

SYNTHESIS, CHARACTERIZATIONS, AND ADSORPTION ISOTHERMS OF CO₂ ON CHROMIUM TEREPHTHALATE (MIL-101) METAL-ORGANIC FRAMEWORKS (MOF)

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ABSTRACT

The concentration of CO₂ in the atmosphere caused by fossil fuels, power plants, and transportation is the most significant environmental issue in the world today. Intensive efforts have been made to minimize CO₂ levels to reduce global warming. Metal-organic frameworks (MOFs), crystalline porous materials, exhibit great potential to adsorb carbon dioxide. In the present study, research was conducted on the synthesis, characterization, and adsorption isotherms of MIL-101. MIL-101, one type of mesoporous MOF, can adsorb enormous amounts of CO₂. The synthesis was carried out using a fluorine-free hydrothermal reaction method. The porous properties, structure, morphology, thermal stability, and chemical functionalities of MIL-101 Cr were measured by N₂ adsorption/desorption isotherms, X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) analysis, respectively. The volumetric uptakes of CO₂ were experimentally measured at temperatures of 298-308 K and pressure of up to 600 kPa. The experimental result was correlated with the Toth isotherm model, showing the heterogeneity of the adsorbent. The heat of adsorption of MIL-101 was determined from the measured isotherm data, indicating the strength between the adsorbent and adsorbate molecule.

Keywords: Adsorbent characteristics; Adsorption isotherms; CO₂ uptakes; MIL-101; Metal-organic frameworks

1. INTRODUCTION

The combination of a strong El Niño has given an impact of global temperature anomaly (GTA) temperature increases up to 0.9°C and carbon dioxide emissions as high as 400 ppm (Szulejko et al., 2017). It is crucial to undertake serious efforts to reduce carbon dioxide emissions to control the rate of global warming. The 21st annual Conference of the Parties, which was held in Paris in 2015 resulted in a negotiated agreement among 195 countries to keep the global temperature below 2°C above pre-industrial levels (Szulejko et al., 2017). Various efforts have been made to reduce the levels of carbon and gas emissions in processing and chemical industries. One such effort is the use of carbon capture technology. Many types of industries have applied this method, such as cement production (Cormos et al., 2017), iron and steel (Cormos, 2016), and power plants (Kanniche et al., 2010). However, many challenges remain in maximizing efficiency and

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economy in implementing this technology.

The adsorption method, which is part of the carbon capture and storage (CCS) technology, is considered an efficient and economical method for replacing conventional technology in the CO₂ scrubbing process, since the technology of amine solvents is deficient in corrosion and toxicity (Kartohardjono et al., 2017; Kusrini et al., 2018). Moreover, large amounts of energy are required to recycle amines, which diminishes the efficiency of energy usage, creates high costs in power plants, and produces corrosion in the pipeline (Ye et al., 2013; Mutyala et al., 2019). Another type of CCS technology is the membrane separation method, but this method is expensive in design and synthesis (Brunetti et al., 2010). Therefore, the most effective method in CCS technology is the adsorption method, which does not require large energy inputs in regeneration, does not cause corrosion, is inexpensive, and has a high capacity and high selectivity of CO₂ gas uptakes (Gargiulo et al., 2014). Recently, the most-studied types of adsorbents have been activated carbon, zeolite, and molecular carbon sieves, as conducted by Sarker et al. (2017), who carried out a comparative study of these three adsorbents in terms of their CO₂ adsorption capacity in equilibrium conditions. The results showed that GCA-1240 activated carbon had a large volumetric uptake of 10 mmol/g at 293 K, followed by Zeolite 13 X, Zeolite 5 A, and a molecular carbon sieve (MSC-3R) with the adsorption capacity reaching to 7, 4.7, and 4.2 mmol/g in sequence (Sarker et al., 2017).

