

Screening of gallate-based metal-organic frameworks for single-component CO₂ and CH₄ gas

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Abstract. Adsorption using porous adsorbents is widely applied in carbon dioxide (CO₂) capture due to its potential energy saving with low operating cost. Metal-organic frameworks (MOFs) are preferable over conventional adsorbents as MOFs have tunable structure properties. Organic linkers from phytochemical-based give a new idea in forming MOFs. Gallic acid is classified under phytochemicals can act as an alternative organic linker in a new family of hybrid framework materials due to low cost, low toxicity, easy availability and naturally abundant. Due to unique property of MOFs that can be tailored, screening using systematic tool is very important. Molecular modeling is proven to play a crucial role in providing an estimation on adsorption capacity, selectivity and adsorbent selection. Grand Canonical Monte Carlo (GCMC) method via Sorption module in Material Studio was performed to compute loading curves of CO₂ and methane (CH₄) in MOFs. Based on the simulation results, it shows that gallate-based MOFs can be a new promising adsorbent in CO₂ capture as the predicted CO₂ loading is significantly higher than CH₄. The highest predicted CO₂ adsorption capacity is achieved by Mg-gallate and the lowest is by Ag-gallate with 7.79 mmol/g and 6.35 mmol/g respectively. The applicability of gallic acid to act as an alternative linker is relevant for practical applications.

1 Introduction

Natural gas represents an excellent choice because of its fuel efficiency and cleanness compared to the other petroleum and coal products like diesel and gasoline. Natural gas is referred as hydrocarbon-rich gas, gaseous fossil fuel that is produced in natural gas fields, oil fields and coal beds [1]. Natural gas found in the reservoirs differs in composition due to the type, depth and location of the underground deposit as well as the geology of the area [2]. Natural gas may consist of diverse hydrocarbon and non-hydrocarbon constituents, leads to inconsistent gas composition consequently [1]. In Malaysia, it is proven that natural gas reserves contain 28-87% of CO₂ content [3]. Over 13 trillion cubic feet of the natural gas reserves remained unexplored because of CO₂ content [4]. Since the energy demands worldwide is rising, made Malaysia to escalate its natural gas production substantially resulting exploitation of natural gas fields with high CO₂ content because of limited natural gas fields with low CO₂ content [3].

This high CO₂ content natural gas fields up to 87% bring new challenges in terms of the CO₂ separation process. There are several processes for CO₂ capture such as solvent absorption, membrane separation, cryogenic and chemical or physical adsorption [5]. Membrane separation is considered as challenging for industrial application since it is high cost while chemical absorption also having problems like high energy consumption for

the solvent regeneration process and equipment corrosion [6]. In addition, cryogenic distillation also has major drawback which is this process requires a large amount of energy [7]. Comparatively, physical adsorption using porous materials is commonly employed in CO₂ capture since it has the benefits of economic viability and environmental friendliness [6]. Besides, it offers promising energy saving with lower operating and capital costs.

Various of solid sorbents is currently under study for CO₂ capture such as zeolite, activated carbon, calcium oxide, hydroxalclites, supported amines and metal-organic frameworks [8]. Recently, MOFs became a promising adsorbent due to their unique properties. MOFs are porous hybrid organic-inorganic materials and consist of a strong coordination bond between connector (metal) and an organic linker. MOFs are preferable over conventional adsorbents as they have the great potential due to their large surface area, well-organized porous structures and various means available for functionalization [9]. Therefore, MOFs can contribute some significant advantages as selective adsorbents since MOFs have large pore sizes to enable rapid diffusion kinetics, tunable binding strengths that can affect adsorption selectivity and high surface area that can contribute in large working capacity [10].

