorption / desorption cyclic performance at 55 °C over five repeated cycles highlighting the thermal stability of the material. It is clear from this figure that the material exhibits the same performance at higher temperatures. Such performance is advantageous over other metal organic materials such as MIL-100 where the uptake is reduced after the first cycle [8].

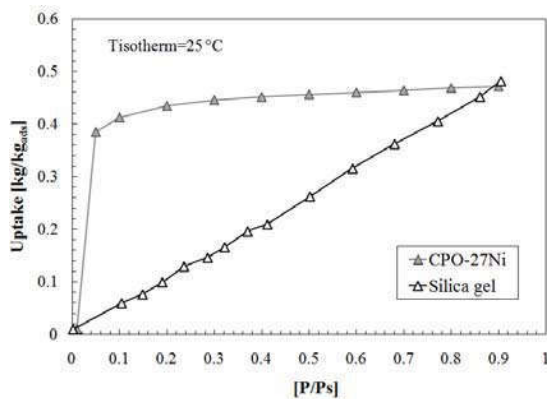


Figure 3(a): CPO-27Ni and silica gel isotherm

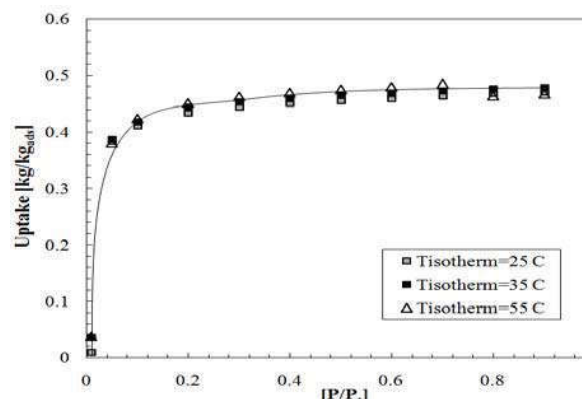


Figure 3(b): Effect of isotherm temperature on uptake

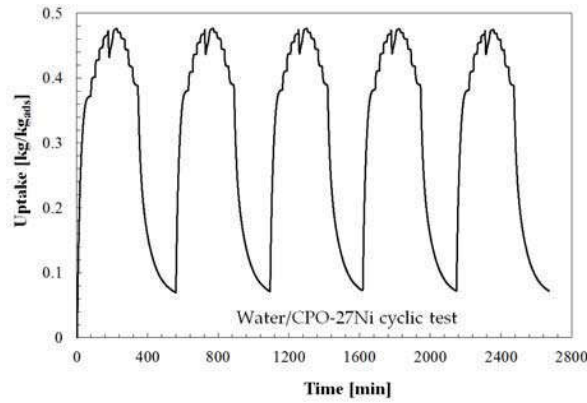


Figure 4: Cyclic test (adsorption/desorption cycles) analysis (Tisotherm=55 °C)

The data has been fitted to adsorption potential using Dubinin equation as shown in Figure 5; such fitting between uptake (x) and adsorption potential (A) (as shown in equation 1) is required for the performance modelling of adsorption systems.

$$x = 0.462248 \cdot \exp(-(A/10019.2)^4) \quad (1)$$

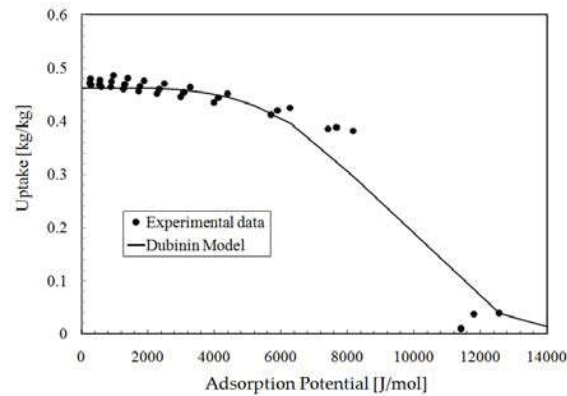


Figure 5: Predicted and measured CPO-27Ni isotherm

4 Adsorption kinetics

Figure 6(a) shows the measured water fractional uptake of CPO-27Ni versus time. This data was fitted in the form of equation 2 to predict the adsorption rate as:

