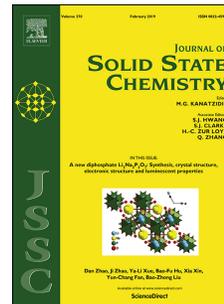


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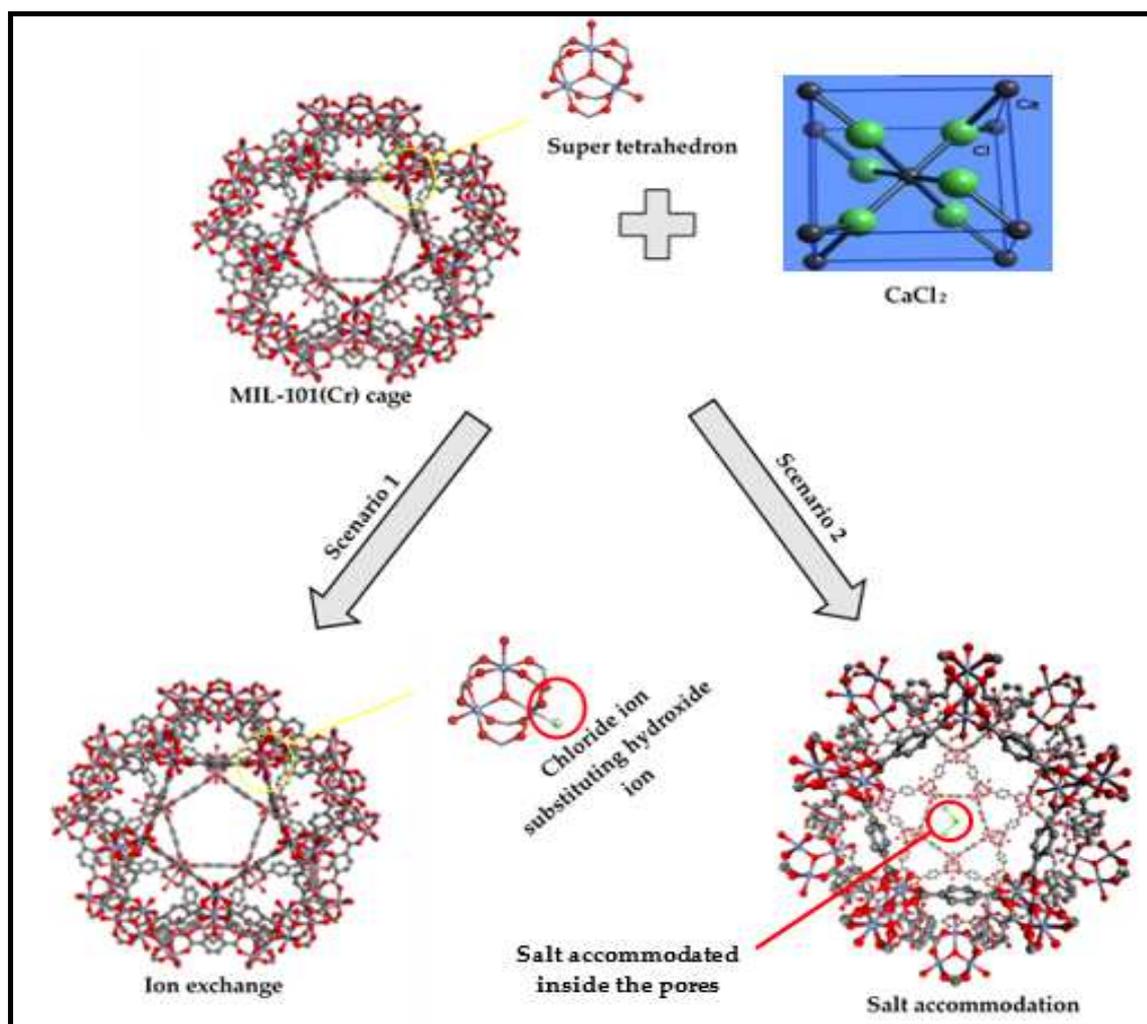
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# MIL-101(Cr)/Calcium Chloride composites for enhanced adsorption cooling and water desalination

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## Abstract:

The adsorption capacity of adsorbent materials at low relative pressure range is a crucial parameter that guarantee the high overall performance and efficiency of adsorption cooling and water desalination systems. MIL-101(Cr) is a metal-organic framework (MOF) material with a high-water vapour uptake of 1.36–1.47  $\text{g}_{\text{H}_2\text{O}} \text{g}_{\text{ads}}^{-1}$ . However, MIL-101(Cr) exhibits an IV isotherm (S-shaped isotherm) which means that the high-water uptake only takes place at high relative pressure ( $\geq 0.5$ ). This drawback makes MIL-101(Cr) impractical for adsorption applications working at lower relative pressure such as adsorption cooling and desalination with cooling effect which operate at relative pressures  $\leq 0.4$ . In this work, MIL-101(Cr)/CaCl<sub>2</sub> composites were synthesized, the unsupported and CaCl<sub>2</sub> supported materials were fully characterized in terms of their structure (XRD), thermal stability, vibrational spectroscopy structure, morphology (SEM), water adsorption capacity and BET surface area. As a result, incorporating CaCl<sub>2</sub> into the MIL-101(Cr) structure significantly enhanced water adsorption characteristics in the desired relative pressure range as the water vapour uptake for Comp\_1:8 CaCl<sub>2</sub> composite increasing from only 0.1  $\text{g}_{\text{H}_2\text{O}} \text{g}_{\text{ads}}^{-1}$  for as-synthesized MIL-101(Cr) to 0.65  $\text{g}_{\text{H}_2\text{O}} \text{g}_{\text{ads}}^{-1}$  at a relative pressure of 0.3.

**Keywords:** Metal-organic framework, MIL-101(Cr), MIL-101(Cr)/CaCl<sub>2</sub> composites, characterization, adsorption cooling.

## 1. Introduction:

Over the past 50 years, a significant increase of almost 22% in the CO<sub>2</sub> emissions has been recorded. This rise was accompanied with an increase in the average global temperature [1-3], resulting in a dramatic increase in the demand for cooling. This demand was largely supplied by systems utilizing chlorofluorocarbon (CFCs) and hydrochlorofluorocarbon (HCFCs) refrigerants before their phaseout [4, 5]. Also, these systems were driven by electricity generated using fossil fuels. An alternative to the common cooling systems is adsorption technology which can be operated using waste heat or renewable energy sources (such as solar and geothermal energy) and uses environmentally friendly refrigerants such as water [6]. Adsorption desalination can also offer an innovative solution to another global crisis which is water scarcity [7] as by 2025, 1.8 billion human being will be living in absolute water scarcity regions [8-10].

Nevertheless, adsorption systems suffer from poorer performance than common cooling systems due to the low water uptake of currently used adsorbents (silica gel and zeolites) at low relative pressures, which limits their application. To solve such problem new adsorbent materials with improved adsorption properties are required [11, 12]. MOFs are crystalline porous materials with exceptional properties such as high BET surface area, versatile pore geometry and tunable pore size and volume [13-15] which can provide high adsorption capacity compared to conventional silica gel [16]. It was shown that due to their tunable properties, MOFs are considered as promising candidates for adsorption heat transformation processes [17]. Using such materials in adsorption systems is expected to improve the performance of the system significantly owing to their superior adsorption capacity.

MIL-101(Cr) is a MOF material that is characterized by its high surface area and adsorption capacity.

. Its capacity of n-alkanes was improved using graphite oxide (GO) while MIL-101(Cr) capacity of acetone was improved through incorporating it with graphene oxide (GrO). Also, a composite of MIL-101(Cr) and multi-walled carbon nanotubes (MWCNT) showed an enhanced carbon dioxide adsorption while another composite using expanded natural graphite (ENG) was used for hydrogen storage. MIL-101(Cr) has a high adsorption capacity of water vapour that can reach up to  $1.47 \text{ g}_{\text{H}_2\text{O}} \text{ g}_{\text{ads}}^{-1}$  and high performance stability [17]. This adsorption capacity was further enhanced by means of combining it with graphene oxide (GrO) and graphite oxide (GO) [18][26]. Nevertheless, all the previously conducted studies focused on improving the equilibrium vapour capacity of MIL-101(Cr) meaning that the entire enhancement took place at high relative pressure range. This makes MIL-101(Cr) and its previous composites impractical for adsorption cooling and desalination applications as the high-water vapour adsorption is only taking place at a relative pressure higher than 0.5. In adsorption cooling and desalination applications, water is used as an adsorbate. To ensure the high performance and efficiency of the system, the adsorbent material should exhibit a high-water vapour capacity at the low relative pressure range (low relative pressure  $\leq 0.4$ ) as shown in Fig. 1.