Despite all the advantages, cost of the MOFs is a significant drawback for scale-up production [11]. Linker is contributed as one of the most expensive materials in

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the production of MOFs [12]. This can be generally caused to the lack of commercialization of MOFs. Gallic acid is classified under phytochemicals can act as an alternative prior to expensive organic linker/ligand in a new family of hybrid framework materials due to low cost, low toxicity, easy availability and naturally abundant [13]. Gallate-based MOFs or known as M-gallate show excellent potential in the industrial applications as they have advantages such as readily available linker, high stability against water vapor and outstanding maintenance of separation performance [14]. The previous study had already proven that gallic acid can act as successful organic linker in a new family of hybrid framework materials [15]. Mostly, gallate-based MOFs are used in biomedical applications and small scopes of chemical industrial applications like olefin/paraffin separations. Gallate-based MOFs are considered as a new alternative material in gas separation applications whereby they are first reported for adsorptive separation of ethylene from ethylene/ethane mixture [14], adsorptive separation of acetylene from acetylene/ethylene mixture [16] and adsorptive separation of geometric isomers of 2-butene [17]. Up to date, the gas separation applications involving the new family gallate-based MOFs are very limited whereby only light hydrocarbon separations have been reported before and none of them related to CO₂/CH₄ separation. Therefore, this circumstance creating a promising opportunity to emphasize more on studies in CO₂/CH₄ separations. Moreover, the selection of gallate-based MOFs for those applications are not based on a systematic approach.

Due to the unique property of MOFs which can be tailored to optimize the interaction between MOFs and guest molecules of interest, screening and understanding of the fundamental structure-function relationships using a systematic tool is very important. Molecular modeling is proven to play a crucial role in this rapidly expanding research field where it can provide an estimation on selectivity of adsorption, working capacity and sorbent selection of MOFs. Nowadays, the growth of fundamental at molecular level in understanding the chemical and physical processes as well as the prediction of physicochemical properties relies greatly on computations. It is known as a powerful tool to comprehend the experimental findings and justify them into novel concepts. Recently, computational chemistry can even replace the experiments so that eventually the experiments are just for validations.

Concerning on the prediction of adsorption isotherm, Grand Canonical Monte Carlo (GCMC) method is widely used for molecular modeling on MOFs for CO₂ capture [18]. GCMC method is the key choice to adsorption matters since it enables the chemical potential of each component in the bulk phase to be identified at the starting stage of the simulation [19]. In GCMC simulation, it is required to specify bulk pressure, composition of the gas mixture and the temperature in favor of calculating the adsorbed amounts of components [20]. Various types of MOFs structure can be tested using this simulation without synthesizing, therefore it offers a cost-effective method to experiment itself. It helps the searching process and allows to discover for a wider number of possible

materials. In addition, molecular modeling can give information about gas adsorption, diffusion and separation in MOFs [21]. GCMC simulation is a great simulation method to evaluate the adsorption behaviors for nonpolar gas molecules in MOFs appropriately and precisely, leading to the interpretation of structure-property relationship [22]. The reliability of employing GCMC is proven whereby the simulated and experimental results are well agreed and almost perfectly overlapped to each other [22]. Since the speedy rising in the database of synthesized MOFs, the computational screening plays a crucial role in identification of MOFs with promising gas separation performance like the previous study done whereby the latest MOF database is screened and enabling the top 20 materials to be listed [23]. In short, GCMC screening enables specific high-performing materials to be identified and indicating the potential of those materials for practical applications [24, 25].

GCMC simulation can be performed using Sorption module in Material Studio [26]. Sorption module is applied to compute a loading curve for guest molecules in MOFs. Loading curve is defined as a series of fixed pressure (grand canonical ensemble) calculations computed over a series of fugacities. Sorption module is designed to compute the sorption of guest molecules, known as sorbates into the host porous 3D frameworks which are normally microporous inorganic structure. Describing the behavior of these materials has important application in separation technology. Output-analysis features of Sorption module like automatic calculation and display of isotherms enable them to be directly compared with experimental results. Therefore, the suitable MOFs that will be used in adsorption can be predicted and selected by using molecular modeling like GCMC.