$$\frac{dx}{dt} = k_0 \cdot \exp\left[-\frac{E_a}{RT}\right] \cdot (x_{eq} - x) \quad (2)$$

k_0 was found to be 5.108 [1/s] and E_a the activation energy is 25125.93 [J/mol], it could be observed the higher the temperature, the smaller time required to reach full capacity of material at certain condition. Lower partial pressures ratio has longer characteristic time to reach the full capacity, i.e., smaller adsorption rate constant and slower adsorption process.

5 Heat of adsorption

The measured isotherms were used to plot the pressure, temperature, concentration diagram (PTX) as shown in Figure 6(b), and the heat of adsorption was calculated using equation 3 as:

$$\Delta H_{ads} = -R_{water} \frac{\partial \ln(P)}{\partial \left(\frac{1}{T}\right)} \quad (3)$$

The heat of adsorption was calculated as 2626 kJ/kg_{ads}.

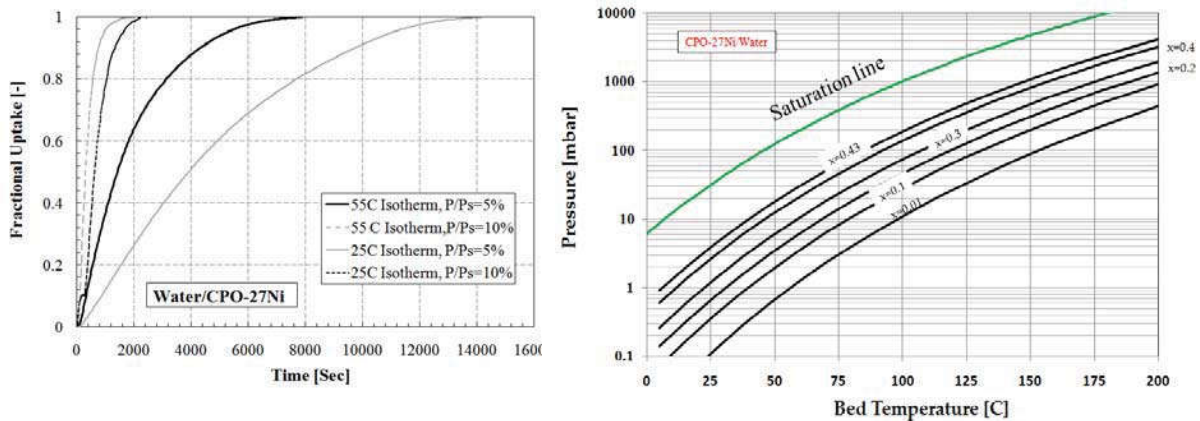


Figure 6(a): Fractional uptake of CPO-27Ni

Figure 6(b): Pressure-temperature concentration CPO-27Ni

6 Full system analysis using Simulink transient model

The predicted isotherms and kinetics of the MOF materials was incorporated in simulink model developed by Elsayed et al. [9] to compare the performance of CPO-27Ni and silica gel under transient operation. Figure 7(a) shows the layout arrangement for the Simulink model used to solve the system of ordinary differential equations representing the transient thermal analysis of adsorption cooling system. Figure 7(b) presents the validation of the modelling. The same model will be utilized to predict both the adsorption and condensation energies that could be stored in case of CPO-27Ni and silica gel. Full details of the model are in reference [9]. Table 2 summarizes the operating conditions for the energy storage where the heat recovered from the condenser and adsorber are of main interest.