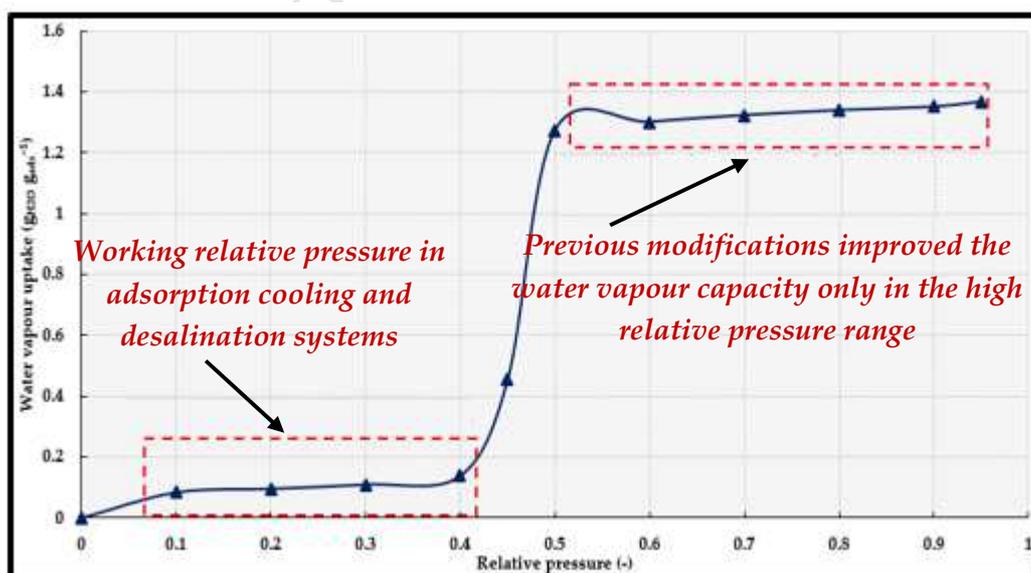


Fig. 1 Water adsorption isotherm of MIL-101(Cr) indicating the relative pressure range of adsorption cooling applications and previous enhancement in the water adsorption capacity.

In this study, the potential of MIL-101(Cr)/CaCl<sub>2</sub> composites in adsorption cooling and desalination systems was investigated. After demonstrating the synthesis of such composites, the produced composites were fully characterized to evaluate the effect of CaCl<sub>2</sub> concentration on the crystal structure of MIL-101(Cr) and how the composites exhibit significantly enhanced performance in the technologically vital low relative pressure range. Also, the mechanism of the incorporation CaCl<sub>2</sub> and water vapour adsorption were explained. This study paves the way for utilizing MOF-based composites in low temperature adsorption applications.

## 2. Methodology:

### 2.1. Synthesis of MIL-101(Cr):

The parent MIL-101(Cr) was synthesized using the hydrothermal synthesis procedures reported by *Yang et al* [17, 19].

### 2.2. Synthesis of MIL-101(Cr)/CaCl<sub>2</sub> composites:

**Fig. 2** illustrates the strategy used to develop the CaCl<sub>2</sub> composites. MIL-101(Cr)/CaCl<sub>2</sub> composites were synthesized by suspending the pre-synthesized MIL-101(Cr) powder in solutions with different CaCl<sub>2</sub> concentrations. The effect of the CaCl<sub>2</sub> concentration was investigated through preparing suspensions with the mass ratio of one-part MIL-101(Cr) to 3, 4, 5, 6 and 8 parts of CaCl<sub>2</sub> salt. The composites were assigned the names Comp\_1:3, Comp\_1:4, Comp\_1:5, Comp\_1:6 and Comp\_1:8. First, the CaCl<sub>2</sub> salt was dissolved in water and MIL-101(Cr) powder was added and left under stirring for 4 hr at the room temperature (**Fig. 2**). Then, each suspension was filtered, repeatedly washed with distilled water and left to dry in air. As the water vapour adsorption capacity is usually used to judge the suitability of adsorbent materials for adsorption applications, the optimum suspension time was determined based on it. It can be noticed from **Fig. 3** that the suspension time had almost no

effect on the water vapour uptake, hence a time as short as 4 hr can be chosen as the optimum suspension time.

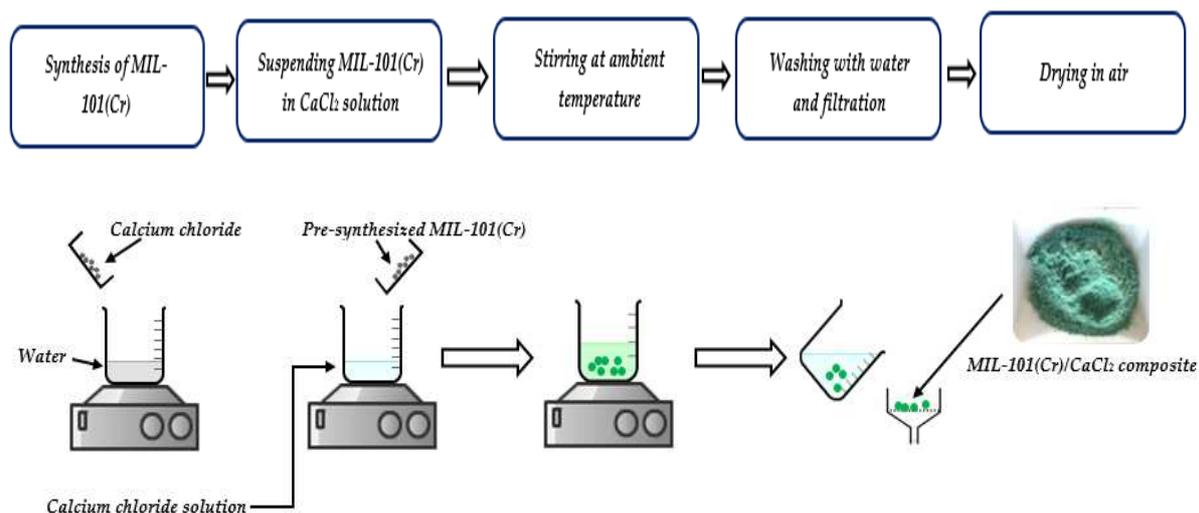


Fig. 2 Synthesis strategy of MIL-101(Cr)/CaCl<sub>2</sub> composites.

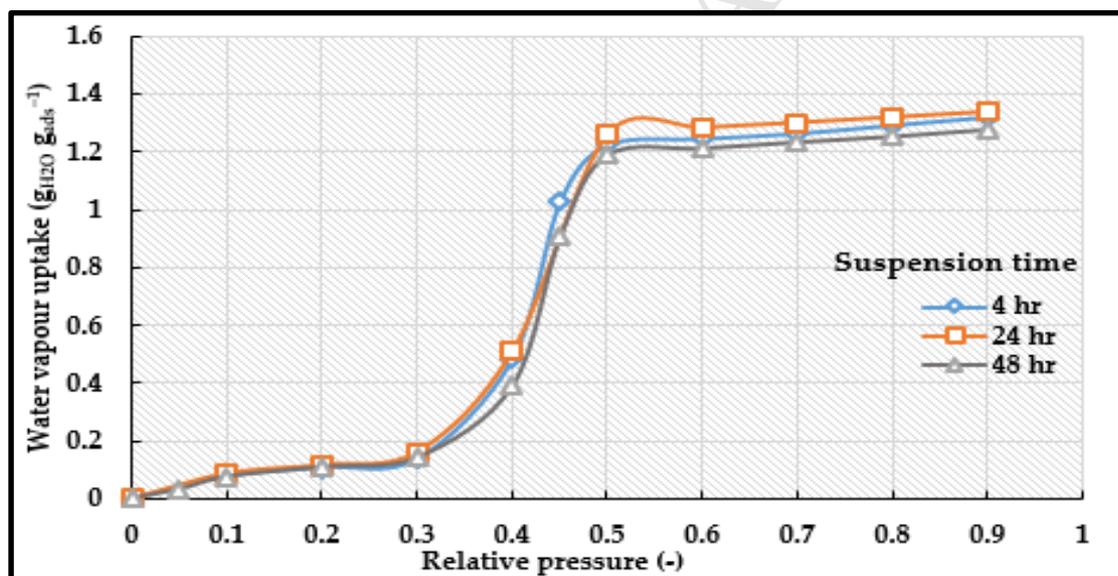


Fig. 3 Effect of suspension time on the water vapour adsorption capacity of Comp\_1:4 CaCl<sub>2</sub> composite.

### 2.3. Materials characterization:

To ensure that suspending MIL-101(Cr) crystals in CaCl<sub>2</sub> solutions did not negatively influence its structural integrity, all the materials were characterized using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) images. The materials were also characterized in terms of their BET surface area through nitrogen adsorption, water

adsorption characteristics, Fourier transform infrared (FTIR) spectroscopy, Raman Spectroscopy and thermal gravimetric analysis (TGA).