The search for the most effective adsorbent has continued for the past five years. Metal-organic frameworks (MOFs) have attracted attention because of their higher thermal stability, good crystallinity, large surface area, and high pore volume (Yulia et al., 2019). MIL-101 is the most attractive MOF for study due to its high thermal and chemical stability, moisture resistance, rapid kinetics, good cyclability, and high adsorption capacity (Liu et al., 2013; Montazerolghaem et al., 2016). MIL-101 is an expected candidate in the future as it is eco-friendly and has better physicochemical properties. MIL-101 has been tested with various types of gas adsorption and coupled by molecular simulation. Llewellyn et al. (2008) conducted experiments on the adsorption of CH₄ and CO₂ gas in MIL-101. Lin et al. (2014) carried out a CO₂ adsorption analysis with polyethyleneimine incorporated MIL-101, and it was found from their report that the CO₂ adsorption capacity reached 4.2 mmol/g at 25°C. Many adsorption experiments are still being conducted on the MIL-101 adsorbent, but different methods and experiments produce various results.

The present research explores the synthesis evaluation of the MIL-101 adsorbent, which is then examined using various experimental techniques to observe porous, structural, morphological, and chemical functionalities and thermal stability by N₂ adsorption/desorption isotherms, X-ray diffraction (XRD) techniques, scanning electron microscope (SEM), thermogravimetric (TGA) analysis, and Fourier transform infrared spectroscopy (FTIR), sequentially. Next, using the volumetric method, measurements of CO₂ adsorption were carried out for MIL-101 Cr adsorbent at temperatures of 298-308 K and pressures of up to 600 kPa. The data obtained from the volumetric test was then regressed with the Toth isotherm model, which represents the heterogeneity of the adsorbent capacity of MIL-101. Analysis of the heat of adsorption was also undertaken for the carbondioxide-MIL-101 system, which depends on the temperature and concentration obtained from the results of the data measurements.

2. EXPERIMENTAL

2.1. Materials

For MIL-101 synthesis, the reactants used were terephthalic acid [HO₂C-(C₆H₄)-CO₂H] and hydrochloric acid (HCL), which were purchased from Sigma-Aldrich (Singapore). Chromium (III) nitrate nonahydrate [Cr(NO₃)₃·9H₂O], N,N dimethylformamide (DMF, 99.5%), and ethanol

(99.7%) were supplied by Merck (Indonesia), and demineralized water (50 mL). All purchased chemicals were used without further purification.

2.2. Synthesis of MOF Adsorbents

The synthesis process used for MIL-101 was a hydrothermal reaction as carried out by (Férey et al., 2005). However, modifications to this process are necessary when an HF-free solvent is implemented as it is corrosive, poisonous, and difficult to manage at high temperatures and pressures if it is necessary to develop the MOF on a large scale (Kayal et al., 2015). The synthesis procedure for MIL-101 Cr was sequentially as follows: terephthalic acid (1.66 g, 10 mmol), chromic nitrate (4 g, 10 mmol), hydrochloric acid (1 ml), and demineralized water (50 ml) were mixed together with a magnetic stirrer for 30 minutes. The resulting mixture was placed on autoclave stainless steel and heated at 200°C for 12 hours. Temperature reduction was undertaken on an autoclave reactor. To remove unreacted terephthalic acid, the mixture was filtered, centrifuged, dried, and purified to obtain a high porosity value with N,N-dimethylformamide and ethanol separately at 80°C. Furthermore, the process was repeated on the MOF MIL-101 crystals obtained after the centrifugation process, followed by a drying process to remove unwanted substances that were still attached to the MIL-101 adsorbent.

2.3. Material Characterization

MOF surface areas were estimated using the Brunauer-Emmett-Teller (BET) equation. The Barrett-Joyner-Halenda analysis was used to determine the porosity parameters. The measurements of pore volume, pore radius, and specific surface area were done with the Micromeritics ASAP 2020 instrument at a temperature of 77 K for N₂ adsorption/desorption. MIL-101 was degassed at 160°C for 8 hours before the adsorption measurement was executed. FTIR was carried out using Thermo Scientific™ Nicolet™ iS™5 at room temperature at a wavelength of 400–4000 cm⁻¹ to determine whether the functional group of the MOF adsorbent was as expected. Scanning electron microscopy (SEM) was carried out using an FEI Inspect F50 microscope at an image resolution of 5 kV to determine the morphology, porosity, and thickness of MOF. TGA was used to determine physical phenomena, chemical phenomena, and thermal decomposition and was conducted using a PerkinElmer TGA 8000 thermogravimetric analyzer, applying N₂ gas at 200 ml/minute with a temperature rise of 10°C/minute in the range of 50°C to 550°C. The weight reduction was then measured with the temperature function. XRD was carried out using a Philips X'PERT MPD diffractometer to determine the structure of the MOF adsorbent with CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) and $2\theta = 4\text{--}70^\circ$ (step width 0.02° in 2θ) and operated at 40kV and 30 mA.