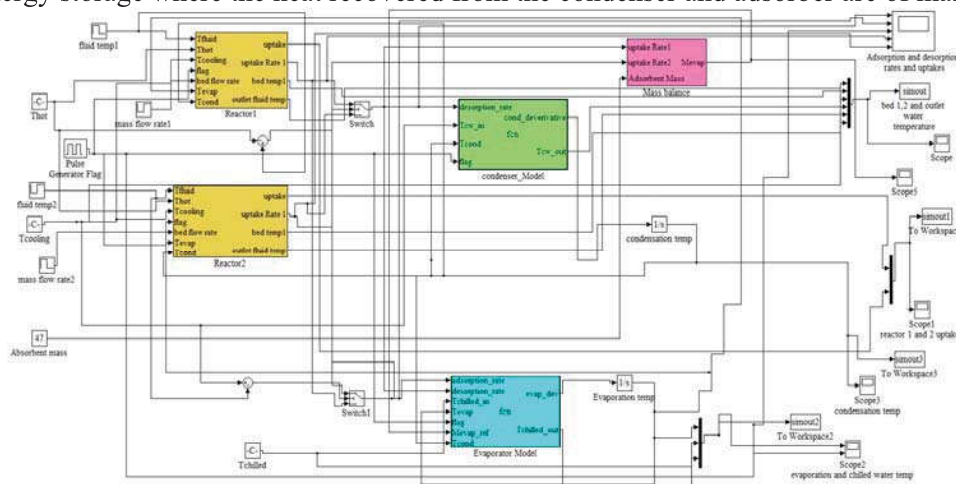


Figure 7(a): Arrangement of chiller component in Simulink simulation environment

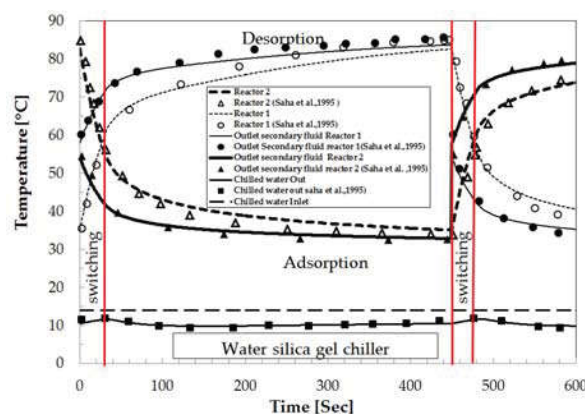


Figure 7(b): Validation of Transient Simulink Model

Table 2: Cycle standard rating condition (Dimensions of the unit [10])

Physical parameter	Value	Units
Chilled water supply	14	°C
Hot regeneration water	85	°C
Cooling water	31	°C
Chilled water flow rate	0.7	kg/s
Hot water flow rate	1.3	kg/s
Condenser cooling water flow rate	1.3	kg/s
Adsorber cooling water flow rate	1.6	kg/s
Half cycle time	420	Sec
Switching time	30	Sec

Figure 8(a) and 8(b) shows the energy distribution for both cooling and energy that could be recovered from condenser and adsorber for both silica gel and CPO-27Ni at different half cycle time. For comparison, 120 sec for both materials was used as switching time as CPO-27Ni has slower kinetics. It is observed that silica gel and CPO-27Ni has similar energy storage from condenser and adsorber for half cycle time 3600 sec. For shorter cycle time silica gel performs better. For longer half cycle time that is more than 1 hr CPO-27Ni outperforms the conventional silica gel adsorbent. Usually energy storage cycles work on long time where CPO-27Ni offers large rates and better performance compared to silica gel.