### 3. Results and discussion:

#### 3.1. X-Ray Diffraction:

The XRD patterns were measured on a Siemens D5005 diffractometer with Cu K $\alpha$  radiation (1.5418 Å). The samples were scanned from 5 to 30° 2 $\theta$  with a step size of 0.02°. **Fig. 4** shows the diffraction patterns of the anhydrous CaCl<sub>2</sub> salt, the unsupported MIL-101(Cr) and the CaCl<sub>2</sub> supported composites. The diffraction peak positions of MIL-101(Cr) were found to be in agreement with previously reported data [20, 21] which indicates that the material was successfully synthesized with its cubic structure. Also, the absence of the reactant peaks indicates that the washing procedures used have effectively removed any traces of both reactants. The peaks at the low 2 $\theta$  indicate the large d-spacing and lattice volume. It can be noticed that the characteristic peaks of MIL-101(Cr) were preserved in all the CaCl<sub>2</sub> composites which indicates that the presence of CaCl<sub>2</sub> did not disrupt or cause any distortion in the MIL-101(Cr) crystal structure. In addition, none of the calcium chloride salt peaks (highlighted) were present in the patterns indicating the successful incorporation of the salt inside the structure of the MIL-101(Cr) and the removal all the excess CaCl<sub>2</sub>. Similar behaviour was observed when graphene oxide was incorporated inside the structure of MIL-101(Cr) [17].

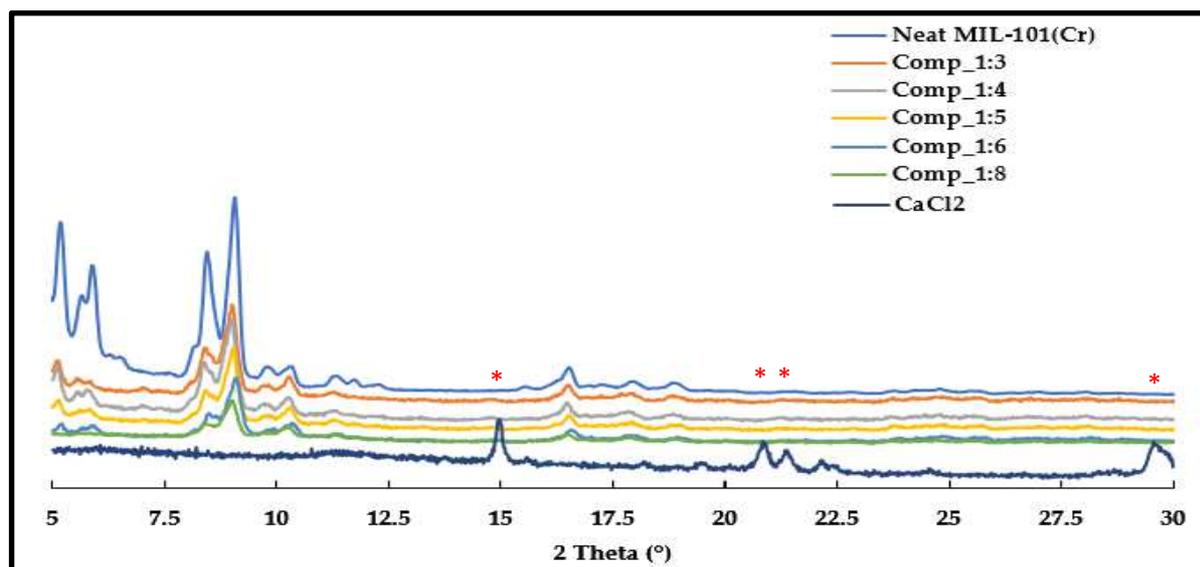


Fig. 4 XRD patterns of MIL-101(Cr), CaCl<sub>2</sub> and synthesized composites.  
(The main peaks of Calcium chloride are highlighted)

### 3.2. Nitrogen adsorption:

The N<sub>2</sub> adsorption isotherm was measured at 77 K was used to measure the BET surface area [22] using a Quantachrome NOVA surface area analyser. Each sample was evacuated at 393 K and the BET surface area was obtained in the relative pressure range from 0.03 to 0.3. This range was chosen as the BET calculation requires a linear plot which is restricted to a limited region of the adsorption isotherm taking place just before what is called ‘the knee’. The knee indicates the completion of single molecular layer (monolayer) coverage of the available pore surface and the beginning of the formation of the multi-molecular layer [23].

The total pore volume was calculated at a relative pressure of 0.95 while the pore size distribution was calculated using the DFT method. The DFT method was chosen as it has the advantage that its underlying molecular modelling approach takes into account the variance in the density of the adsorbed phase as a function of pore size, the BJH (Barrett, Joyner, and Halenda) neglect.

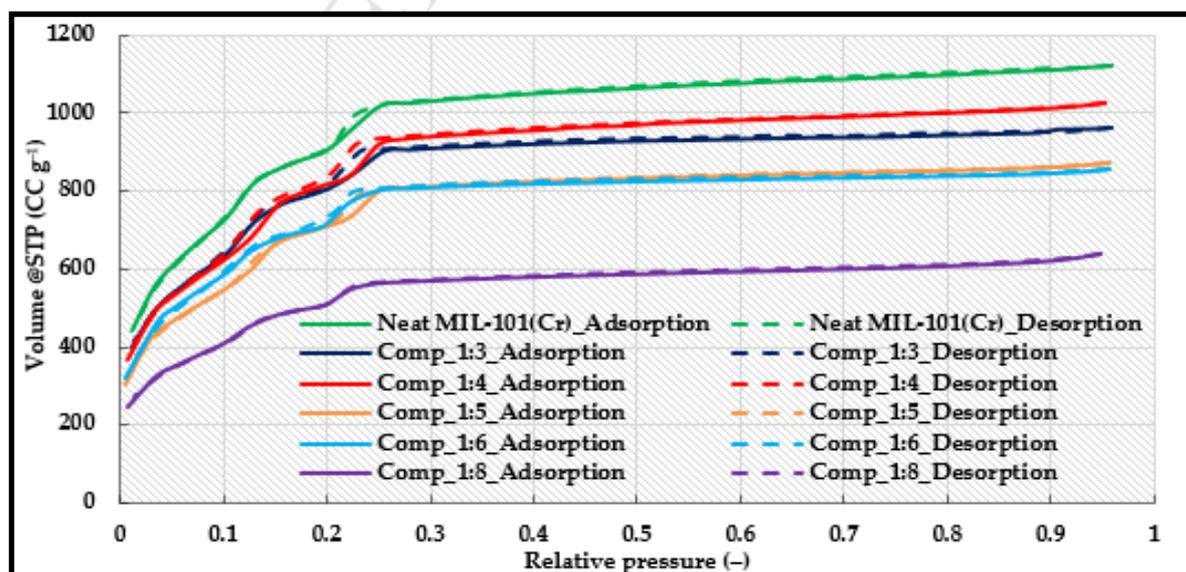
**Fig. 5** shows the nitrogen adsorption isotherms of the MIL-101(Cr)/CaCl<sub>2</sub> composites. It was found that the surface area of the synthesized MIL-101(Cr) was 3355 m<sup>2</sup> g<sup>-1</sup> and its pore volume was 1.73 cm<sup>3</sup> g<sup>-1</sup>. The measured values are in good agreement with the previously reported values using the same synthesis procedures which were 3197 m<sup>2</sup> g<sup>-1</sup> and 1.73 cm<sup>3</sup> g<sup>-1</sup>, respectively [20].

It can be noticed that introducing CaCl<sub>2</sub> to MIL-101(Cr) in Comp\_1:3, Comp\_1:4 and Comp\_1:5 composites slightly decreased the BET surface area and the total pore volume as illustrated in **Table. 1**, while for the Comp\_1:6 and Comp\_1:8 composites, the surface area significantly decreased. The decrease in the pore volume and surface area are due to a number different of effects as shown in **Fig. 6**. There are two potential scenarios or hypothesis, the first is assumed to be an ion exchange mechanism where the ions of the salt replace the ions of the framework. In this case, the chlorine ion could substitute for the hydroxide ion which co-ordinates to the chromium cluster and the decline in the pore volume and surface area would be caused by the difference in size of ions (1.81Å for Cl<sup>-</sup> vs 0.958Å for OH<sup>-</sup>). A similar mechanism was observed when the CaCl<sub>2</sub> was incorporated in zeolite

13X [24]. The second potential hypothesis is the incorporation of the  $\text{CaCl}_2$  would cause the salt accommodation inside the pores of the MIL-101(Cr) which would lead to a reduction in the available pore volume. Such mechanism is similar to when  $\text{CaCl}_2$  was incorporated in silica gel to produce SWS-1L [25]. Still, the pore size distribution calculated *via* DFT showed that even though the unsupported material had the highest pore volume, incorporating MIL-101(Cr) with  $\text{CaCl}_2$  had almost no effect on the pore size of all the composites as shown in Fig. 7.

