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RESEARCH PAPER

High Performance MIL-101 Nanoadsorbent for the Natural Gas Dehydration

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ABSTRACT

In this study, the possible usage of MIL-101 as an attracting adsorbent for natural gas dehumidification is investigated via static and dynamic water vapor adsorption. On this principle, MIL-101 nano-adsorbent with different types of additives were synthesized by solvothermal method. The framework and morphology of the adsorbents were characterized by SEM, PXRD and BET techniques. For these novel desiccants, higher regenerability and drying efficiency were acquired compared to those of the commercial silica gel and zeolite 3A. The results showed that the MIL-101 is an effective sorbent for drying the natural gas for which the water capacity at $P/P_0 = 0.9$ was 1.41 wt.%(300-400% more than counterparts). The experiments confirmed that the nanoadsorbents for both type of powder and shaped forms are water stable, and no remarkable loss in adsorption capacity was observed even after tenth adsorption/desorption cycles. Thus, it could be simply regenerated at low temperatures.

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INTRODUCTION

Natural gas has been used widely as fuel in domestic and industry applications. Adsorption capacity and efficient regeneration of water are the key factors which limit the performance of the commercially used desiccants such as 3A molecular sieve and silica gel in natural gas dehydration [1,2].

Natural gas is saturated with water vapor under exploration and production circumstances. For side effects prevention such as corrosion and deactivation of catalysts, water vapor must be removed. There are two major desiccants used today.; silica gel and molecular sieves. They have distinctly different properties and the choice of these desiccants depends on the inlet feed properties and the outlet requirements. Silica gel has the highest water capacity of any adsorbent, often as high as 40 kilos of water per 100 kilos of gel. It is used when there is very high concentration of inlet water in the gas and the outlet dryness need be no lower than -50°C dew point. Molecular sieves have the lowest capacity under saturated feed conditions but are by far the strongest adsorbent. They can produce an outlet dew point of better than -100 °C [3,4].

However, the two main disadvantages of common desiccants are low capacity for water adsorption and high temperatures for regeneration

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while consuming a large amount of energy. Thus, the energy cost should be considered in the process of natural gas drying, for which the lower cost resources should be introduced [5,6].

Researches were led to find new structures that not only have high uptake capacity but also low energy consumption for regeneration. Metal-organic frameworks (MOFs) are a type of hybrid porous materials that contain inorganic clusters and organic linkers. We propose MOF as high capacity and energy-efficient desiccants for natural gas drying. Removal of the water as unwanted material by MOFs has been shown to be an excellent possibility for a wide range of applications such as gas separation and dehumidification [7-10].

These materials have been considered in various applications specially for gas storage, separation and dehumidification due to some of their unique properties such as wide free surface, high thermal and mechanical strength, low density and very high porosity structure [6].

One of the most important series of MOFs, is MIL (Matériaux de l'Institut Lavoisier), that has been recognized for its micro/meso porosity and high surface area. MIL-101 is widely studied nanomaterials with high capacity adsorption for gas drying, storage of CH_4 and H_2, CO_2 capturing, the separation of C_2H_6/C_2H_4 and removal of H_2S because of high water stability, large cavities, high uptake and recyclability [11-18] .

Many studies have been dedicated on the static water adsorption isotherms using the MOFs as a nanoadsorbent [19-21]. However, a few researches have focused on dynamic dehumidification of natural gas by MOF based nanomaterials [21]. Investigation of natural gas dehumidification on microporous absorbents in order to design a model for natural gas dehumidification were studied and the results showed that the model design was in good agreement with the experimental data [22]. Separation of acid gases from methane in the presence of water were studied and the results showed that it is possible to separate H_2S and CO_2 from natural gas in the presence of water by MOF, but the amount of water adsorption by the adsorbent is not very impressive [23].

The use of MOFs in the dehydration of natural gas shows its innovative atmosphere and promising materials for the treatment, since it meets the main requirements.

Thus, the reviews showed that the dehydration of natural gas by using MOFs may consist many advantages compared to the technologies already existing in the commercial, showing great potential for use in the future [24,25].

We considered, both dynamic and static water adsorptions using MIL-101 adsorbents and distinguished them from those of industrial silica gel and zeolite. MIL-101 was chosen for this purpose because it has large porosity, reasonable stability and good performance in gas separation [13,14].

MIL-101 is constructed by trimers of Cr octahedral with terminal ligands linked by fixed carboxylate ligands. It has two forms of mesoporous cages (29 and 34 Å in diameter) with microporous windows (12 and 16 Å in diameter).

The unique structural properties of MIL-101 inspired us to evaluate its applicability for natural gas dehumidification which requires high water stability. Here, MIL-101 nanoadsorbent with different additives (modulators) were synthesized via hydrothermal method under different synthesis conditions. The frameworks were characterized and surveyed for dehydration of natural gas saturated by water for several static and dynamic adsorption /desorption cycles and studied their water stability and adsorption capacity.

Also, the properties of MIL-101 adsorbents for water adsorption were studied and compared with commercial ones; Silica gel and 3A zeolite. Meanwhile MIL-101 carried out as effective water adsorbent and energy-efficient dehydration, it was shaped with a polymeric binder with the goal of use in industrial applications. Also, the effective parameters for dehumidification process among the powder and shaped samples were considered and compared.

MATERIALS AND METHODS

Synthesis of MIL-101 nanoadsorbents

Particles of MIL-101 were synthesized via a scaled-up procedure using chromium (III) nitrate nonahydrate [$Cr(NO_3)_3.9H_2O$, 99%], terephthalic acid or benzene dicarboxylic acid (H_2BDC,98%), acetic acid (36%), hydrofluoric acid (40-45%) and nitric acid (65%), were all prepared from Merck Chemical Co. All other solvents and chemicals were supplied from commercial grades and were of the maximum purity accessible.

In this work, MIL-101 frameworks were prepared hydrothermally, using a chromium

salt and H_2BDC with the aid of small amount of additive (modulator) in a Teflon-lined autoclave under autogenous pressure, reported in literatures [11,26,27].

MIL-101 particle

$Cr(NO_3)_3.9H_2O$ (4.0 gr), H_2BDC (1.66 gr) and deionized water (40 ml) were mixed and sonicated to achieve a blue-colored suspension. The mixture was located in an autoclaved and retained in the oven at 491 K for 18 h. The solids were separated from water using a centrifuge and was further washed by water, methanol and acetone. The solids were placed in 40 ml of N,N-dimethyl formamide and the suspension was sonicated for 10 min and then retained under vacuum at 298 K for 2 days[28].