In this study, the applicability of gallic acid as alternative linker in MOF family is investigated by using computational chemistry approach and their predicted performances are evaluated and benchmarked with available literature data. The predicted results are expected to provide substantial information on the CO₂ adsorption ability for practical applications.

2 Methodology

Adsorption isotherm for single-component (static adsorption) was calculated using GCMC algorithm via Sorption module in Material Studio in order to study the adsorption performance of CO₂ and CH₄ pure components in gallate-based MOFs. At the specific pressure and temperature, this simulation calculated the average number of adsorbate molecules that having similar chemical potential with the bulk phase [27]. The screening was based on gallate-based metal-organic frameworks whereby the focus was on gallic acid as the organic linker and covered nine metals including magnesium (Mg), cobalt (Co), manganese (Mn), titanium (Ti), nickel (Ni), zinc (Zn), iron (Fe), chromium (Cr) and silver (Ag).

The simulation was started by drawing the structure of components involved including CO₂, CH₄ and gallate-

based MOFs as shown in Figure 1. The CO₂ and CH₄ components were drawn inside the Material Studio while the structure of gallate-based MOFs were imported from Cambridge Crystallographic Data Centre (CCDC). The structure of the components should be cleaned and linked to each other. Purple, gray, red and white represent metal, C, O, and H atoms respectively. During the sorption process, those structures were assumed to be rigid and maintain fixed in their initial optimized positions.

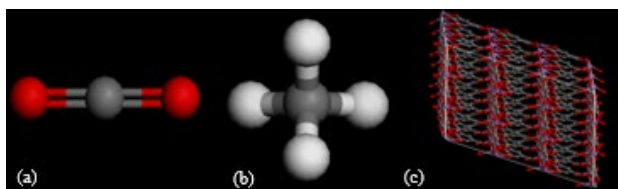


Fig. 1. Structure of components. (a) CO₂, (b) CH₄ and (c) M-gallate.

Then, the parameters for the calculation was set up. The COMPASS force field was applied to the framework atoms to calculate the adsorbate-adsorbent interaction parameters. The charges was set as forcefield assigned. The Ewald summation was employed for computing the electrostatic interactions. The van der Waals summation was denoted as atom based. The amount of attached molecules can be calculated at equilibrium once the fugacity and temperature of the adsorbates in GCMC method were specified, [28]. The size of the simulation box was set to 3x3x3 crystallographic unit cell [29]. Lastly, the Sorption calculation was run accordingly. The selection of gallate-based MOFs was done by considering the promising capacity and selectivity in capturing CO₂.

3 Results and discussion

At lower pressure range (≤ 1 bar, 298 K), the selective adsorption behavior and binding affinity of CO₂ over CH₄ had been predicted in order to study the possible impact of the porous nature of gallate-based MOFs on the CO₂ and CH₄, as illustrated in Figure 2 and Figure 3 respectively.

3.1 Single-component adsorption isotherms

The predicted isotherm data of gallate-based MOFs for single-component CO₂ and CH₄ adsorption are fitted with the Langmuir model within the operational conditions. Based on Figure 2, the amount of CO₂ adsorbed is significantly increasing as the pressure increases for all gallate-based MOFs, with a type I isotherm shape. At the initial phase of adsorption (lower pressure range), CO₂ molecules are in contact with gallate-based MOFs surface and formed a monolayer gradually. Moreover, a steep CO₂ loading over all gallate-based MOFs can be detected at low pressure range.

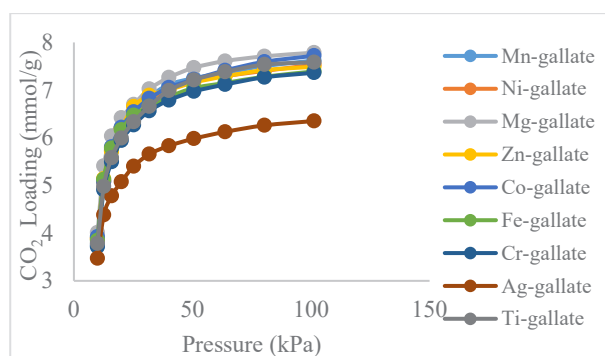


Fig. 2. Predicted CO₂ adsorption isotherm.