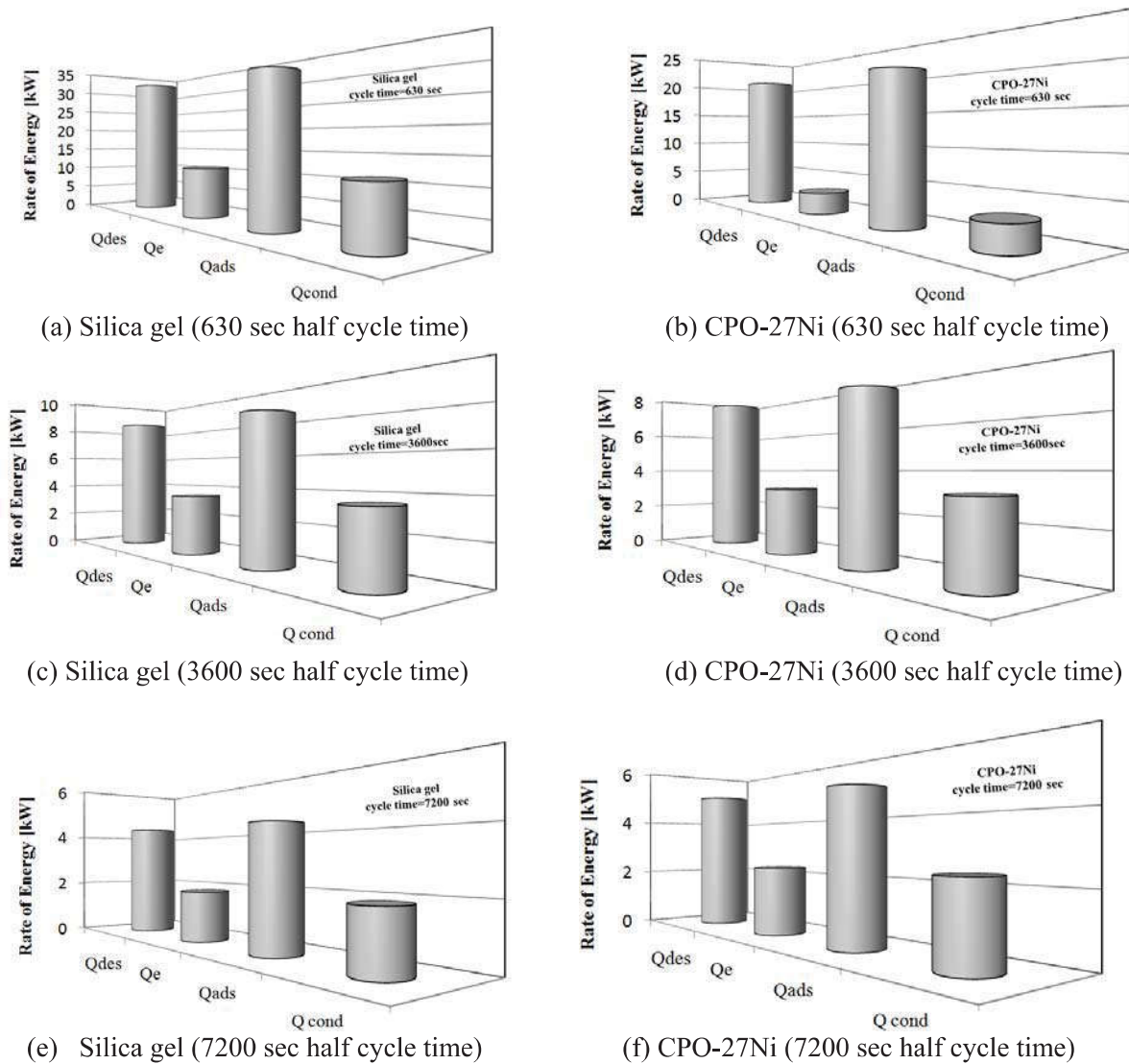


Figure 8: Energy distribution during cooling and storage mode

7 Conclusions

Metal organic frame work materials offer potential for energy storage and cooling applications. CPO-27Ni is a commercially available MOF material that has been reported to have good adsorption characteristics. Complete characterization of this MOF material was performed using laser diffraction, SEM, XRD analysis and dynamic vapour sorption test facility. The particle diameter varied between 125 micron to 355 microns. Leadhillite, Strontium titanate and aluminium oxychlorid were found as the main constituents of the CPO-27Ni. The isotherms were found to approach 0.47 kg/kgads over wide range of partial pressures. The CPO-27Ni was found to outperform silica gel for half cycle time larger than 1 hour.

Acknowledgement

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