MIL-101 with hydrofluoric acid as modulator

$Cr(NO_3)_3.9H_2O$ (4.0 gr), H_2BDC (1.66 gr) and HF (2 ml) in deionized water (48 ml) were stirred for 30 min at ambient temperature and subsequently heated to 493 K for 8 h. Multi-step solvent treatments by using water, hot ethanol, dimethyl formamide (DMF) and aqueous NH_4F solutions are necessary for the removal of impurities such as unreacted H_2BDC present both outside and within the pores of MIL-101 [11].

MIL-101 with nitric acid as modulator

$Cr(NO_3)_3.9H_2O$ (4.0 gr) and H_2BDC (1.66 gr) were dissolved in 0.4 ml of nitric acid 65%. The mixture was heated at 473 K for 12 h and then the solid was separated and washed with deionized water and dried in the oven overnight at 423 K. The washing step with ammonium fluoride has been eliminated [27,29].

Preparing shaped MIL101

The powders of MIL-101 (90 wt%) and of alginate (10 wt%) were premixed well. Then the mixture dropped into the 2 wt% calcium chloride solution to make uniform beads. After 15 minutes, shaped material washed by demineralized water and then undertakes a maturation step at 393 K for 10 h. In order to find the water uptake and reversibility of the shaped sample, water adsorption tests were performed. The formed samples were used for dehydration of natural gas, up to five adsorption-desorption sequential cycles. The shaped samples for the desorption step were heated at 343 K for 2 h.

Static and Dynamic Adsorption Apparatus

BELSORP Aqua 3 BEL device was used to measure water vapor absorption on synthesized nanoadsorbents. Absorption measurement in this device is based on a volumetric method. Measurements of dynamic adsorption were studied by using the packed-bed column which have been designed and made-up in-house [25].

RESULTS AND DISCUSSION

Three usual MIL-101 structures were synthesized via a hydrothermal method which are listed in Table 1.

Characterization: porosity of MIL-101 and Other Porous Solids

The Powder X-Ray Diffraction (PXRD) pattern indicates whether the structure of the material is crystalline or not. The published PXRD pattern for MIL-101 was used as the reference pattern to compare the aforementioned properties.

Fig. 1 shows the crystallographic information and purity of the MIL-101 phase using the X-ray diffraction method. The MIL-101 diffraction patterns are consistent with previous reports which underlined the similarity of the crystal structure [11]. Broad-wide Bragg reflections in material X-ray diffraction patterns are attributed to effects due to very small particle sizes. As the particle size decreases, the lines become wider, so MIL-101 (C), has the smallest particle. According to the diffraction patterns, the synthesized sample without adding acids has sharper peaks which means the larger particle size in this synthesized material.

Fig. 2 shows the FE-SEM images of the MIL-101 nanoparticles. It can be seen that all the

Table 1. Representative MIL-101 synthesis conditions

Sample	Metal	Ligand	Solvent	Additive	Synthesis Conditions
A	$Cr(NO_3)_3.9H_2O$	H_2BDC	H_2O	-	491K,18hr
B	$Cr(NO_3)_3.9H_2O$	H_2BDC	H_2O	HF	493K,8hr
C	$Cr(NO_3)_3.9H_2O$	H_2BDC	H_2O	Nitric acid	473K,12hr

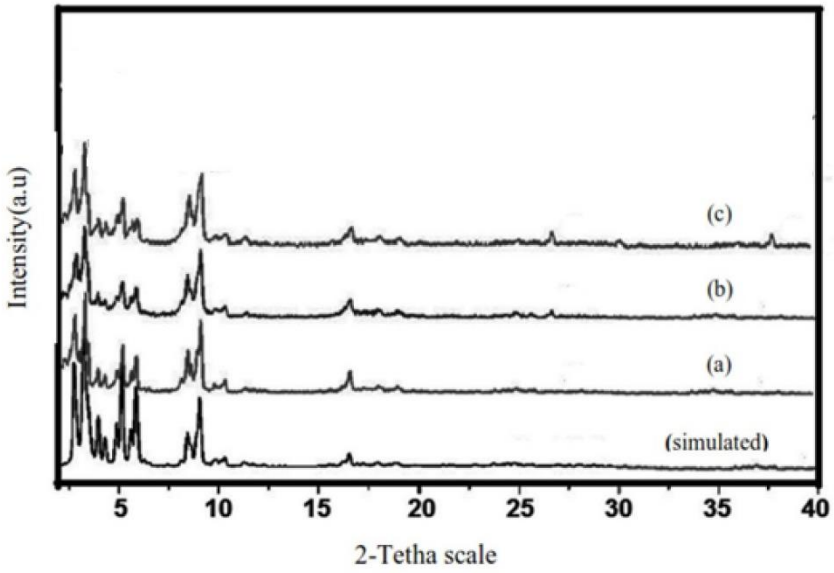

Fig. 1. X-ray diffraction pattern of MIL-101

synthesized samples have the shape of polyhedral crystals which is completely consistent with previous reports [29,32]. In addition, there is no needle-shaped crystal (indicating unreacted HBDC) in the powder, indicating that the purification processes are complete. The images show that the use of modulators (i.e. HNO_3 and HF) leads to an increase in the average particle size, uniformity and octagonal shape of the crystals [1].

The surface characteristics of the MIL-101 with different additives and other porous materials in terms of surface area and pore volume were measured using a N_2 adsorption/desorption isotherms. Isotherms for all samples of MIL-101 structures are shown in Fig. 3.

This indicates that N_2 uptake in all synthesized samples, except MIL-101 (A), which shows a significant hysteresis loop at $P / P_0 > 0.87$, is acceptably reversible with a slight hysteresis loop.

Generally, the presence of a hysteresis ring at high relative pressures can be an indication for the concentration of mesopores in the structure. According to the IUPAC classification, all isotherms presented in Fig. 3 can be classified as type I isotherm protocols. It is found that the two slopes observed in the range of $P/P_0 = 0.1$ and $P/P_0 = 0.2$ in the nitrogen adsorption isotherm, due to the presence of two types of microporous windows in the structure of MIL-101 [30].

