

Gas Adsorption and Storage at Metal-Organic Frameworks

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ABSTRACT

Dry gas is considered one of the most environmentally friendly sources of energy. As a result, developing an efficient strategy for storing this gas has become essential. In this work, MOF-199 was synthesized and characterized in order to investigate the MOF-199 in dry gas adsorption using a built-in volumetric system (methane, ethane, and propane from Basrah gas company). The MOF-199 (metal organic framework) was synthesized using the solvothermal method at 373K for 24h, and then it was characterized. The dry gas adsorption on MOF-199 was studied under various conditions (adsorbent dosage, contact time, temperature, and pressure). The isothermal adsorption of the dry gas had been studied on MOF-199 using two types of models: Freundlich and Langmuir. The results of the isothermal adsorption shown corresponded to the Freundlich model with a correlation coefficient (R^2) of 0.9426. Also, the rate of adsorption kinetic of the first and second-order was studied, and the results showed that the reaction rate was second-order.

Keywords: gas adsorption, mof-199, dry gas.

امتزاز الغاز وتخزينه في الهياكل المعدنية العضوية

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الخلاصة

يعتبر الغاز الجاف من أكثر مصادر الطاقة الصديقة للبيئة. نتيجة لذلك، أصبح تطوير استراتيجيات فعالة لتخزين هذا الغاز أمراً ضرورياً. تم تحضير الأطر العضوية وفحصها في امتزاز الغاز الجاف باستخدام نظام حجمي مدمج ويتكون الغاز من الميثان الأيثان والبروبان من شركة غاز البصرة تم استخدام الطريقة الحرارية المذبذبة المستخدمة عند 373 كلفن لمدة 24 ساعة. تمت دراسة امتصاص الغاز الجاف على MOF-199 تحت ظروف مختلفة (جرعة الممتزات، وقت التلامس، درجة الحرارة، والضغط). تمت دراسة الامتزاز متساوي الحرارة للغاز الجاف على MOF-199 باستخدام نوعين من النماذج Freundlich:

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و Langmuir. تم عرض نتائج الامتزاز متساوي الحرارة مع نموذج Freundlich مع معامل الارتباط (R^2) حوالي 0.9426. كما تم دراسة معدل حركية الامتزاز للدرجة الأولى والثانية وأظهرت النتائج أن معدل التفاعل كان من الدرجة الثانية. الكلمات الرئيسية: امتصاص الغاز ، MOF-199 ، الغاز الجاف

1. INTRODUCTION

Natural gas and dry gas of which methane is one of their most significant components, can be stored and delivered as a compressed gas (CG), liquified gas (LNG). In the case of CG, the gas is stored at a pressure of 250 bar in low-cost steel tanks and delivered as a fuel (Schoedel, et al., 2016) and (Bae, et al., 2017). However, an extremely pressurized tank raises safety concerns in the case of accidents and has an energy cost associated with compression. For LNG, the resources and costs associated with liquefaction (-162 C) have several disadvantages, which present substantial technical barriers (Dobrota, et al., 2013) and (van Biert, et al., 2016). Therefore, there is an economic necessity to devise and use alternative methods that are safer, less costly, and economically feasible. Nowadays, the gas can be stored in the form of adsorbed natural gas (AG). For AG, various groups of adsorbents, such as activated carbons, zeolites, porous coordination polymers(PCPs), and metal-organic frameworks (MOFs) (Morris, et al., 2008), have been developed and tested for natural gas storage (Chui, et al., 1999).

The presence of sorbent materials in high-pressure tanks decreases the tank pressure requirements, makes it safer to store and deliver, and enables single-stage compressors to be used (Liang, et al., 2017). The pipelines are used to transport natural gas and oil derivatives (Fattah, et al., 2016), the tubes can be used to store the adsorbed gas (AG).

Gas adsorption is an exothermic process in the AG system, and desorption is endothermic, leading to potentially significant temperature shifts that decrease the amount of gas stored and distributed. Physical adsorption takes place when the adsorbent layer is attached to the adsorption surface by certain forces similar to those responsible for the liquefaction of gases or the cohesion forces in the liquid (between the molecules of a single liquid), these forces are called physical forces or Van der Waals force. Chemical adsorption is achieved when the surface of the steel is covered with one layer of the adsorbed gas, but it has been found that there is physical adsorption on this layer (Howarth, et al., 2016).