**Table. 1** Surface area of MIL-101(Cr) and  $\text{CaCl}_2$  composite

Material	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
<i>Neat MIL-101(Cr)</i>	3354.84	1.73
<i>Comp_1:3</i>	2976.77	1.49
<i>Comp_1:4</i>	3117.14	1.58
<i>Comp_1:5</i>	2675.9	1.35
<i>Comp_1:6</i>	2641.5	1.32
<i>Comp_1:8</i>	1876.01	0.99



**Fig. 5 Nitrogen adsorption isotherms of MIL-101(Cr) and CaCl<sub>2</sub> composites at 77 K.****3.3. Thermal gravimetric analysis (TGA):**

The thermal stability of the materials was investigated by thermal gravimetric analysis (TGA) with Perkin Elmers Pyris 1. **Fig. 8** shows the change in mass as a function of temperature for the unsupported MIL-101(Cr) and MIL-101(Cr)/CaCl<sub>2</sub> composites. It can be noticed that all the materials had three stages of weight loss. In the first stage, the materials lose the water trapped in their pores. In this stage, MIL-101(Cr) lost almost 50% of its weight at a temperature of 137°C while all the CaCl<sub>2</sub> composites showed slightly lower weight loss except for the Comp\_1:8 composite. Comp\_1:8 composite showed a significantly lower weight loss than other composites due to the higher content of CaCl<sub>2</sub>. In the second stage, the materials lose their co-ordinated water molecules hence a lower weight loss is expected [26]. For MIL-101(Cr), this stage took place in the temperature range of 137–337°C. In the second stage, it can be noticed that all the composites showed a higher thermal stability over the temperature range of 123–423°C which is higher than MIL-101(Cr) emphasising the higher thermal stability of the CaCl<sub>2</sub> composites. The higher stability of the CaCl<sub>2</sub> composites is due to the substitution of -OH CaCl<sub>2</sub> the or accommodate inside the pores. This means that the content of the free water and the coordinated water are reduced and hence a lower weight loss is expected, and the decomposition of the structure is shifted to a higher temperature which means a higher thermal stability. The combustion of the terephthalic acid caused the weight loss in the final stage [26]. It can be concluded from the thermal gravimetric analysis that as the CaCl<sub>2</sub> concentration in the composite increased, the thermal stability of the composite was also increased.

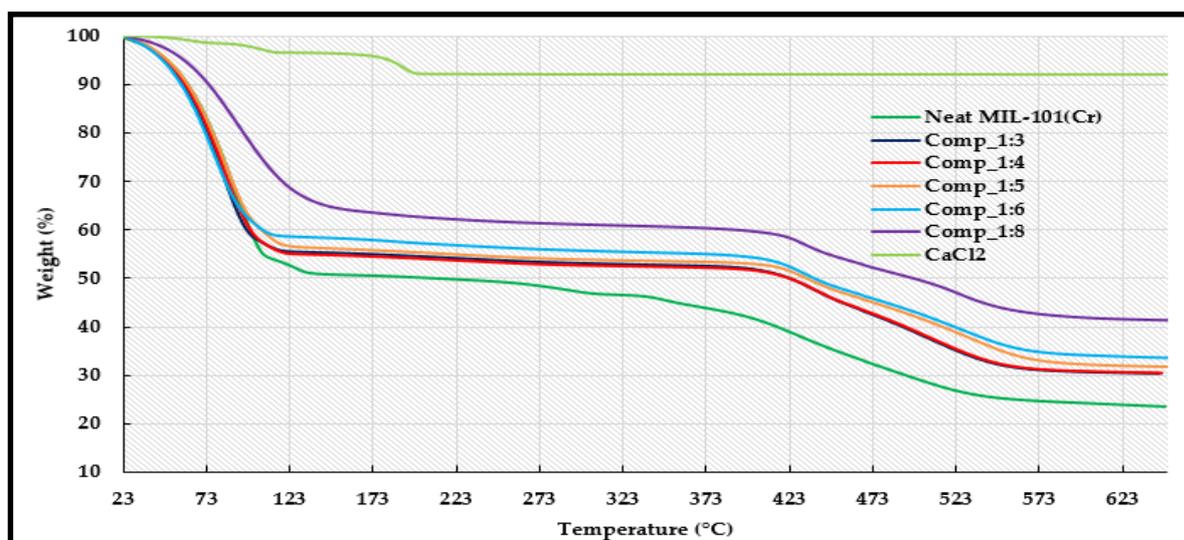


Fig. 8 Thermal gravimetric analysis of MIL-101(Cr) and CaCl<sub>2</sub> composites.

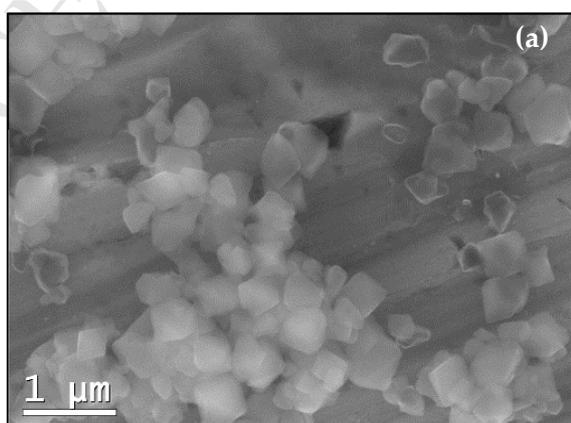
### 3.4. Scanning Electron Microscopy (SEM):

Scanning electron microscopy (SEM) images were taken using a CFEI Quanta 3D FEG FIB-SEM, elemental analysis was carried out using EDX and an S8 Tiger X-ray fluorescence (XRF) spectrometer. The morphology of MIL-101(Cr) and effect of CaCl<sub>2</sub> on its crystals were investigated using SEM. MIL-101(Cr) had been reported to exhibit well defined octahedral crystals [26]. In the case of MIL-101(Cr)/CaCl<sub>2</sub> composites, **Fig. 9** shows that all the composites preserved the defined octahedral crystal shape of the parent MIL-101(Cr). This proves once again that the presence of CaCl<sub>2</sub> did not degrade the pre-synthesized MIL-101(Cr) crystals. Nevertheless, as the CaCl<sub>2</sub> concentration increased, the presence of the salt may have caused the formation of agglomerates which is a side effect of using CaCl<sub>2</sub> [27]. The crystal size of the MIL-101(Cr)/CaCl<sub>2</sub> was measured from SEM images. It can be noticed that that the crystal size in case of all the composites was in the range of 0.5µm. This is in a good agreement with the crystal size of MIL-101(Cr) previously measured [26, 28]. The elemental analysis of the different CaCl<sub>2</sub> composites was performed using both EDX and XRF techniques. It can be noticed that with low concentration of CaCl<sub>2</sub> salt, there was almost no traces of Ca<sup>2+</sup>. This supports the suggestion that in the case of low CaCl<sub>2</sub> content

composites, the incorporation mechanism is done through ion exchange as shown in scenario 1 (**Fig. 6**). In this mechanism, the salt is not accommodated in the pores but rather the  $\text{Cl}^-$  replaces the  $\text{OH}^-$  on the chromium cluster. As the salt concentration increased, the concentration of the calcium ion increased where the second scenario is expected to take place. In this case both salt anions and cations are accommodated inside the pores of the MIL-101(Cr). The concentration of Cl and Cr was also measured using both techniques; good agreement was observed between the EDX and XRF results as the ratio between Cr and Cl is shown in **Table 2**.