The physical parameters of the synthesized

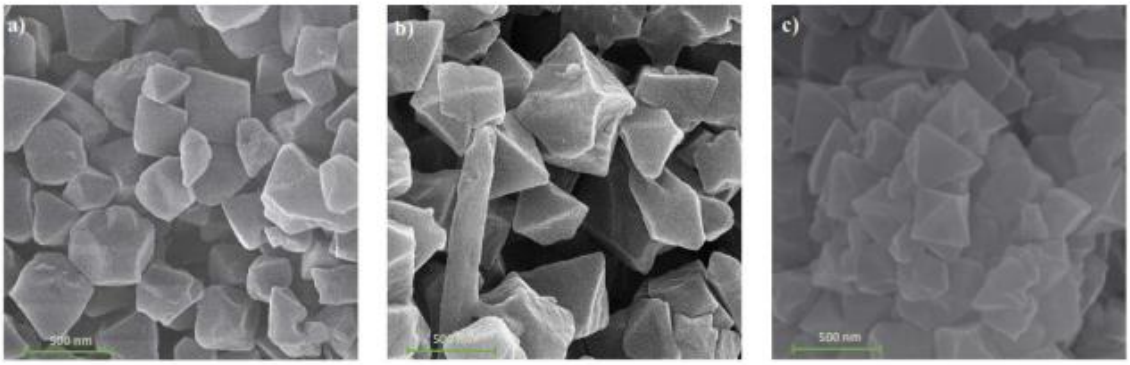

Fig. 2. FE-SEM images a) MIL-101 (C) b) MIL-101 (B) and c) MIL-101 (A)

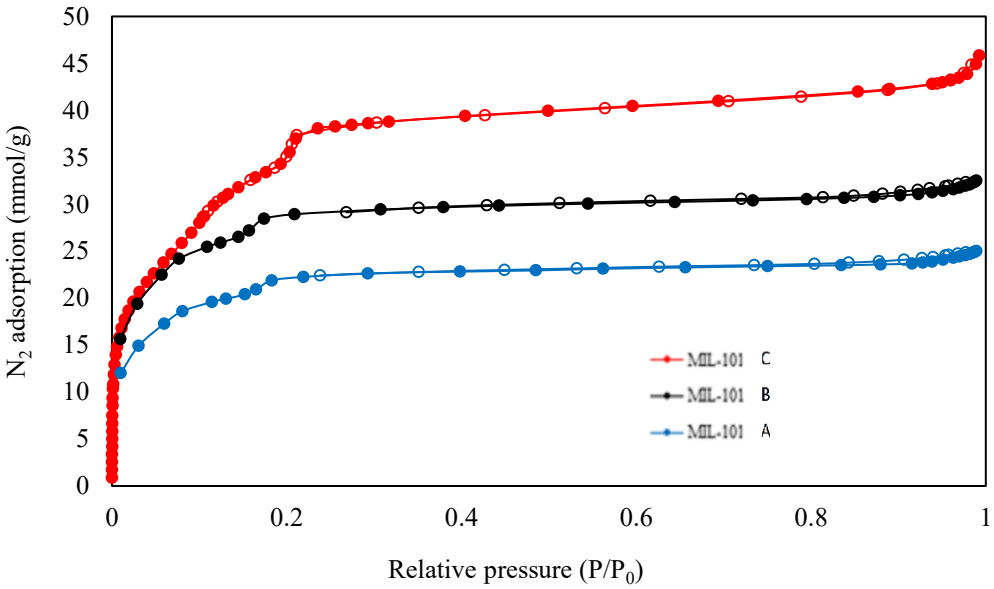

Fig. 3. Nitrogen adsorption/desorption isotherm for MIL-101 samples at 77 K

Table 2. Physical parameters of synthesized MIL-101

Samples	Surface area(m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
MIL-101 (A)	1758	0.85	7.44
MIL-101(B)	2132	1.18	1.24
MIL-101(C)	3129	1.51	2.11

MIL-101 structures obtained from BET and BJH analysis are presented in Table 2.

The use of HNO_3 and HF as modulator leads to an increase in surface area, pore volume, pore size, and the ratio of micropore volume to total pore volume. Regardless of the disadvantages of HF in human health, it has suggested HF as an excellent modulator. Since the synthesis of MIL-101 (C) leads to much better material properties, we see HNO_3 could be an even better alternative to HF. HNO_3 slowed the nucleation speed and, at a lower pH environment, would yield larger crystals of MIL-101. When adding the HNO_3 as additive, the particle size of would increase. It is assumed that the nitric acid as additive affects the particle growth, yielding material with a larger particle size, thus, outstanding to material that is more effective [31,32]. Here, the performance of MIL-101(C) was evaluated by FT-IR, TGA, water uptake assessment (powder and shaped, static and dynamic), stability and so on. For simplicity, we called MIL-101 (C) as MIL-101 for the rest of the article.

Fig. 4 shows the FT-IR spectrum of the prepared MIL-101 of the previous studies, in which the both types of the spectra are similar [33,34]. In the distance of 2500-3300 cm^{-1} we see the signals related to the OH bond, so the peak is not wide and differs from its ligand state. This shows that H atom has been lost and replaced by metal in the MIL-101, and this shows the formation of the MOF structure. The Strong signals in 1623.94 and 1403.42 cm^{-1} indicate the structure of O-C-O, and confirmed the presence of dicarboxylic acid as linker.

Typically, in the TGA profile of MIL-101, three distinct stages of weight loss are observed: the first weight loss (temperature below 150 ºC) is related to the loss of adsorbed water and organic solvent molecules. As the temperature rises further, the water molecules that are chemically bonded are removed. In the third stage (325 ºC < T <470 ºC), weight loss of approximately 57% is attributed to the removal of OH groups and the decomposition of the framework [35].

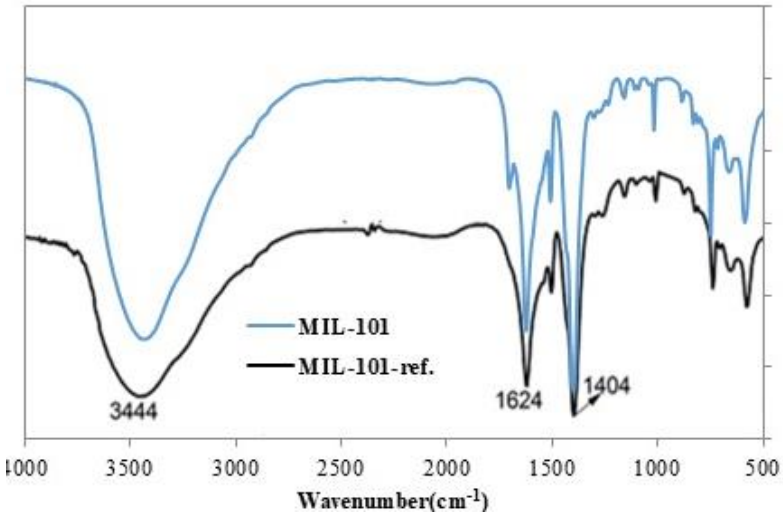

Fig. 4. FTIR of synthesized MIL-101

Experimental results of water uptake assessment

In order to evaluate the performance of synthesized metal-organic structures, adsorption isotherms were prepared at 25 ºC. Fig. 6 shows the water adsorption isotherm of the MIL-101 nanoadsorbent. Here we have two different slopes that are attributed to the filling of micro and meso cavities, respectively. The maximum water uptake at P / P_0 = 0.9 is more than 1.4 g / g.