Fairly wide volumetric measurements Capacities of 4-6 MJ L⁻¹ at pressures of about 35 bar at room temperature have been achieved for various adsorbents (Szilágyi, et al., 2016). To this end, strategies such as MOFs can also be used. One benchmark MOF material is MOF-199 is composed of Cu₂(-COO)₄ secondary building units (SBUs) with a paddlewheel shape. It has a high surface area. For MOF-199, the amount of methane adsorbed and desorbed between 65 bar and 5 bar (Peng, et al., 2013). There are several challenges to implementing MOFs for natural gas storage, which can reduce up to 50 percent storage (Mason et al., 2014). Mason and coworkers addressed these implementation issues, including: thermal management, losses in storage or deliverable capacity densification, and impurities of natural gas.

This research is an experimental study of Iraq dry gas adsorption on the MOF-199 adsorbent at pressures of up to (31 bar) had been done to investigate the adsorption equilibrium and kinetic data in order to find the isosteric heat of adsorption and adsorption isotherm for the dry gas on MOF-199.



2. EXPERIMENTAL WORK

2.1 Characterization of the Synthesized MOF-199

The MOF-199 was prepared using the solvothermal process (Hill et al., 2015). Fig. 1 a and b show the prepared MOF-199 before and after vacuum activation. It was clear that MOF-1999 triggered the blue color in following activation, the removal of covalently was changed to dark violet due to water boundary molecules from copper centers (Kareem, 2018).

The prepared MOF-199 samples have been tested in an XRD diffractometer using a 5-70 deg scan range with 40 Kv tube voltage, 30 mA tube current with radiation under equal conditions for all tested samples. The surface area of the prepared adsorbent was investigated using (ASAP 2020). The BET surface area, the volume, and pore volume were measured by N₂ physical adsorption at N₂ liquid temperature 77 K after sample degassing process to extract moisture and some airborne gases that cause blockage and decrease surface area. The infrasound (IR) test is primarily used to assess improvements in the absorption of BTC ligand-possessed carboxyl groups, the type of device used FTIR 8400S Shimadzu type with (600-4000cm⁻¹) wavenumber range.

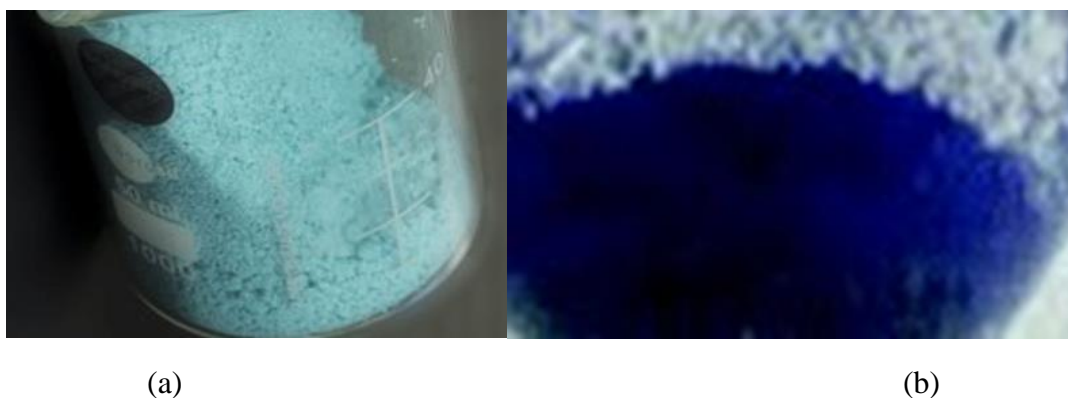


Figure 1. Prepared MOF-199 (a) before activation (b) after activation.

2.2 DRY GAS Adsorption by (MOF-199) as Sorbent

The adsorption equilibrium of dry gas was calculated on MOF-199 using the volumetric method. For MOF-199, each sample isotherm and kinetics data of Dry gas was measured at a temperature ranged from 298.15 to 313.15 K. The adsorption kinetics of Dry gas on MOF-199 were measured using rig shown in Fig. 2.