**Table 2** Elemental analysis of  $\text{CaCl}_2$  composites derived from EDX and XRF data

Material	EDX		XRF	
	Cr/Cl	Ca/Cl	Cr/Cl	Ca/Cl
Comp_1:3	7.18	0	7.1	0.01
Comp_1:4	5.42	0.04	5.2	0.05
Comp_1:5	3.5	0.20	3.56	0.21
Comp_1:6	2.5	0.25	2.9	0.29
Comp_1:8	0.54	0.48	0.7	0.5



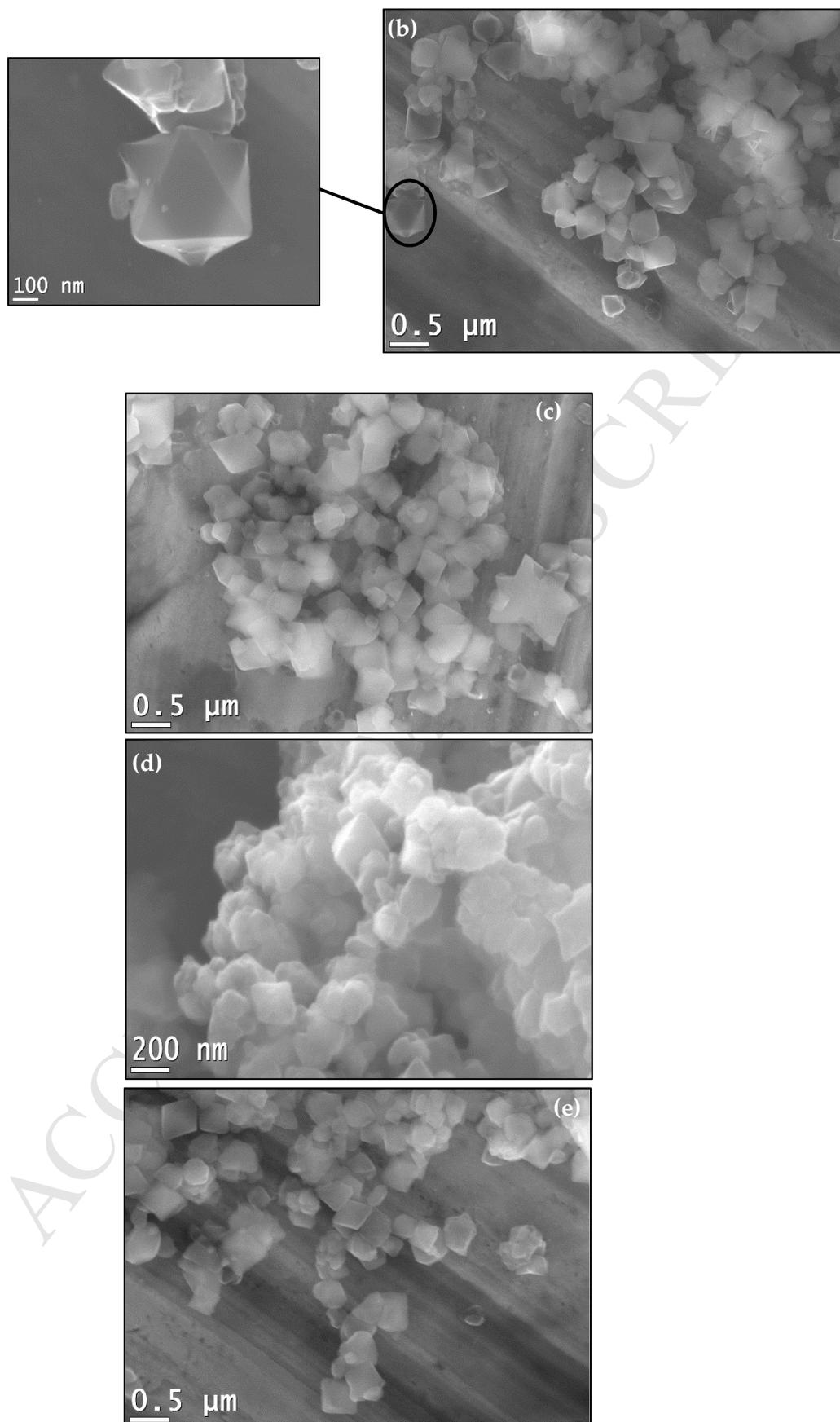
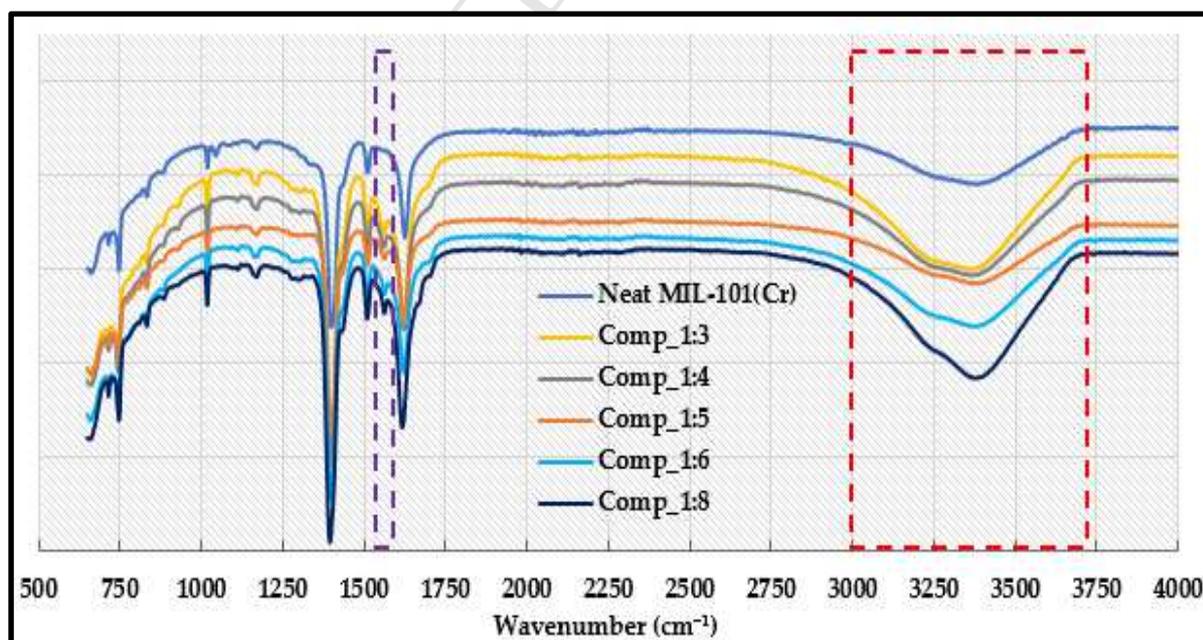


Fig. 9 SEM images of MIL-101(Cr)/CaCl<sub>2</sub> composites a. Comp\_1:3, b. Comp\_1:4, c. Comp\_1:5, d. Comp\_1:6 and e. Comp\_1:8.

### 3.5. Fourier Transform Infrared Spectroscopy (FTIR):

FTIR measurements were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer in the wavenumber range of  $650\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . **Fig. 10** shows the FTIR spectra of MIL-101(Cr) and its  $\text{CaCl}_2$  composites where it can be observed that all the composites preserved the same spectrum of the parent material, proving once again that the addition of the  $\text{CaCl}_2$  salt did not affect the structural integrity of the MIL-101(Cr) framework. The spectra showed the presence of the characteristic vibrational bands of the carboxylate group (O-C-O) at  $1400$  and  $1620\text{ cm}^{-1}$  which confirms the presence of the dicarboxylate ligand within the MIL-101(Cr) framework while the absorption band between  $3250$  and  $3500\text{ cm}^{-1}$  confirms the presence of water. The band at  $1500\text{ cm}^{-1}$  is for the vibration of (C=C) while the bands between  $600$ - $1200$  confirms the presence of the benzene ring (C-H) [21, 29].

Also, a new band appeared at  $1570\text{ cm}^{-1}$  which may be attributed to the change of the functionality coordinated to the metal sites in the MOF framework due to addition of the salt [28] proving the successful incorporation of  $\text{CaCl}_2$  into the structure of MIL-101(Cr).

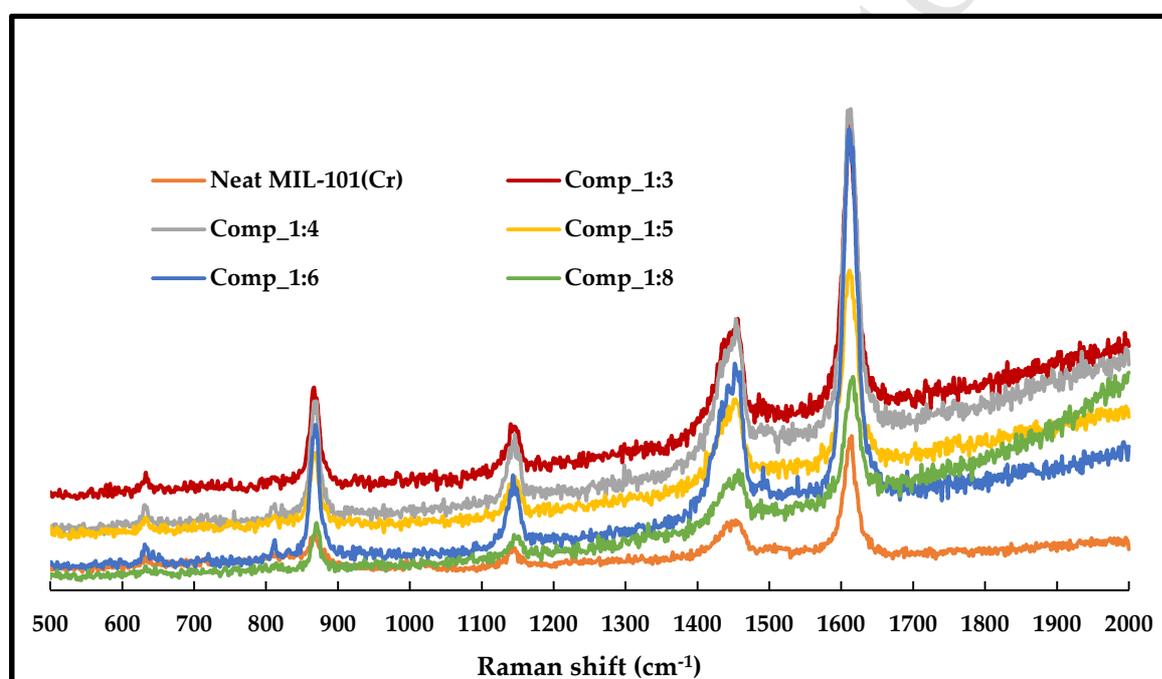


**Fig. 10 FTIR spectra of MIL-101(Cr) and different CaCl<sub>2</sub> composites.  
(The bands of water and new functionality are highlighted)**