As mentioned earlier, the MIL-101 is a structure with two different pore sizes, including micro and meso cavity. The steep slope of the adsorption diagram in the range of P / P_0 = 0.4 to P / P_0 = 0.5 indicates the water filling of mesopores.

Filling of mesopores begins first by pentagonal windows with a diameter of 11.7 Å and then by hexagonal windows with a diameter of 16 Å. At P / P_0 = 0.5 the adsorption of the water is completed and there is only a slight increase in the volume of water uptake due to the adsorption of water molecules in the cavities of the crushed powder particles [36]. The water uptake of MOFs and industrial desiccants were compared in Table 3. Data related to UiO-66 and UiO-66-NH_2 was taken

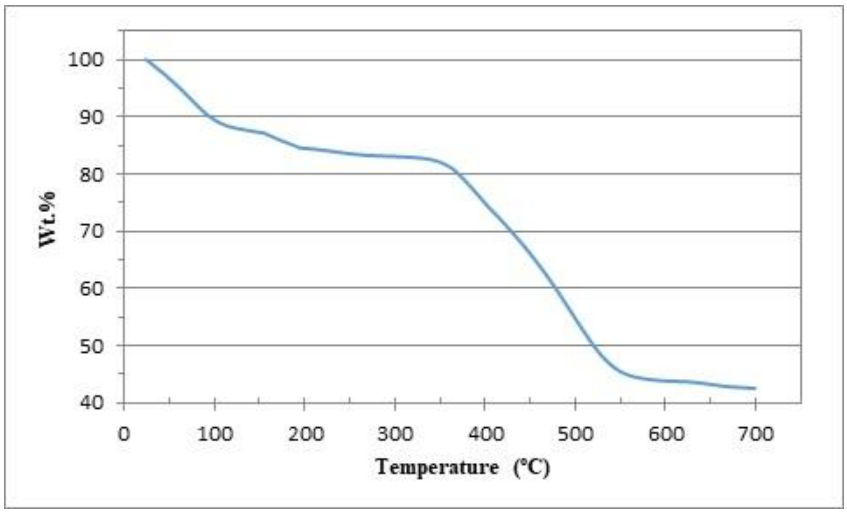

Fig. 5. TGA curve of MIL-101 nanoadsorbent

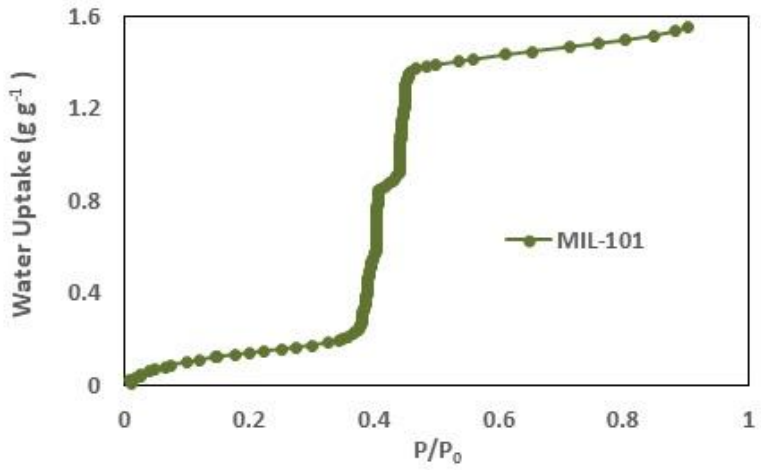

Fig. 6. Water adsorption performance of the MIL-101 measured at 298 K

Table 3. Summary of the Water Uptake of the Studied MOF and other desiccants

Water uptake (wt%)	Adsorbent				
	Desiccants		MOFs		
	Silica gel	3A	MIL-101	UiO-66	UiO-66-NH2
P/P_0=0.6	27.4	24.1	137.3	35.7	33.1
P/P_0=0.9	35.9	24.5	141.7	41.0	36.1

from previous published study [25]

Regeneration and Recyclability of MIL-101

As shown in Fig. 7, the water uptake of MIL-101, Silica gel and 3A zeolite for 5 cycles were studied (in each cycle regeneration of samples were performed at 80 ° C for 15 minutes). According to this study, there is no significant change for

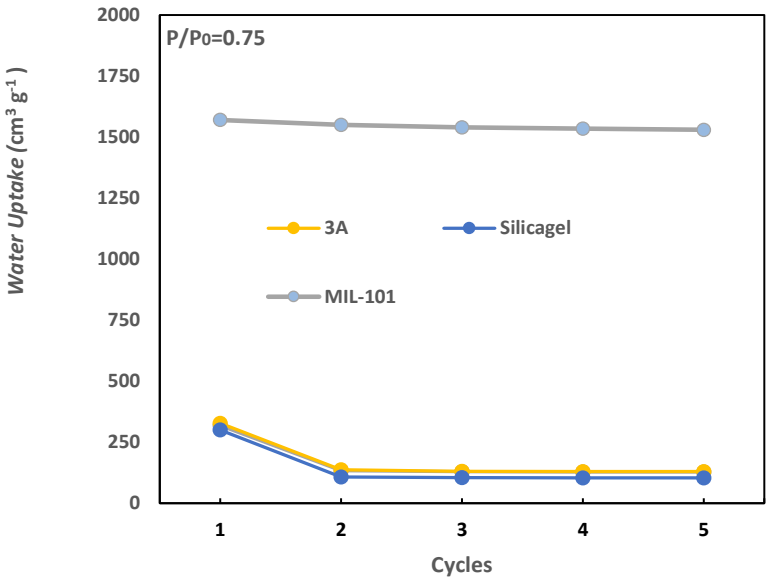

Fig. 7. Water uptake performance of MIL-101 and 3A zeolite and Silica gel at P/P_0=0.75 (298 K)