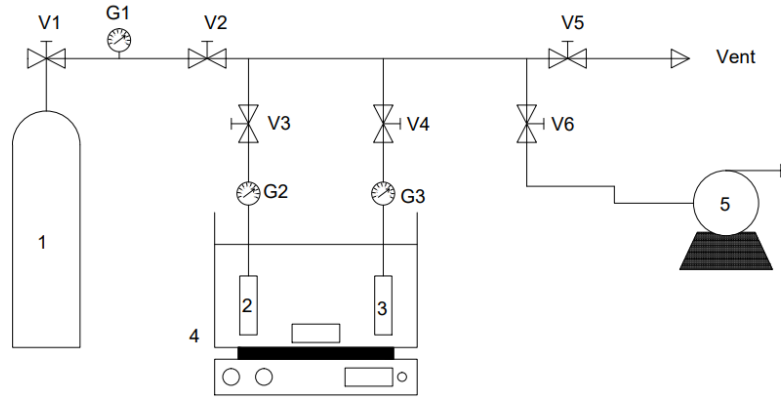


Figure 2. Schematic diagram of apparatus used for adsorption equilibrium measurement.

Table 1. The components of the adsorption device

1. Gas cylinder	3. Adsorber bomb	5. Vacuum pump	G1, 2, and 3 = pressure gauge No.1, 2 and 3
2. Reservoir bomb	4. Water bath	V1, 2 and 3 = Manual valve	

3. Results and discussion

3.1 General properties of the adsorbent

Physical properties of the prepared adsorbent had been measured, and the surface area had been measured using the BET process; pore volume adsorbent was measured by N₂ physical adsorption at N₂ liquid temperature 77 K after sample degassing process to extract moisture and some airborne gases that cause blockage and decrease surface area. A high surface area value means an improvement in adsorbent activity by increasing the site of activity (Chui, et al., 1999).

The pore volume is another significant property measured by N₂ adsorption and expressed in cm³/g (a measure of the pore space in the adsorbent).

The MOF-199 was prepared and had the high crystallinity purity phase at 373.15 K, which was the same as the sample prepared by Kareem, who showed 100 percent crystallinity under the same conditions (Kareem and Alrubaye, 2019). The acquired surface area and pore volume values for the prepared samples from MOF-199 are shown below:

$$\text{Surface area} = 3600 \text{ m}^2/\text{g}$$

$$\text{Pore volume} = 0.7 \text{ cm}^3/\text{g}$$

These obtained values are not far from the values obtained by Kareem (3635 m²/g for a sample prepared for 30 h) (Kareem and Alrubaye, 2019).

The surface area was high compared to the sample prepared by (Alyassiry A., and Alrubaye, 2020), who showed that surface area is 3400 m²/g at the same conditions (prepared sample at 100 °C for 24 h).



The IR spectrum of MOF-199 revealed the heavy stretching vibration of the presence of the reaction of COOH groups in 1,3,5-benzenetricarboxylic acids with metal ions is demonstrated by carboxylate anions at 1612.38cm⁻¹. The presence of water and OH groups in the material structure was indicated by the wideband at 3600-2800cm⁻¹. The peaks at 410, 500, 610, and 615 cm⁻¹ indicate a CuO and Cu₂O-free synthesis product. In MOF-199, the loss of bond to water molecules was shown by extending and shifting the carboxyl uptake in MOF-199 from 3,100 to 3600 (Alyassiry A., and Alrubaye R, 2020).

3.2 Adsorption Isotherm

The relationship between the sum of adsorbed gas in the adsorbent and its equilibrium concentration in the solution at a constant temperature is an adsorption isotherm. By analyzing an isotherm, the mechanisms of the adsorption molecules distributed between the solid and the gas phase during equilibrium can be obtained. The Langmuir and Freundlich models are the two most common models to use.

3.2.1 Langmuir Isotherm

It is a model that allows adsorption only for homogeneous surfaces, i.e., an adsorbate occupies each site and for one site called Langmuir Isotherm, no more than one adsorption occurs (Delavar et al., 2015). The model defined by the equation can be seen below (Mahmood, 20.19)

$$q_e = (q_m K_L C_e) / (1 + K_L C_e) \quad (1)$$

where q_m is the maximum amount of an adsorbate per unit weight adsorbent to form complete monolayer coverage on the surface, K_L is adsorption equilibrium constant(l/mg), C_e is the equilibrium concentration of the adsorbate.

By rearranging the above equation, a linear form results as shown below:

$$1/q_e = 1/q_m + 1/(q_m K_L C_e) \quad (2)$$

As shown in **Fig. 3**, the isothermal data fits the equation of Langmuir. well ($R^2 = 0.7981$). The q_m and K_L values were estimated from the data and were found to be 17.544 mg/g and 18.387 L/mg, respectively. However, K_L values suggest that this model is useful for explaining equilibrium adsorption (Guoheng Liu et al., 2016).