2.4. Carbon Dioxide (CO₂) Uptake Measurements

The examination of the CO₂ adsorption was carried out using a volumetric apparatus at temperatures of 298–318 K with pressure variations of up to 600 kPa. Isothermal adsorption done on the test rig consisted of two SS 304 stainless steel enclosures, one a measuring cell and the other a charging cell. The enclosures were then connected using a stainless steel tube and submerged in fluid that was regulated by a thermal bath with 0.1°C accuracy. Pressure on both cylinders was measured using a pressure transmitter with a 0–40 absolute bar range (Druck PTX 1400) with 0.15% accuracy. A class A type K thermocouple was used to measure the temperatures of the adsorbate (CO₂) and adsorbent (MIL-101). Pressure and temperature data were then saved using a National Instrument Data Acquisition tool. The experimental investigation consisted of five steps:

- 1) Loading the adsorbent sample into an adsorption cell.
- 2) Regenerating heat at 140°C for degassing.
- 3) Supplying helium gas to decrease humidity and remove unwanted adsorbent.
- 4) Conducting the isotherm process of the CO₂ study.
- 5) Conducting the desorption process before conducting another CO₂ study.

The adsorbent sample was loaded into the adsorption cell after its dry mass was measured. The adsorbent was then vacuumed until the pressure was 0.01 mbar. Adsorbent regeneration was conducted at 140°C. Next, a calibration of the helium gas was conducted to measure the effective volume of adsorption cells for gas adsorption. The system was then vacuumed once more to remove the helium gas before another study was conducted (Alhamid et al., 2015). The first in a set of processes was degassing to remove unwanted materials (impurities) from the adsorbent (Kayal et al., 2018). A measuring cell filled with MOF MIL-101 was connected with a charging cell. The measuring cell was fitted with a heater to heat it to 140°C to 150°C. Simultaneously, the measuring cell was also vacuumed until the pressure was 0.01 mbar. This process was conducted for 2 hours. Helium was passed into the system until the pressure reached 7 bar. Helium was selected because of its small molecule size, which enabled it to enter the pore of the adsorbent and “push” impurities so that the vacuum pump could then discharge the impurities. The vacuum pump was again used to discharge the remaining impurities (Martin et al., 2011).

Next, the charging cell and the measuring cell were submerged in water circulated by a HUBER thermal circulating bath with a 0.1°C accuracy to keep the temperature constant. When the desired temperature was achieved, CO₂ gas insertion was started after closing the first connection between the measuring cell and the charging cell. The initial process of isothermal adsorption was conducted when the connection was opened. The measurement for the next pressure was only conducted when the charging cell temperature had been stabilized. This process was repeated until the test pressure reached 600 kPa. The entire process was repeated at different isothermal temperatures. The adsorption isotherm experiment was carried out at least three times at each temperature until accurate data were obtained. A schematic diagram of the measurement of isothermal adsorption is presented in Figure 1. The analysis of the heat of adsorption was measured using the data with the smallest deviations. It was essential to analyze the heat of adsorption to predict how much heat was needed for the adsorption process, leading to the prediction of the amount of energy needed to adsorb CO₂ gas at a certain pressure and temperature.