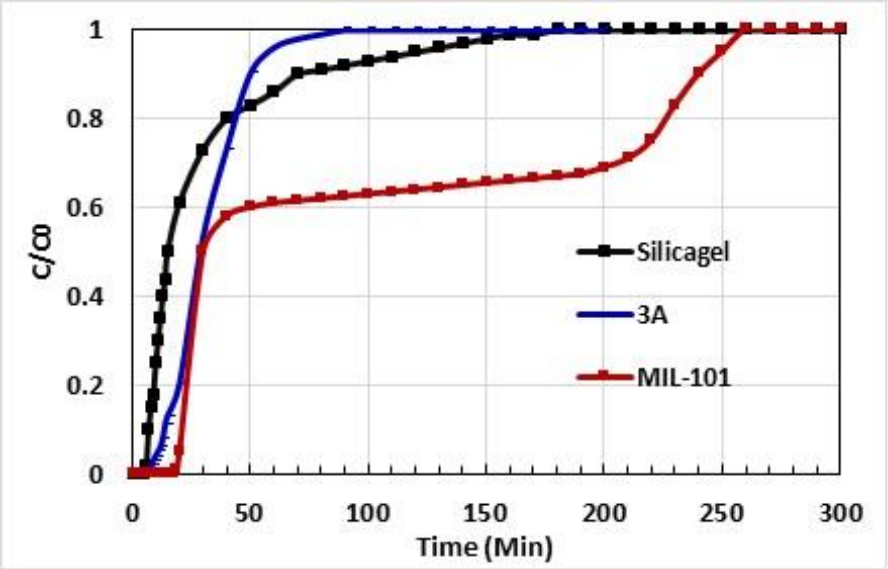

Fig. 8. Dynamic diagram of the water adsorption for MIL-101, Silica gel and 3A zeolite.

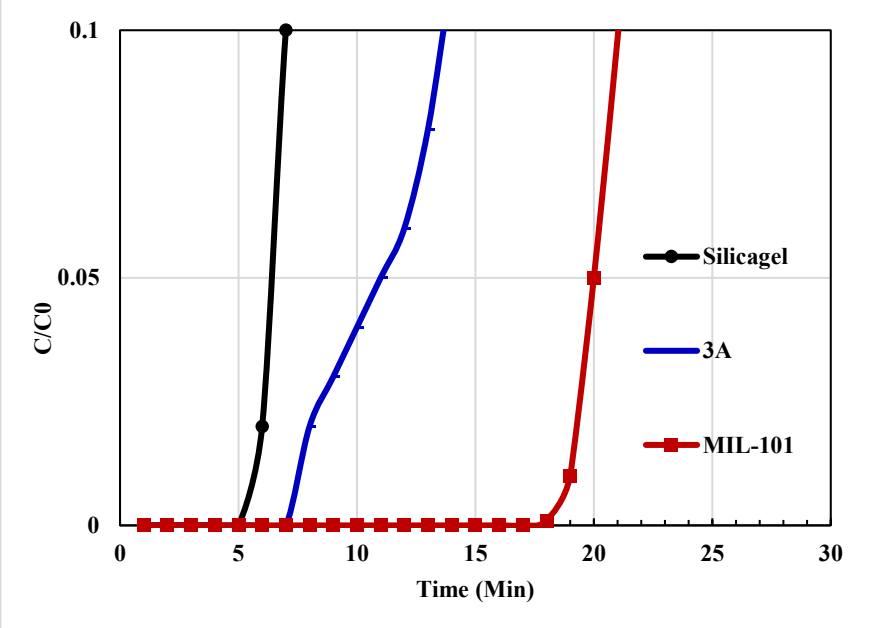

Fig. 9. Break through diagrams of MIL-101 and industrial desiccants (75% RH)

uptake for MIL-101 even after 5 cycles. Comparing conventional industrial attractions such as Silica gel and 3A zeolite, it is observed that the adsorption rate decreases significantly after the first cycle (they lose more than 50% of the initial capacity).

Experimental results of dynamic adsorption and breakthrough point

A comparison of the dynamic adsorption of MIL-101 structure and commercial adsorbents (3A zeolite and silica gel) at 75% relative humidity and

Table 4. Total Water Capacity, Equilibrium and Dynamic Breakthrough time for the MOFs and other adsorbents

Desiccant	Breakthrough Time (Min.)	Dynamic Equilibrium Time (Min.)	Total Water Capacity (Wt.%)
MIl-101	18	258	141
UiO-66	4.5	175	40
UiO-66(NH_2)	8.3	135	35
3A	7.2	100	26
Silica gel	5.5	155	34
Alumina	4.5	115	22

298 K was shown in Fig. 8. Industrial adsorbents were reached to the equilibrium saturation capacity before 150 minutes, meanwhile MIL-101 after about 250 minutes had potential for the water uptake. High water adsorption capacity was expected in the MIL-101 because the high surface area and situation of the water molecules that adsorbed in the structure.

The equilibrium saturation capacity is always more than the breakthrough capacity but essential factor for industrial measurements is breakthrough capacity because the desiccant must be regenerated before reaching the breakthrough point.

The break through diagrams of MIL-101 and commercial structures at 75% relative humidity and 298 K are shown in Fig. 9, Breaking points were determined for the silica gel and 3A zeolite after 5 and 7 minutes respectively and for MIL-101 after 18 minutes.

Dynamic equilibrium, breakthrough time and total capacity of water adsorption for MIL-101, 3A zeolite, silica gel, UiO-66 and UiO-66(NH_2) are summarized in Table 4. Data related to UiO-66 and

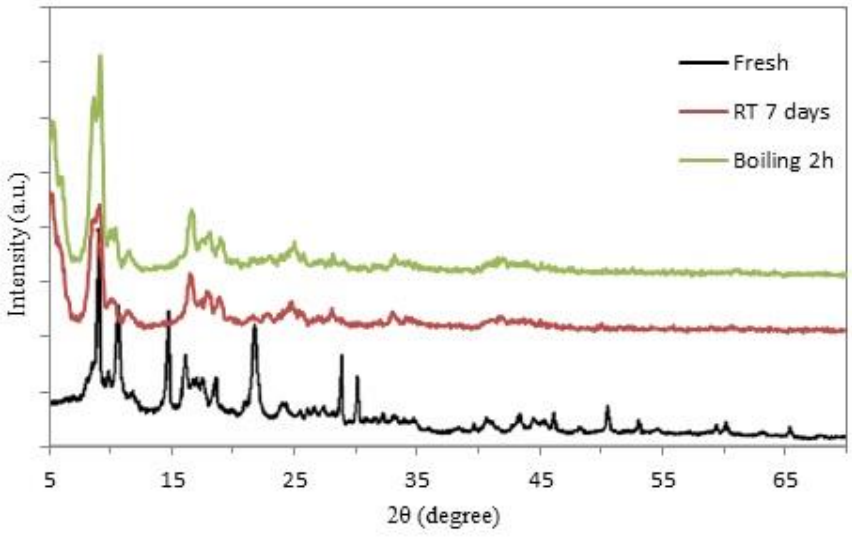

Fig. 10. XRD patterns of MIL-101 samples (fresh, in water for 7 days at room temperature and in boiling water for 2 hours)