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### 3.6. Raman spectroscopy:

Raman spectra were measured using Renishaw in Via Raman Microscope ( $\lambda = 633$  nm). **Fig. 11** shows the Raman spectra of MIL-101(Cr)/CaCl<sub>2</sub> composites. It is evident that all the MIL-101(Cr)/CaCl<sub>2</sub> composites preserved all the main bands of the neat MIL-101(Cr) at 1611, 1454, 1142, 864 and 632 cm<sup>-1</sup> [17]. These peaks are consistent with the absorption bands observed in the FTIR spectra. Furthermore, this indicates the successful incorporation of CaCl<sub>2</sub> into the MIL-101(Cr) structure without causing distortion or destruction to the pre-synthesized MIL-101(Cr) crystals which is in good agreement with all the previous results.



**Fig. 11** Raman spectra of MIL-101(Cr) and its CaCl<sub>2</sub> composites.

### 3.7. Water vapour adsorption:

Water adsorption characteristics were measured using a dynamic vapour sorption (DVS) gravimetric analyser (Advantage DVS, Surface Measurement Systems, UK) using the methodology previously described [30].

One of the important features of MIL-101(Cr) is its exceptional high-water capacity. **Fig. 1** shows the water adsorption isotherm of MIL-101(Cr) exhibiting a type IV isotherm. At low relative pressure  $\leq 0.4$ , the water vapour adsorption is caused by the unsaturated metal centres

(UMCs). UMCs are formed due to the removal of guest ligands from metal atoms in the framework. These sites attract water molecules especially at low relative pressure ranges. Nevertheless, the low water vapour capacity in this range reflects the hydrophobic effect of the organic linker [26]. At higher relative pressure (0.4-0.5), the water vapour uptake took a steep increase as the capillary condensation phenomenon took place [31]. This phenomenon also causes the hysteresis loop between the adsorption and desorption processes [32, 33]. For relative pressure  $\geq 0.5$ , the material exhibited a stable uptake as the pores were almost filled. As it was highlighted earlier, adsorption cooling and desalination systems can only employ adsorbent materials with high water vapour uptake in the low relative pressure range. This means that MIL-101(Cr) is only suitable for applications working at high relative pressure and that it is not practical applications such as adsorption cooling and desalination owing to the limited uptake in the low relative pressure range. **Fig. 12** shows the water adsorption isotherms of the neat material, the Comp\_1:3, Comp\_1:4 and Comp\_1:5 composites that also exhibited type IV isotherms. It can be noticed that introducing the  $\text{CaCl}_2$  significantly enhanced the water vapour uptake in this range especially for the Comp\_1:5  $\text{CaCl}_2$  composite. This is attributed to the hygroscopic nature of  $\text{CaCl}_2$  which outweighs the hydrophobic effect of the organic ligand. At a relative pressure higher than 0.5, all the composites had lower water vapour capacity. This can be attributed to the reduction in the accessible pore volume and surface area as highlighted in the nitrogen adsorption measurements causing the water vapour uptake to decrease. **Fig. 13** shows the water adsorption isotherm of the Comp\_1:6 and Comp\_1:8 composites. It can be noticed, that the Comp\_1:6 maintained the type IV isotherm, while increasing the concentration of the  $\text{CaCl}_2$  further changed the isotherm to a type II in the Comp\_1:8 composite. This may be a result of the increasing salt concentration changing the impregnation mechanism from ion exchange to salt accommodation. A similar adsorption isotherm was also observed in the case of SWS-1L.

The water vapour adsorption mechanism is explained by that at a relative pressure lower than 0.3, the anhydrous salt accommodated in the pores of the structure started forming a low hydration phase of the salt; this may be similar in composition to the bulk phase ( $\text{CaCl}_2 \cdot 0.33\text{H}_2\text{O}$ ). A plateau was observed in the range (0.3-0.5), where the water content may correspond to two water molecules per calcium ion as in the solid stable crystalline hydrate  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . As the relative pressure increased, the water vapour capacity increased and a higher degree of hydration comparable to that in ( $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ) was achieved [25, 34]. In the case of MIL-101(Cr), it is clear that introducing the  $\text{CaCl}_2$  significantly enhanced the water adsorption characteristics at the low relative pressure range. **Fig. 14** shows the amount of enhancement by introducing  $\text{CaCl}_2$  to the MIL-101(Cr) structure through presenting the water loading difference (the difference between the adsorption phase and desorption phase) which reflects directly to the adsorption system performance. It can be noticed that the unsupported MIL-101(Cr) had a water loading difference of  $0.026 \text{ g}_{\text{H}_2\text{O}} \text{ g}_{\text{ads}}^{-1}$  which increased to  $0.35 \text{ g}_{\text{H}_2\text{O}} \text{ g}_{\text{ads}}^{-1}$  in case of Comp\_1:8. This increase means that the adsorption system outcomes and performance are expected to improve up to 11 times compared to the unsupported MIL-101(Cr) which highlight the great potential of such composites in the adsorption applications.

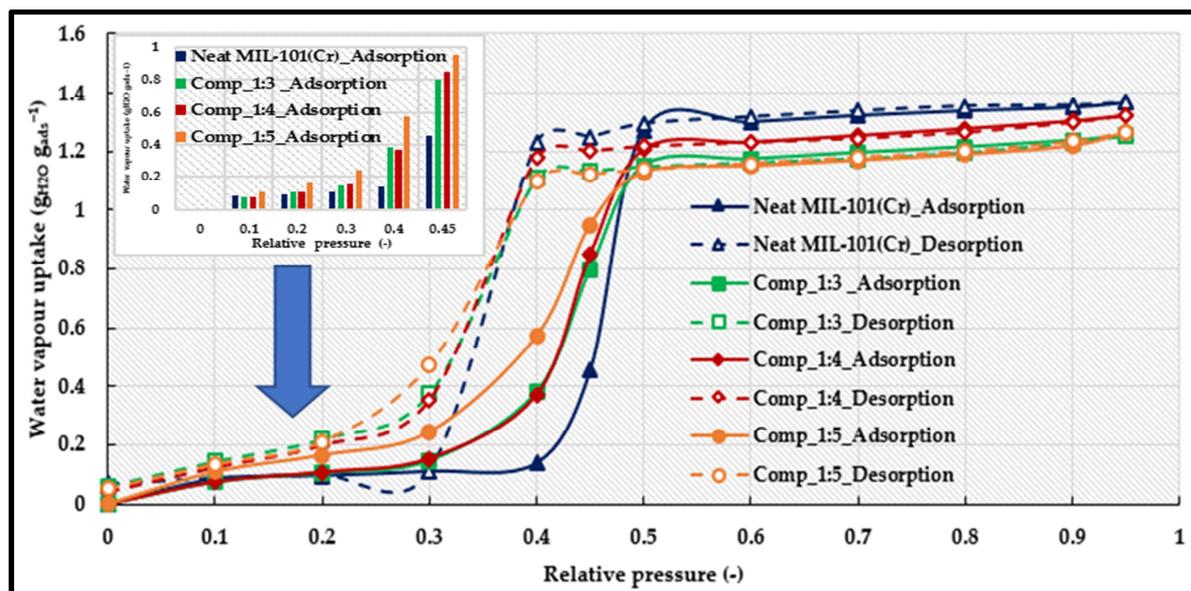


Fig. 12 Water adsorption isotherms of neat MIL-101(Cr) and  $\text{CaCl}_2$  composites: Comp\_1:3, Comp\_1:4 and Comp\_1:5 at 25°C.