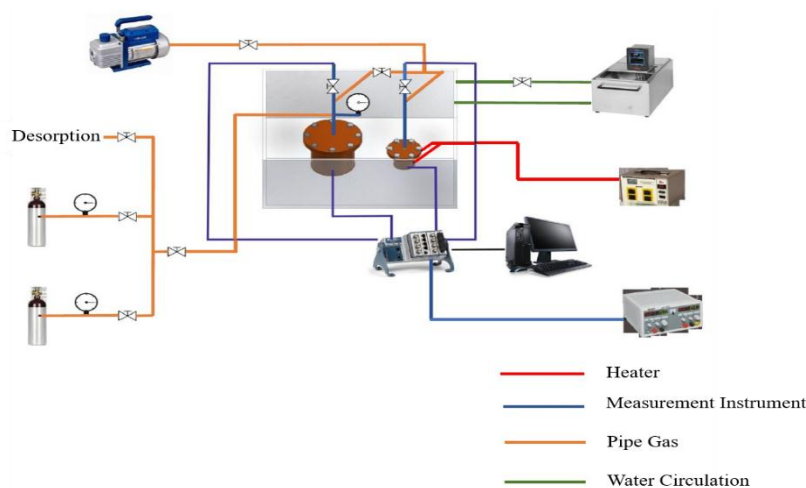


Figure 1 Schematic diagram of volumetric apparatus for adsorption isotherm

3. RESULTS AND DISCUSSION

3.1. Synthesis

The adsorbent MIL-101 BDC was synthesized using thermal processes. To enhance the rate of chemical reaction, it is essential for the mixture of chrome nitrate, terephthalic ligand acid, HCL, and demineralized water to be stirred. The MIL-101 was heated in an oven at 200°C so that the substances reacted perfectly. The MIL 101 was then subjected to gradual temperature cooldown

to form a crystal adsorbent. An adsorbent in the form of green crystal was acquired after the adsorbent and the liquid were separated by centrifuge. For purification purposes, DMF and ethanol were used. First, DMF was added to solid MIL-101, heated to 80°C, and centrifuged. Second, ethanol was added to the MIL-101 and the substance was heated to 80°C for 5 hours, being rinsed every 2.5 hours. Finally, the MOF was heated to 80°C for 12 hours. The character of the crystalized MOF is presented in the following sections.

3.2. Phase Identification

The synthesized MOF was analyzed using XRD to verify its identity and check its purity. Impurities that hamper CO₂ adsorption are indicated by the apex of the XRD pattern. The XRD pattern of the sample (presented in Figure 1) indicated that it is similar to an apex of MOF MIL-101 BDC that has been reported (Kayal et al., 2015). This indicated that a good crystallinity phase existed in the synthesized MOF. A considerable number of pores inside the MOF structure were indicated at 2 θ degrees on the XRD pattern where the intensive apex was visible. Two kinds of interior structures with diameters of 29 and 34 Å existed in the MIL 101-BDC (Hong et al., 2009).

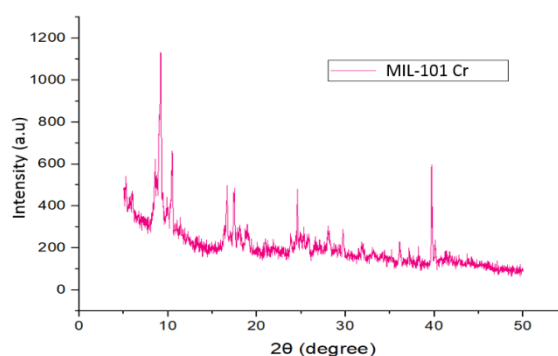


Figure 2 XRD profile of chromium terephthalate

3.3. Surface Area and Porosity

The MOF's surface area and porosity were calculated from the N₂ isothermal adsorption/desorption at 77 K. The calculated surface area of the MIL-101 BDC was 1367.74 m²/g (using the BET method) and 2096,65 m²/g (using the Langmuir-Blodgett method). The total pore volume (V_p) of the MIL-101 was 0.74 cm³/g at a relative pressure (P/P₀) 0.98. The pore size distribution of the MIL-101 was calculated from the N₂ isothermal adsorption/desorption at 77 K. The pore size distributions confirmed that two type of pore size exist (18 and 12 Å), which is similar to its lattice structure (Kayal et al., 2015). Porosity parameters, such as pore volume, pore radius, and surface area, are essential since increases in pore volume and surface area are linked to increases in the CO₂ adsorption rates. Increases in pore volume are also linked to increases in condensed CO₂ capacity.