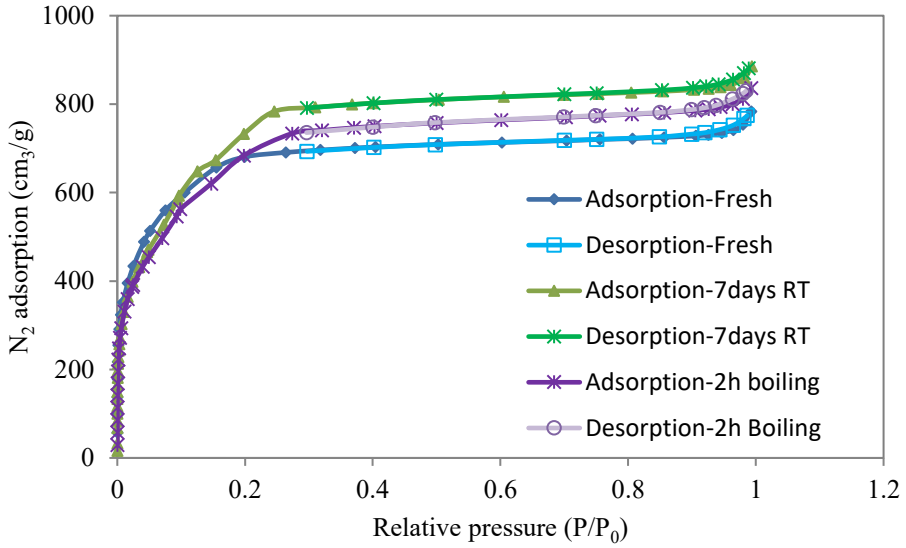

Fig. 11. Nitrogen adsorption/desorption isotherms (fresh, in water for 7 days at room temperature and in boiling water for 2 hours)

UiO-66-NH_2 was taken from previous published study [25]

Having a long breakthrough time is critical for choosing desiccant as natural gas dehumidifier because it determines the service life of a solid to adsorb moisture and could significantly reduce initial investment, energy required for regeneration and other operational costs. Thus, the MIL-101 is a good option due to its high breakthrough capacity.

MIL-101 has a trivalent chromium metal with unsaturated parts and two types of mesoporous cavities with an inner diameter of 2.9 and 3.4 nm. The presence of unsaturated metal parts in this material leads to very strong places to bond with the water guest molecules, in this material the penetration and adsorption of water into the cavities occurs very quickly. For this reason, a suitable break through time and high water adsorption capacity can be seen in this material. Despite the mesopores, it requires a certain amount of water to fill the cavities, so at a relative humidity of about 0.6, the curve becomes a plateau until the solid becomes saturated.

Stability of MIL-101 in humid environment

In order to evaluate the stability of the synthesized sample in this study in the presence of water, the sample was placed in water at room temperature once for 7 days and again in boiling water for two hours and then XRD and ASAP tests were studied to evaluate possible changes in structure, surface area and volume of cavities.

The results of XRD (Fig. 10) and ASAP (Fig. 11 and Table 4) tests indicate the stability of the sample under the conditions mentioned above.

The surface area of MIL-101 is more than 3000 m^2/g and has one of the largest pore volumes among the MOFs. The MIL-101 adsorbent has a strong water isotherm of type V, which indicates the high energy interaction between water and MOF structure [34,36]. Previous study confirmed that MIL-101 is very stable and its specific BET and

Table 5. Total pore volume, Average pore diameter and Surface area for the MIL-101

Samples		Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
MIL-101	Fresh	3100	1.50	2.11
	7 days RT	3150	1.28	1.97
	2 h Boiling	3050	1.35	2.32

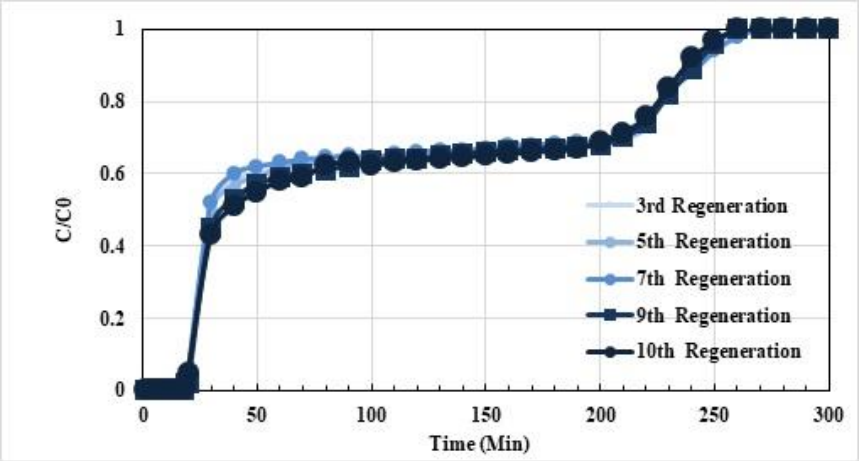

Fig. 12. Ten cycles of dynamic moisture adsorption/desorption of MIL-101 at 75% RH

XRD pattern are maintained even after one week of immersion in boiling water [12].

In order to evaluate the stability of MIL-101 powder in water for 7 days at room temperature and in boiling water for 2 hours, the structural parameters such as Surface area, Average pore diameter and Total pore volume was measured by N_2 adsorption at 77 K and the results was mentioned in Table 5.

A survey of consecutive dynamic moisture adsorption cycles on MIL-101 powder at 75% relative humidity showed a slight change in the adsorption cycle, indicating the maintenance of water adsorption capacity after ten cycles (Fig. 12).