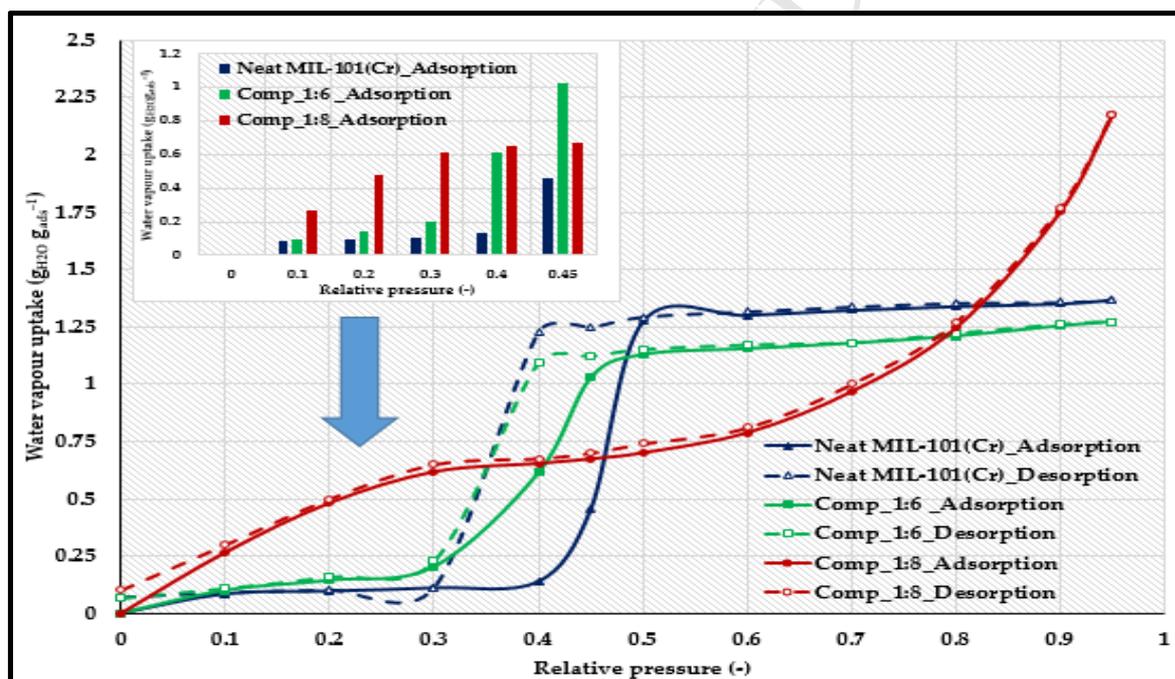


Fig. 13 Water adsorption isotherms of neat MIL-101(Cr) and  $\text{CaCl}_2$  composites: Comp\_1:6 and Comp\_1:8 at 25°C.

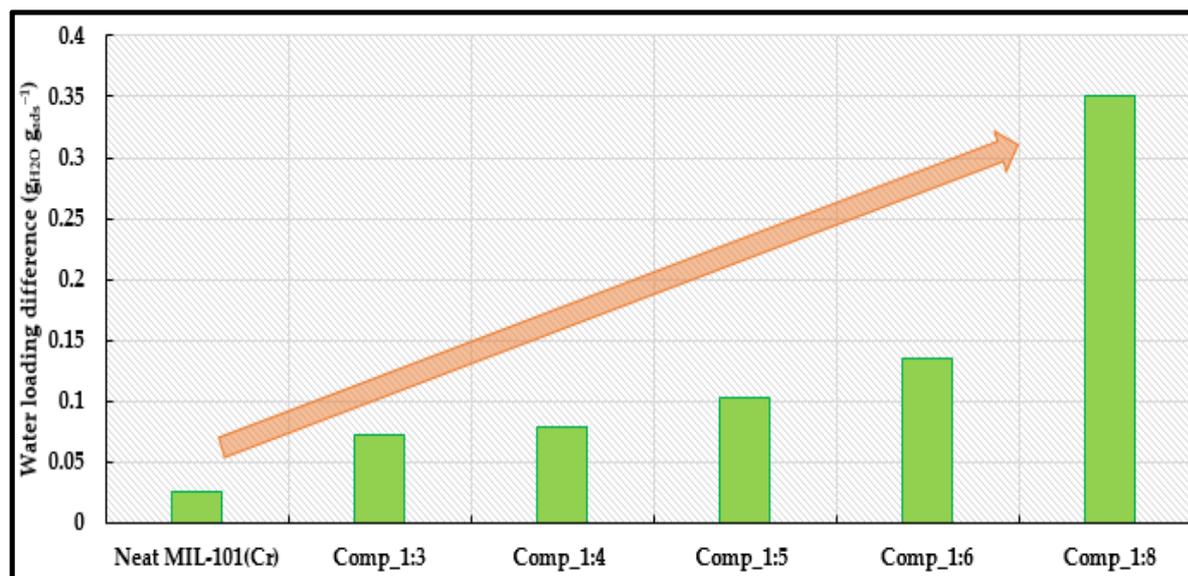


Fig. 14 Water loading difference for neat MIL-101(Cr) and  $\text{CaCl}_2$  composites.

Also, an important feature of any adsorbent material is its performance stability. The performance stability of the  $\text{CaCl}_2$  composites was investigated through subjecting the materials to ten successive adsorption/desorption cycles. Three MIL-101(Cr)/ $\text{CaCl}_2$  composites were selected, Comp\_1:4, Comp\_1:5 and Comp\_1:8. As the main improvement in the water uptake took place below a relative pressure of 0.5, the cyclic analysis was investigated for 10 successive cycles in the range 0-0.45. As shown in **Fig. 15**, the composites showed excellent performance stability, maintaining a steady performance over the tested cycles with the high uptake not affected by the successive adsorption/desorption processes.

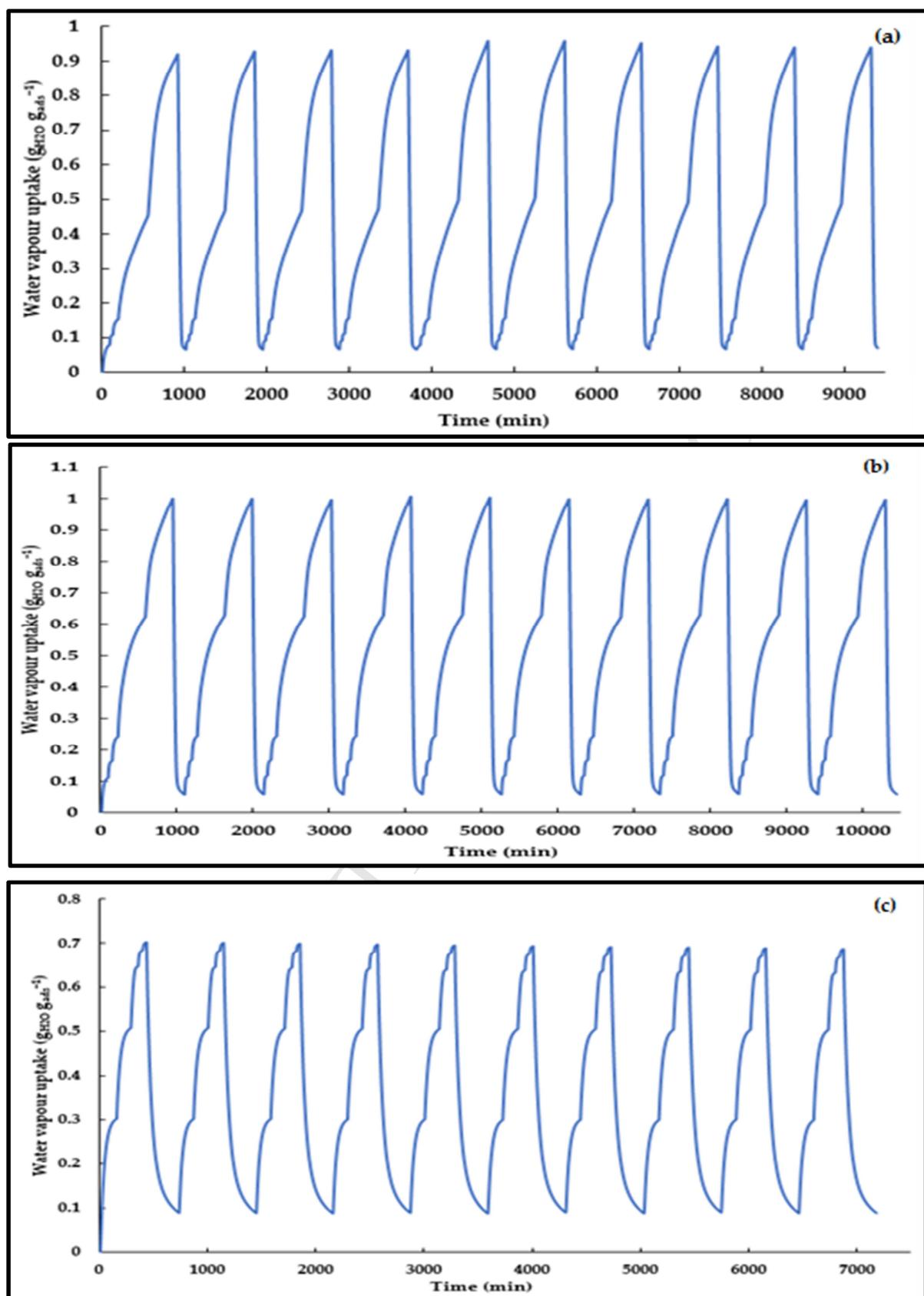


Fig. 15 Cyclic analysis (10 adsorption/desorption cycles) of CaCl<sub>2</sub> composites: a. Comp\_1:4, b. Comp\_1:5 and c. Comp\_1:8 at 25°C.