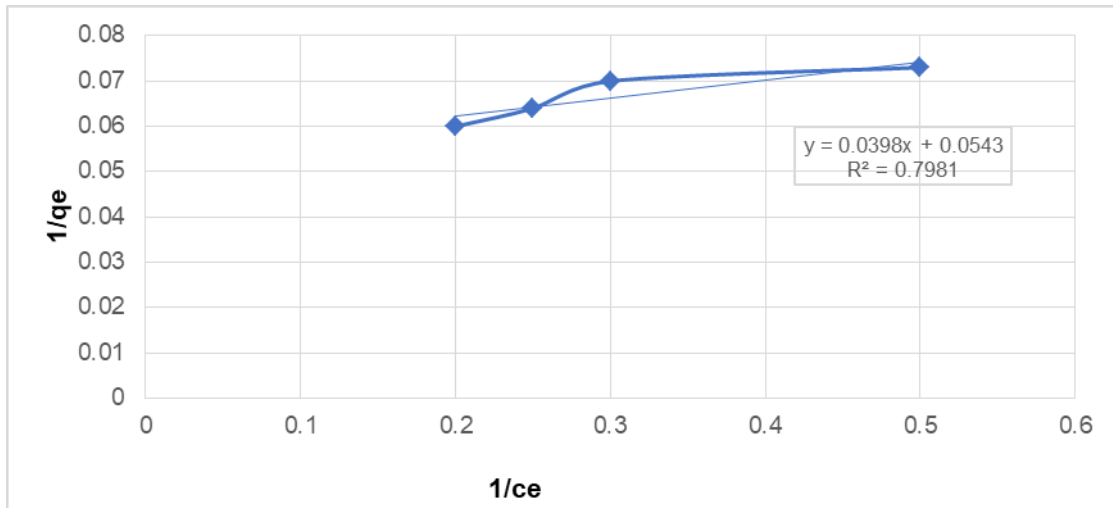


Figure 3. Langmuir isotherm.

3.2.2 Freundlich Isotherm

It is a model that imposes adsorption equilibrium for heterogeneous surfaces, i.e., several adsorbates with many adsorption energies are occupied by each site, and more than one adsorption occurs for one site called Freundlich Isotherm. The model defined by the equation can be seen below.

$$q_e = k_f C_e^{1/n} \tag{3}$$

Where q_e is the amount adsorbed at equilibrium (mg/g), the Freundlich constants are k_f , C_e is the adsorbate equilibrium concentration, and the rate of adsorption (1/mg) is $1/n$. This equation, in linear form, is shown:

$$\text{Log } q_e = \text{Log } k_f + 1/n \text{ Log } C_e \tag{4}$$

From intercepts and slopes of a plot of $\log q_e$ versus $\log C_e$, the Freundlich constants (k_f and $1/n$) can be calculated. A clear picture of the adsorption process can be seen by knowing the value of n , where $n < 1$ indicates that the adsorption process is favorable under the specified conditions.

A linear plot of $\log C_e$ vs. $\log q_e$ is shown in **Fig. 4**, which was used to calculate the intercept value of $\log K_f$ and the slope of $1/n$. As shown in **Fig. 4**, the isothermal data (correlation coefficient = 0.9426) matches well with the Freundlich equation. The K_f and n values were estimated from the figure and were found to be 12.897 and 6.831, respectively. The $1/n$ slope reflects the rate of adsorption, while the K_f intercept value is an indicator of the adsorption capability of the adsorbent. The value of n showed that the preferred adsorption conditions were $n < 1$ (**Guoheng Liu et al., 2016**).