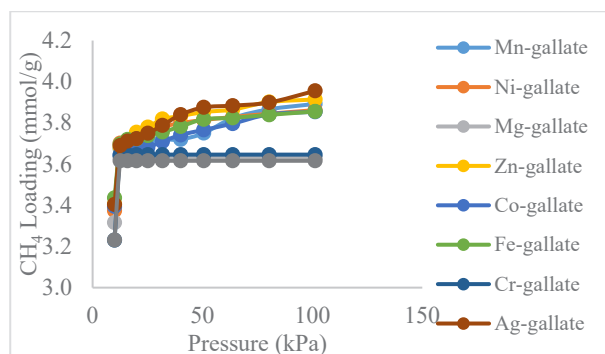


Fig. 3. Predicted CH₄ adsorption isotherm.

For CH₄ adsorption isotherms as shown in Figure 3, most of gallate-based MOFs exhibit roughly linear plots of adsorption against pressure, showing that the frameworks are not saturated at these operational conditions [26]. It shows that gallate-based MOFs do not prone to adsorb CH₄ in this case. The influence of microporous nature of gallate-based MOFs on CO₂ loading can be observed at 298 K which shows that the gallate-based MOFs have CO₂ adsorption loading higher than CH₄ adsorption loading. Therefore, based on Figure 2 and Figure 3, the amount of CO₂ adsorbed is significantly higher than CH₄, indicating that these are potential adsorbents for CO₂/CH₄ separation.

3.2 Adsorption capacity and selectivity

Single-component gas adsorption capacity is normally evaluated from the pure gas sorption isotherm at certain conditions. The adsorption capacity is an important factor in identifying MOFs for CO₂ capture and it is the major evaluation tool for gas capture application. Determining the adsorption capacity of CO₂ and CH₄ for MOFs is essential for comprehending the CO₂ capture and CH₄ desorption process. However, this approach cannot evaluate the binary/mixed gas adsorption behaviors because the competitive adsorption among different components in the mixture is not taken into account. Therefore, it is known as a preliminary screening tool to evaluate the relative gas capture capacity. Based on the predicted adsorption isotherms, adsorption capacity (loading) and selectivity of gallate-based MOFs at ambient conditions can be determined as shown in Table 1.

Table 1. Adsorption capacity and selectivity of M-gallate.

M-gallate	CO ₂ Capacity (mmol/g)	CH ₄ Capacity (mmol/g)	CO ₂ /CH ₄ Selectivity
Mg-gallate	7.79	3.63	2.14
Co-gallate	7.72	3.85	2.00
Mn-gallate	7.62	3.89	1.96
Ti-gallate	7.58	3.62	2.10
Ni-gallate	7.53	3.86	1.95
Zn-gallate	7.49	3.91	1.91
Fe-gallate	7.39	3.86	1.92
Cr-gallate	7.36	3.65	2.02
Ag-gallate	6.35	3.96	1.61

It shows that the gallate-based MOFs can be a new promising adsorbent in CO₂ capture as the adsorption capacity of CO₂ is significantly higher compared to CH₄. Based on the previous work, the aperture size of gallate-based MOFs is in the range of 3.47-3.69 Å [16]. Meanwhile, the kinetics diameter of CO₂ and CH₄ are 3.3 Å and 3.8 Å respectively [30]. Theoretically, this fact would explain gallate-based MOFs can significantly capture CO₂ prior to CH₄. In addition, CO₂ has a larger polarizability (29.1 x 10⁻²⁵ cm³ for CO₂, 25.9 x 10⁻²⁵ cm³ for CH₄) and quadrupole moment (4.30 x 10⁻²⁶ esu cm² for CO₂, 0 for CH₄), which lead to a stronger interaction between CO₂ and MOFs [30]. The highest predicted CO₂ adsorption capacity is achieved by Mg-gallate which is 7.79 mmol/g and the lowest is by Ag-gallate with 6.35 mmol/g. This indicates that the highest interaction is occurred between CO₂ molecules and open metal Mg²⁺ sites.