3.4. Morphology and Particle Size

Morphology and particle size were determined from micrograph images using SEM. The SEM process indicates whether homogenous MIL-101 crystal particles have been acquired and whether any impurities have adhered to the MIL-101 structure. Impurities could cover the MOF and hamper the rate of adsorption. The symmetric cube shapes of particles of MIL-101 Cr. are shown in Figure 3. Various magnifications of up to 100,000 times were used to provide a clear visualization of the crystal symmetry. As can be seen in the figures, octahedral particles with double-sided, pyramid-type geometry and a uniform size of 1 μm are visible. Lebedev et al. (2005) reported that MIL-101 crystal synthesized using a hydrothermal method with HF solvent at 220°C for 8 hours has a length ranging from 0.1 to 0.4 μm. Kayal et al. (2015) also reported the octahedral shape of crystal MIL-101 having the uniform size of 1 μm. Thus, the synthesized MIL-101 matched the crystal length reported in previous research.

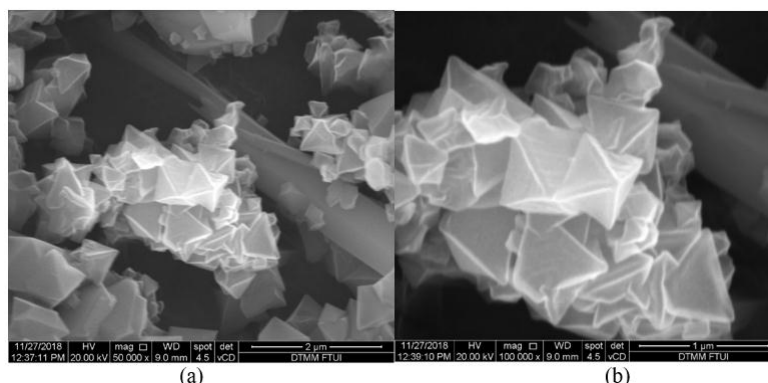


Figure 3 (a) SEM test of MIL-101 BDC showed that particles have octahedral shape at 50,000× magnification; (b) SEM test of MIL-101 BDC showed that particles have octahedral shape at 100,000× magnification

3.5. Thermal Stability

The result of TGA (as shown in Figure 4) showed the plot of mass decline of the sample to temperature that measures MIL-101 thermal stability when the samples were heated to 550°C. During the early process of heating to 100°C, rapid mass decline of as much as 50% occurred because of water molecule release from the larger MOF structure cage (34 Å diameter) (Hong et al., 2009). Mass decline during the second stage of the heating process up to 250°C occurred as water molecules were released from smaller cages (~29 Å) (Kayal et al., 2015). During the later heating process (above 350°C), mass decline of as much as 20% occurred due to degradation of the benzene dicarboxylate (BDC) binder. This process demolished the MOF structure, leaving metal residue of Cr₂O₃. It can be concluded from this result that the material formed is MOF since the material can defend itself to temperatures above 300°C and this property is possessed by MOF.

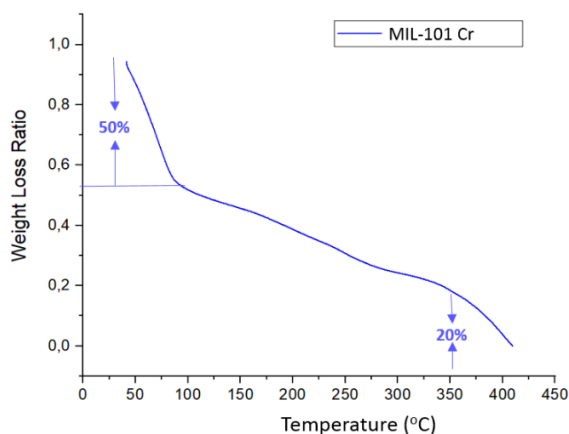


Figure 4 Result of thermogravimetric analysis of MIL-101 BDC

3.6. FTIR Analysis

FTIR analysis was conducted to identify the functional groups in MOF MIL-101, as represented in Figure 5. The MIL-101 pattern was measured before the isothermal adsorption process. Vibration was indicated at a value of 3372.91 cm⁻¹, and evidence of vibration by adsorbed water molecule on the MOF surface particle was indicated at an apex value of 1624.92 cm⁻¹. O-C-O bonds as linkers from the BDC in the MOF MIL-101 are represented at an apex value of 1402 cm⁻¹. Representation of the BDC linker ring is visible at an apex value between 600 dan 1600 cm⁻¹ including vibration of C=C at 1540.09 cm⁻¹ and vibration deformation (C-H) at 1101.90, 1016.32, and 740.15 cm⁻¹ for MIL-101 BDC. FTIR analysis on the MIL-101 BDC was used as a