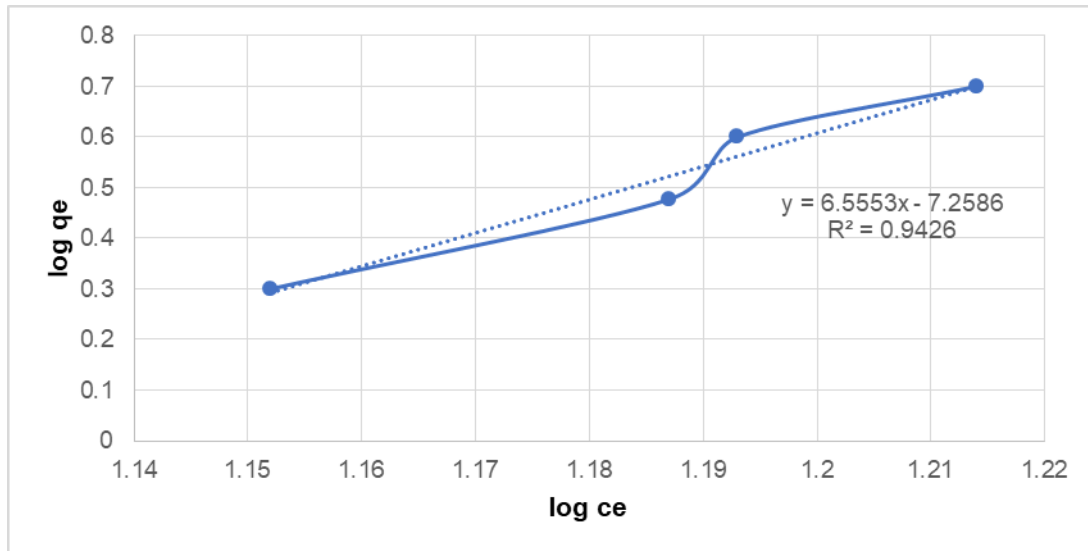


Figure 4. The Freundlich isotherm model.

3.3 Adsorption kinetics

The study of adsorption kinetics helps to know the time needed to reach equilibrium as well as the controlling mechanism knowledge of the adsorption processes such as chemical reaction and mass transfer. The pseudo-first-order and pseudo-second-order equations were studied to model the kinetics of dry gas adsorption onto MOF-199. The best fit model is then selected based on the linear regression correlation coefficient, i.e., R^2 , and the value of q_{cal} close or not to q_{exp} (Simonin, 2016).

3.3.1 Pseudo-first-order kinetic model

The pseudo-first-order rate expression was introduced initially by Lagergren {Lagergren (1898) cited in (Simonin, 2016)}. It is generally used in the form proposed after integration of the initial conditions of

$q = 0$ at $t = 0$ and $q = q_t$ at $t = t$ for :

$$dq/dt = K_1 (q_e - qt) \tag{5}$$

The following equation is obtained:

$$\ln [q_e - qt] = \ln q_e - K_1 t \tag{6}$$

Where K_1 is the pseudo-first-order rate constant, q the amount of adsorbed solute, q_e its value at equilibrium, and t the time.

The pseudo-first-order constants (k_1) and q_e can be calculated from the slope and intercept of the line obtained by a linear relationship of $\ln (q_e - qt)$ versus t for experimental data.



The resulted form of this equation is given below:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{7}$$

The pseudo-first-order model does not match well with the experimental results based on the correlation coefficient of 0.8929 relative to the pseudo-second-order model. **Fig. 5** shows the pseudo-first-order kinetic model for dry gas adsorption. Furthermore, the measured concentration of equilibrium ($q_{e,cal}$) does not agree well with the experimental value.