A high selectivity for CO₂ over the other guest molecules in a gas mixture is necessary for CO₂ capture applications [31]. The improved CO₂ binding affinity may be due to the reactive nature of sites of gallate-based MOFs which is encouraged by the high charge density sites. In terms of selectivity, Mg-gallate also shows the highest value which is 2.14. The adsorptive selectivity (thermodynamic separation) occurs due to the difference in affinity of the different components of the gas mixture to be attached on the porous surface of the MOF [31]. Selectivity can be simply understood as the affinity of gallate-based MOFs to adsorb CO₂ compared to CH₄. Selectivity calculated by the single-component isotherm method represents a simple point of comparison for evaluating the performance of different adsorbents but does not represent the actual selectivity of a mixed gas. As the loading of CO₂ is higher than CH₄ and all the values of CO₂/CH₄ selectivity are more than unity, therefore, it can be concluded that the gallate-based MOFs are prone to selectively capture CO₂ instead of CH₄.

3.3 Comparison of gallate-based MOFs with other adsorbents

The gas capture and separation involving the new family gallate-based MOFs are very limited up to date whereby only light hydrocarbon separations have been reported before and none of them related to CO₂/CH₄ separation

[14, 16, 17]. Since the experimental results on the adsorptive separation of CO₂/CH₄ using gallate-based MOFs are not available in the literature, therefore the predicted CO₂ adsorption capacity for gallate-based MOFs is compared with the other adsorbents in the previous experimental works at 1 bar as shown in Table 2.

Table 2. Comparison of CO₂ adsorption capacity.

Adsorbents	CO ₂ Adsorption Capacity (mmol/g)	Temperature (K)	Reference
Mg-gallate	7.79	298	This work
Mg-MOF-74	8.00	298	[11]
UiO-66-NH ₂	2.97	298	[32]
PPN-SO ₃ Li	3.70	295	[33]
SIFSIX-2-Cu-i	5.41	298	[34]
Zeolite 13X	1.66	298	[35]
ZIF-8	0.84	298	[35]
Mg ₂ (dobdc)-(N ₂ H ₄) _{1.8}	5.51	298	[36]
Zn-MOF-74	5.50	296	[37]
Ni-MOF-74	5.80	296	[37]
Co-MOF-74	7.00	296	[37]
HKUST-1	4.10	298	[38]
MOF-5	2.10	296	[39]
IRMOF-1	1.92	298	[40]
MIL-101	1.60	298	[41]
Activated carbon	2.92	298	[42]

In terms of CO₂ adsorption capacity, Mg-MOF-74 becomes the top of the list of all the adsorbents. However, when it is compared to gallate-based MOFs, Mg-MOF-74 is so costly. Nevertheless, Mg-gallate shows higher predicted CO₂ adsorption capacity compared to the rest of other adsorbents in Table 2.

4 Conclusion

In this study, the performance of gallate-based MOFs has been studied by using a computational chemistry tool. The CO₂ loading and CH₄ loading have been predicted using GCMC simulation via Sorption module in Material Studio. Gallate-based MOFs can be a new promising adsorbent in CO₂ capture as the predicted CO₂ loading is significantly higher than CH₄. The highest predicted CO₂ adsorption capacity is achieved by Mg-gallate and the lowest is by Ag-gallate with 7.79 mmol/g and 6.35 mmol/g respectively. The applicability of gallic acid to act as an alternative linker in a new family hybrid metal-organic framework is relevant for practical applications.

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