guide to determine whether the synthesized adsorbent had produced the desired atom bonds to indicate MOF synthesis. The analysis also revealed remaining unwanted solvent, such as DMF and ethanol, which could hamper MOF adsorption rates.

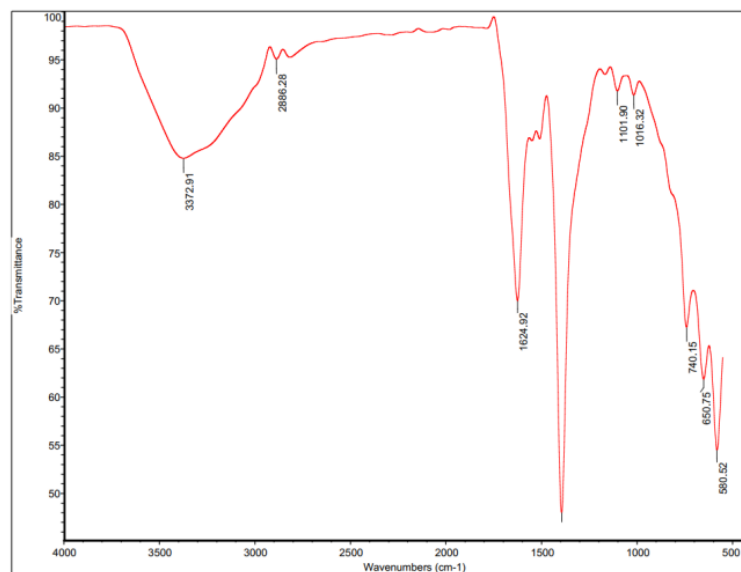


Figure 5 Result of FTIR analysis conducted on MIL-101

3.7. CO₂ Adsorption on Adsorbent MIL-101 (Cr)

The synthesized MIL-101 was investigated for its capability to adsorb CO₂ adsorbate. The experiments were carried out at the variations of pressure and temperature shown in Figure 6. The isothermal data obtained were plotted for temperature variations of 298–308 K. Figures 6a–6c shows increases in storage capacity as the pressure increases, but it is inversely proportional to the temperature increases, reflecting the fact that the adsorption in MIL-101 is physical adsorption. These charts show the highest capacity obtained at high pressure and low temperature operating conditions, which reached 2.28 mmol/g at a temperature of 298 K and pressure of 600 kPa.

Carbon dioxide uptakes are also significantly affected by the temperature isothermal adsorption process; the lower the temperature during the isothermal adsorption process, the larger the adsorption capacity. It occurs as in the adsorption process; the adsorbate flowing to the surface of the MIL-101 will pound and stick to its surface. Further, it condenses on the porous solid surface. Thus, at a lower temperature, the amount of adsorbate condensed on the surface of the MOF will be greater. Therefore, more adsorbate is also adsorbed in the MIL-101.

Measurements at temperatures of 300 K and 308 K were also carried out. The maximum capacity obtained at a temperature of 300 K was 2.26 mmol/g at a pressure of 600 kPa. Furthermore, at a temperature of 308 K, the maximum capacity obtained was 2.24 mmol/g at a pressure of 600 kPa. The adsorbent density plays an important role in determining volumetric uptake (Kayal et al., 2018). The overall adsorption is affected by pore volume and adsorbent density. A high temperature change will cause difficulty in the attachment of adsorbed molecules to the surface of the MOF. In the adsorption process, there is a possibility of adsorbate adsorption, which is followed by heat release.