#### 4. Conclusion

In conclusion we report the synthesis of a series of MIL-101(Cr)/CaCl<sub>2</sub> composites through post-synthetic modification of MIL-101(Cr). The synthesized composites were methodically characterized in terms of their structure, morphology, water adsorption uptake, BET surface area, thermal stability, FTIR and Raman spectroscopy.

Results showed that the water adsorption capacity in the important low relative pressure range significantly enhanced while preserving the crystal structure of the unsupported MIL-101(Cr). The mechanism of the water adsorption phenomenon was also explained and supported with the elemental analysis data. It was also shown that the new composites can improve the adsorption system outcomes and performance up to 11 times compared to the neat MIL-101(Cr). Also, one of the main advantages of CaCl<sub>2</sub> salt is its availability and low price which means using this salt will not increase the cost of the adsorbent material. Not only that but using the new CaCl<sub>2</sub> composites will make the adsorption systems not as bulky as the conventional systems. This means that using the new MIL-101(Cr)/CaCl<sub>2</sub> composites a cost-effective approach regarding the material itself and the whole adsorption system.

This work demonstrates that post-synthetic modification with CaCl<sub>2</sub> is an effective way to manipulate and control the adsorption characteristics of MOF materials and paves the way for the use of a new generation of adsorbent materials facilitating higher performance and compact adsorption systems.

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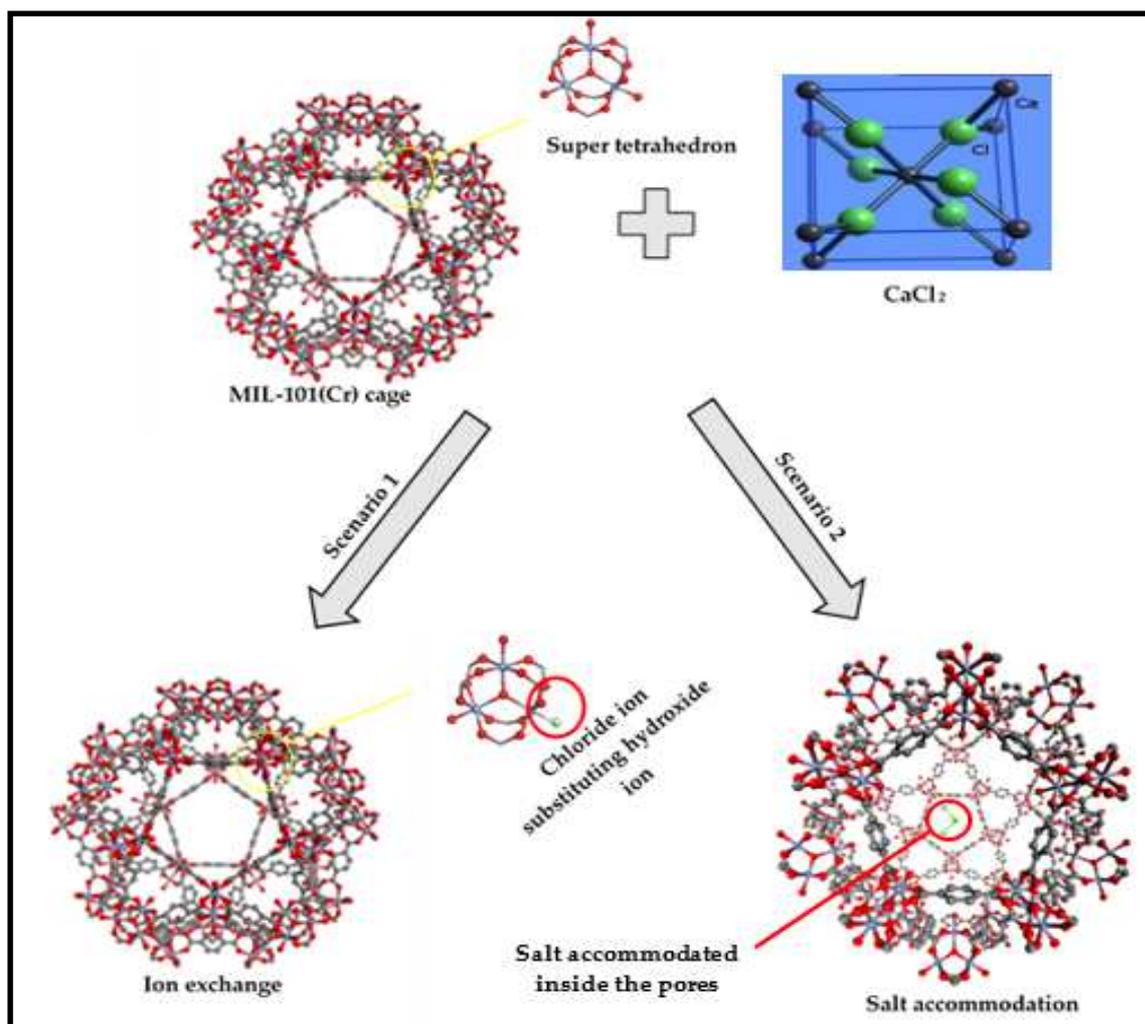


Fig. 6 MIL-101(Cr) cage and configuration of the CaCl<sub>2</sub> on the MIL-101(Cr)/CaCl<sub>2</sub> composites. (Figure was developed using Materials Studio software)

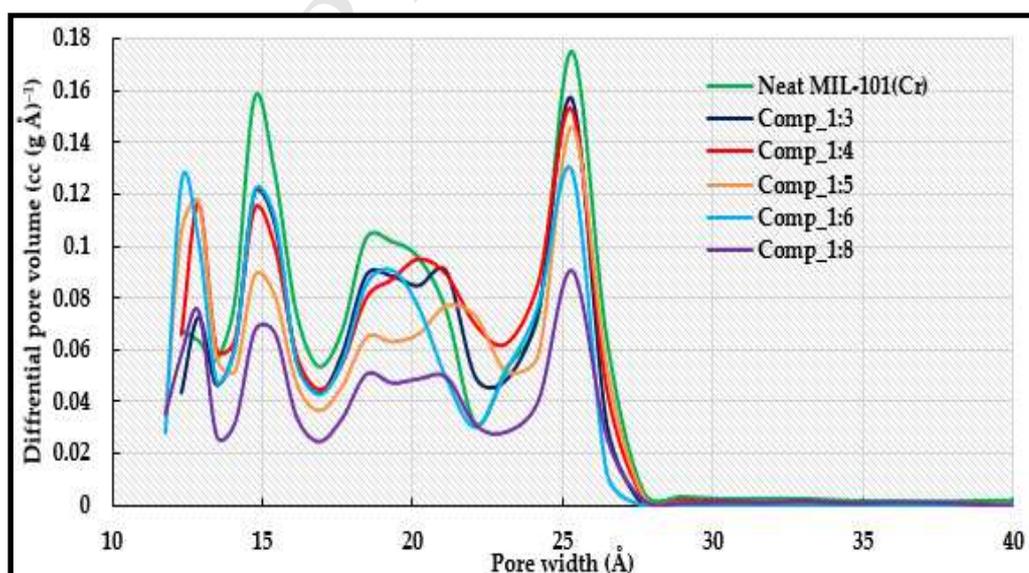


Fig. 7 Pore size distribution of MIL-101(Cr) and CaCl<sub>2</sub> composites.

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**Highlights:**

- $\text{CaCl}_2$  was incorporated on MIL-101(Cr) structure using post-synthetic modification.
- $\text{CaCl}_2$  increased water vapour capacity from  $0.1 \text{ g}_{\text{H}_2\text{O}} \text{ g}_{\text{ads}}^{-1}$  to  $0.65 \text{ g}_{\text{H}_2\text{O}} \text{ g}_{\text{ads}}^{-1}$ .
- $\text{CaCl}_2/\text{MIL-101(Cr)}$  is a practical for adsorption applications at low relative pressure.