Shaped Structure studies

In the meantime, the powder form of MIL-101 showed high water uptake capacity and stability, it was shaped for the purpose of industrial applications. High pressure drop, inlet ducts

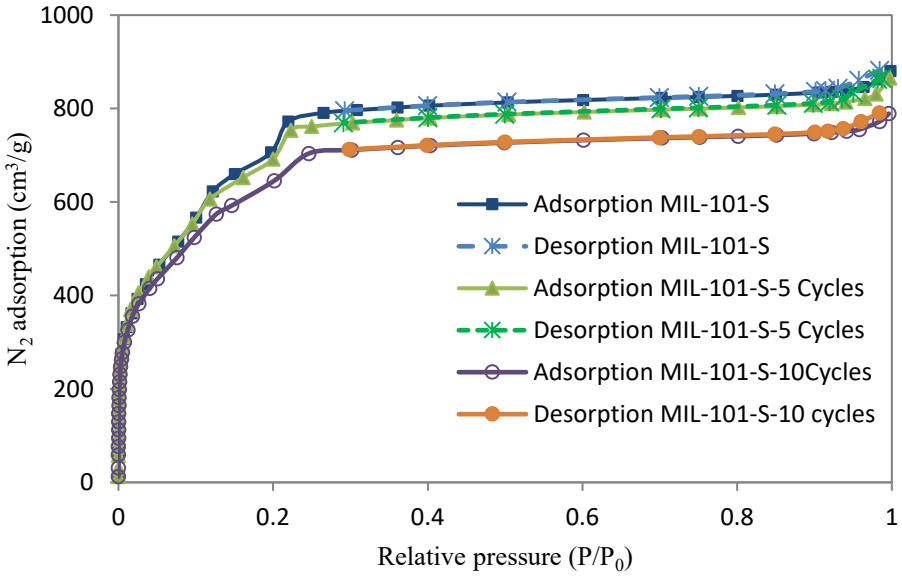

Fig. 13. Nitrogen adsorption-desorption isotherms for formed MIL-101

Table 6. Specification of MIL-101 Formed after 5 and 10 Adsorption Cycles

Number of cycles	0	5	10
Surface area [m2 / g]	2833	2677	2441
Cavity volume [cm3 / g]	1344	1316	1207
Initial weight [mg]	150	150	120
Final weight [mg]	290	290	230
Weight difference [mg]	140	140	110
Percentage of initial capacity	100	100	98

blockage and wasting by output stream are main challenges of powder form. In this study, the MIL-101 powder was shaped with alginate and investigated by a dynamic system. Natural gas was passed from saturated NaCl solution and the relative humidity exceeded to 75%, then the amount of water adsorption at 298 K was measured by gravimetric method. In the regeneration step, the sample was placed at 373 K for 150 minutes and the weight of the samples was measured. After 5 and 10 adsorption cycles, the ASAP test was performed. Fig. 13 shows the adsorption-desorption isotherm. After 10 cycles, nitrogen uptake decreased by less than 10%. In addition, the pore volume and water adsorption capacity at 75% relative humidity were determined after adsorption cycles (Table 6). As can be seen, the water adsorption capacity does not decrease more than 2%. The surface area after 5 and 10 cycles decreased by about 5 and 14%, and the volume of cavities decreased by 2 and 10%, respectively.

Dynamic adsorption of the powder (P) and shaped (S) form of MIL-101 was compared in Fig. 14 and Table 7. Decreasing the surface area, Total water capacity and Break through time are justified by increasing the resistances of the solid phase and barrier the matrix-forming substance (here alginate).

Regeneration of MIL-101

One of the key principles which should be considered for selection and actual applicability of MOFs is ease of regeneration and stability to minimize the operational cost and maximize the efficacy of water removal.

To evaluate this factor, after water adsorption in 75% relative humidity, the samples were regenerated in two different temperatures (80 and 120 ºC for 30 minutes) and the weight loss of the samples was measured as a function of time.

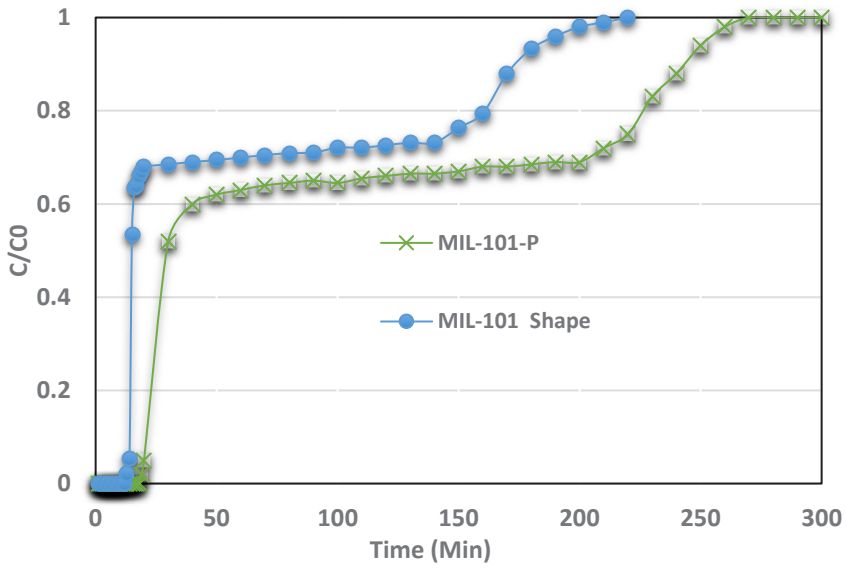

Fig. 14. Adsorption isotherms for powder and shaped forms of MIL-101

Table 7. Total Water Capacity, Dynamic equilibrium and Breakthrough time of MIl-101 for powder (P) and shaped (S) forms

Desiccant	Breakthrough Time (Min.)	Dynamic Equilibrium Time (Min.)	Total Water Capacity (Wt.%)
MIL-101-P	18.1	260	141
MIL-101-S	12.3	220	100

According to the results, the samples under the 75% relative humidity condition, adsorb the water about 98% of initial weight and during the regeneration at different temperatures (80 and 120 ºC), the samples lost more than 48.2% and 43.5% of their weight, in the other words, 95 and 88% of the adsorbed water were removed from the samples, respectively.

The weight changes of the samples at the two different regeneration temperatures as well as the weight loss over time are shown in Fig. 15. The weight remained constant after 10 and 15 minutes at 120 and 80 ºC respectively. It means that the saturated samples with water vapor can be regenerated in a very short time (maximum 15 minutes).

Although regeneration at 80 ºC required more time but the adsorbent was better regenerated and the samples excreted more than 95% of the adsorbed moisture. Comparison of time and regeneration temperature of organic-metal structure (80 ºC and 15 minutes) with industrial ones for examples silica gel (260 ºC and 8 hours) shows a significant reduction in energy and time.