The adsorption of adsorbate occurs due to the electrostatic force, such as the London force or the Van der Waals forces, which results from dipole-dipole induction. This bond can also be influenced by physical characteristics of the adsorbent such as porosity. The distribution of forces between molecules is the effect of fluctuations, which are the very rapid induction of electron

charges from the adsorbent and adsorbate molecules. Physical adsorption in gases occurs when intermolecular attractions between solid molecules with gas are greater than the intermolecular force between the solid molecules themselves. This causes exothermic phenomena in adsorption process (heat release). The regression of isotherm data from the Toth isotherm model can be seen in Figure 7 for the temperature variations of 298 K to 308 K. The regression error value has also been calculated by comparison of experimental data. The Toth model describes isothermal adsorption data that show the heterogeneity of adsorbents. Furthermore, the isosteric heat of adsorption can be determined from the Toth isotherm model, which is represented in Figure 8 with the uptake as the dependent variable. The value of h_{st} decreases when the vapor uptake increases, which is caused when carbon dioxide molecules directly penetrate the pore of MIL-101, affecting the larger interaction between the adsorbate and adsorbent at lower loading.

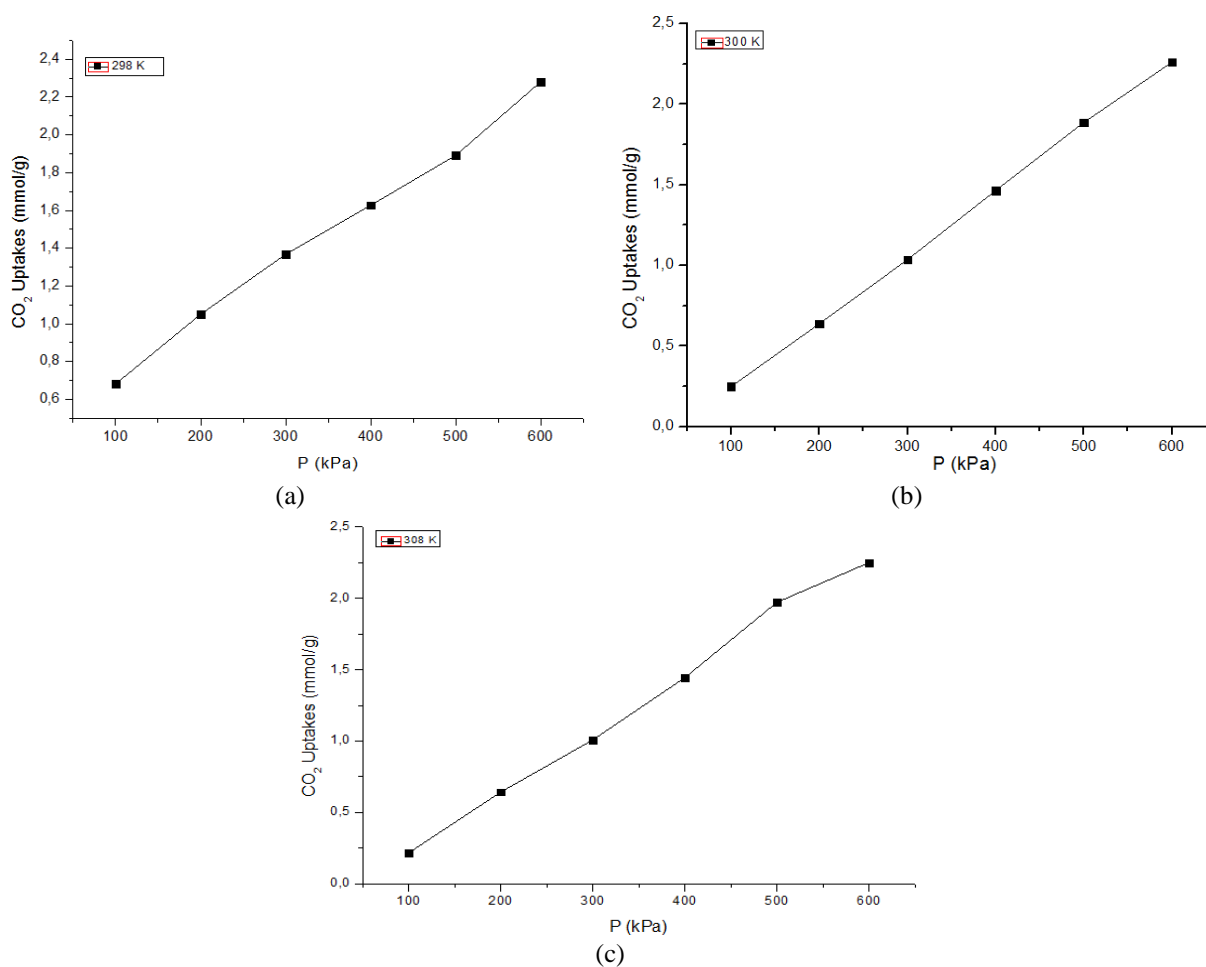