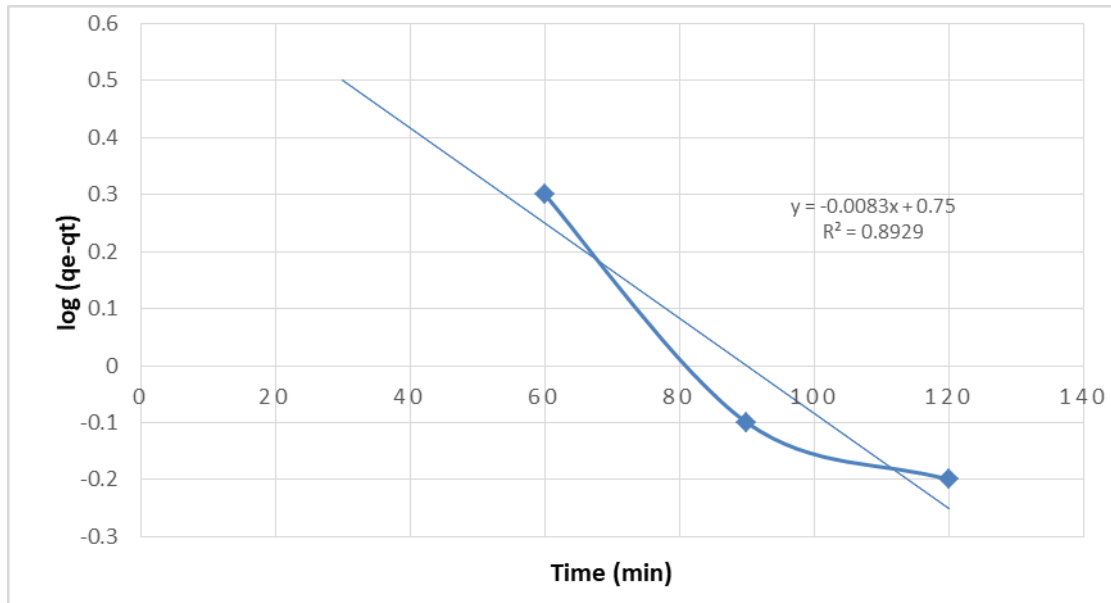


Figure 5. Pseudo-first-order kinetic model for dry gas adsorption.

3.3.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is shown as below :

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{8}$$

The following equation is obtained by integrating the initial conditions, as above, for the Pseudo-first-order kinetic model.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{(k_2 q_e)^2} \tag{9}$$

Where K_2 is the pseudo-second-order rate constant, for experimental data, a linear relation of t/q_t versus t means that this model is applicable.

The pseudo-second-order model suits experimental data very well as the pseudo-first-order model based on the correlation coefficient of 0.9984. **Fig.6** shows the Pseudo-second-order kinetic model



for dry gas adsorption at pressure 31 bar. In addition, for the pseudo-second-order model, the measured equilibrium adsorbed amount of dry gas (q_e , cal) is very similar to the experimental values.

The findings indicate that dry gas adsorption on MOF-199 follows the adsorption kinetics, pseudo-second-order. This contributes to physical adsorption controlling the overall dry gas adsorption process. It takes more time to reach equilibrium, so the kinetics of the reaction is considered pseudo-second-order (Tsivadze et al., 2019) and (Yang et al., 2014).

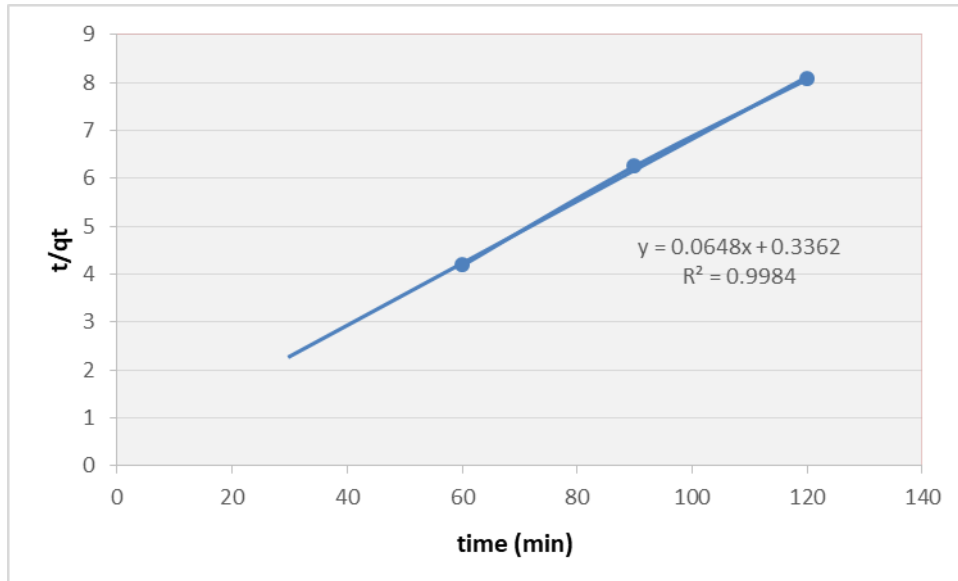


Figure 6. Pseudo-second-order kinetic model for dry gas adsorption at pressure 31 bars.

4. CONCLUSIONS AND OUTLOOK

From the present experimental research, the following can be concluded:

- 1-The Freundlich isotherm is successfully fitted with Equilibrium isotherms for adsorption of dry gas on MOF-199
2. Kinetic study shows that the pseudo-second-order model can describe the adsorption kinetics.
3. The adsorption process, according to the nature of the attraction forces between the adsorbed gas molecules and the adsorption surface, is of the type of physical adsorption. Because increasing the pressure of the adsorbent (gas) increases the rate of increase of the natural adsorption, as well as the physical adsorption, is instantaneous. It does not need much time to occur. Notably, the physical adsorption can occur in a fraction of a hundred between a second.



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