Adsorption modeling with kinetic model

In equilibrium modeling of adsorption, prediction of adsorption parameters as well as quantitative comparison of surface adsorption behavior for different systems and different laboratory conditions are considered. The linear squares method is widely used to determine the isotherm parameters.

As previously stated, water vapor uptake on the MIL-101 is described by a type V isotherm (Fig. 4)

One of the related models that can be well used for type V isotherms is the Dubinin-Astakhov equation (DA); This equation is based on the assumption that the adsorption process follows the mechanism of filling the cavities [38].

$$V = V_0 \exp\left[-(A / E)^n\right] \quad (1)$$

V is the adsorbed volume at relative pressure (P / P_0), V_0 is the maximum adsorbed volume) and E is the adsorption energy. Power “n” depends on the non-uniformity of the size distribution and the

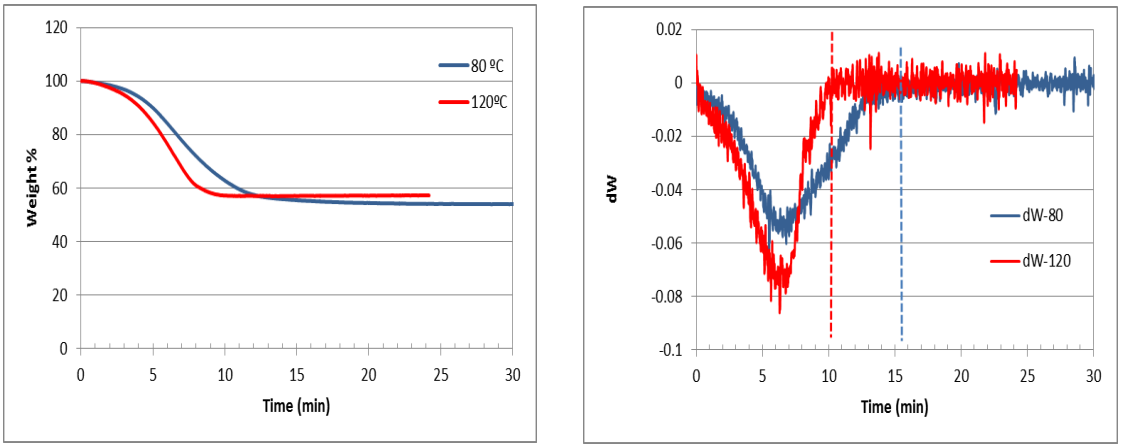

Fig. 15. Weight changes (Left) and Weight loss (Right) of the saturated sample over time

adsorption potential (A) defined as:

$$A = -RT * \ln (P / P_0) \quad (2)$$

The reason for the relatively good agreement of the data with the Dubinin-Astakhov model (DA) is due to the large cavities of MIL-101 adsorbent micropores and the volume of mesoporous cavities, which is one of the main assumptions of the DA model. The cavities have a variety of distribution in micro dimensions that are consistent with the adsorbent data, so this model can be used in calculations for design of the adsorption column. (Fig. 16)

In this study, using the analysis based on industrial parameters, we showed that the chromium (III) terephthalic MIL-101 could be a remarkable adsorbent for natural gas dehumidification.

Three samples with different additives (HF, HNO_3 and one sample without additive)) were synthesized hydrothermally and characterized with PXRD, SEM and ASAP. The results showed that the MIL-101 nanoadsorbent has a high efficiency in terms of high water absorption capacity (more than 140% by weight) and an interesting breakthrough time of more than 260 minutes, is a more desirable option than other solid sorbents.

The synthesized sample of MIL-101, shows high thermodynamic stability with a high level of reliability of this structure in the presence of water. The stability of the MIL-101 in the presence of water was investigated and the results showed that MIL-101 that was exposed to water for 7 days and in boiling water for 2 hours is stable and the essential performing parameters such as PXRD and ASAP almost remained constant.

Comparing the MIL-101 sample with conventional industrial adsorbents such as Silica gel and 3A zeolite, was observed that during 10 consecutive cycles, no significant change in the moisture adsorption of the samples was observed during 10 consecutive cycles.

The amount of energy required to regenerate the adsorbents were measured and the results showed that at a temperature of 80 ° C for 15 minutes, the MIL-101 was released more than 95% of its moisture. The energy required to regenerate these materials is far less than conventional adsorbents.

Analysis of nitrogen adsorption-desorption isotherms for MIL-101 powder and shaped form showed that after 10 cycles, nitrogen uptake decreased by less than 10%.

Adsorption study on the shaped form of MIL-101 with alginate in the dynamic system and in several cycles showed that the formation of shaped samples reduced the adsorption rate and

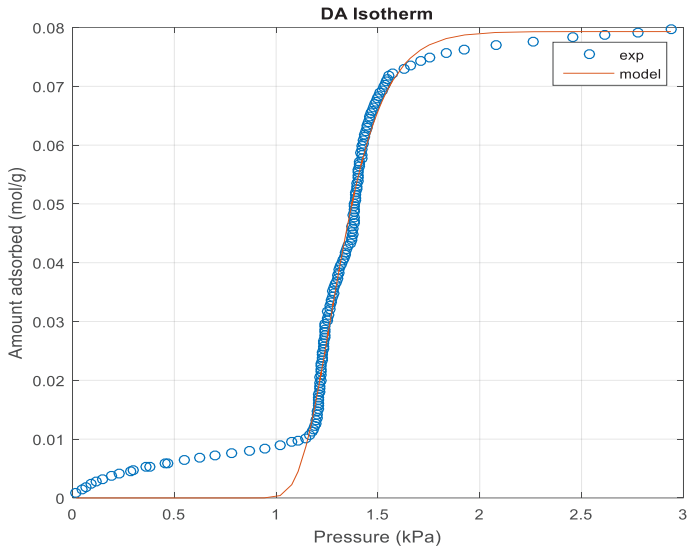

Fig. 16. Correlation of kinetic adsorption model with experimental results for MIL-101

breaking point due to the common resistance to penetration from the gas to solid phase. The specific surface area of the shaped samples is reduced by about 15-20%, but in any case it is competitive with conventional adsorbents in terms of adsorption and breaking point.

CONCLUSION

In conclusion, according to the results obtained in this study, organic-metallic structures can be proposed as reliable materials for dehumidification of natural gas. In this study, in addition to static adsorption, which has been discussed in previous studies, dynamic adsorption studies were performed as an important parameter in the selection of adsorbents for industrial applications and showed that MIL-101 can be used for dehumidification of natural gas.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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