Figure 6 Volumetric uptakes for CO₂ adsorption in MIL-101 at: (a) 298 K; (b) 300 K; (c) 308 K and pressures up to 600 kPa

4. CONCLUSION

The synthesis of the MOF chromium terephthalate with a hydrothermal reaction without using HF solvents was performed. We evaluated the characterization of the adsorbent MOF with various experimental methods, such as XRD, SEM, TGA, FTIR, and N₂ adsorption/desorption isotherms. The experiment using the volumetric apparatus was carried out with a CO₂ gas adsorbate. Temperature and pressure variations were observed in isothermal adsorption tests at temperatures of 298 K to 308 K and pressures of up to 600 kPa. The maximum capacity in the isothermal adsorption test occurred at a temperature of 298 K, reaching 2.28 mmol/g at a pressure

of 600 kPa. The experimental data was also regressed with the Toth isotherm adsorption model representing the heterogeneity of the adsorbent. In addition, a decreasing trend was found in the calculation of the isosteric heat of adsorption due to a strong heterogeneity in the surface structure.

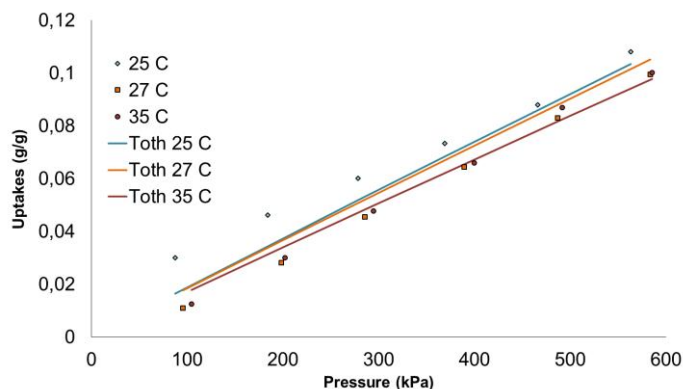


Figure 7 Adsorption isotherms of CO₂ on MIL-101 (♦, 298 K; ■, 300 K; ●, 308 K). Solid lines represent the Toth model for CO₂ adsorption

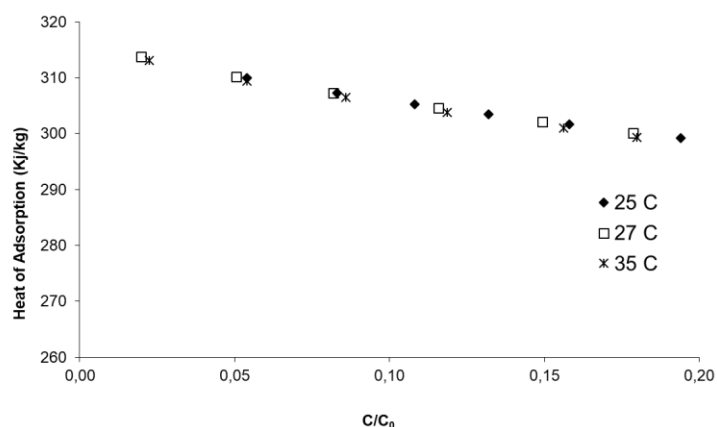


Figure 8 Isosteric heat of adsorption for CO₂ on MIL-101

5. ACKNOWLEDGEMENT

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