Insights into the Adsorption of VOCs on a Cobalt-Adeninate Metal–Organic Framework (Bio-MOF-11)

Ruofei Chen, Zhengxin Yao, Ning Han, Xiancheng Ma, Liqing Li,* Shaomin Liu, Hongqi Sun, and Shaobin Wang*

Cite This: ACS Omega 2020, 5, 15402−15408

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: With increasingly severe air pollution brought by volatile organic compounds (VOCs), the search for efficient adsorbents toward VOC removal is of great significance. Herein, an adenine-based metal–organic framework, namely, bio-MOF-11 [Co2(ad)2(CH3CO2)2·0.3EtOH·0.6H2O, ad = adeninate], was synthesized via a facile method, and its VOC adsorption was reported for the first time. This novel bio-MOF-11 was investigated by employing four common VOCs (i.e., methanol, acetone, benzene, and toluene) as adsorbates. The saturated adsorption capacity of these targeted VOCs on bio-MOF-11 was estimated to be 0.73−3.57 mmol/g, following the order: toluene < benzene < acetone < methanol. Furthermore, with the adsorption temperature increasing from 288 to 308 K, the saturated adsorption capacity was reduced by 7.3−35.6%. It is worth noting that acetone adsorption is most sensitive to temperature ascribed to its low boiling point and strong polar nature. Meanwhile, owing to the molecular sieve effect, the adsorption capacity appears negatively correlated to the size of VOC molecules. Besides, the abundant exposed nitrogen atoms and amino groups in bio-MOF-11 cavities facilitate the adsorption of polar VOC molecules. This work promotes the fundamental understanding and practical application of bio-MOF for adsorptive removal of VOCs.

INTRODUCTION

The control of volatile organic compounds (VOCs) from industrial and natural sources has raised ever increasing public concern on account of their potentially harmful effects on the environment and human beings even at low concentrations and hence prompted more stringent legislation and regulations.1,2 Great efforts have been made to eliminate the emission of VOCs.3−5 Among various techniques for VOCs abatement from polluted air, adsorption by porous materials has been well established and proved effective.6−8 With high-efficiency removal of VOCs by adsorption yet to be achieved, the development of specialized adsorbents toward targeted adsorbates is crucial, which still remains a major challenge.

Thus, metal–organic frameworks (MOFs), an emerging class of porous materials, have attracted extensive attention because their textural structure and chemical functionality could be facilely tailored for specific applications through the variation of metallic clusters and organic linkers,9,10 which are regarded as promising alternatives for addressing many limitations experienced by classical adsorbents.11 MOFs have some inherent superiorities such as a well-developed porous structure, controlled pore size, homogenous dispersion of components, and facile functionalization, presenting bright prospects for catalysis, photocatalysis, liquid- and gas-phase adsorption, and so forth.12−16 Attempts by several researchers have been made to achieve efficient adsorption of VOCs using MOFs. For instance, Zhu et al.17 reported an enhanced hydrophobic MIL(Cr)-Z1 material with high adsorption capacity and selectivity for benzene series VOCs by grafting naphthalene dicarboxylic acid as the ligand. MIL(Cr)-101 exhibited favorable adsorption of VOCs containing aromatic ring or heteroatoms, especially the amines such as n-butylamine.18 Besides, MOF-177 was discovered to be a potential adsorbent for the removal of acetone and benzene series VOCs,19 while fluorous MOFs were found to possess high adsorption capacity and affinity to C6−C8 hydrocarbon vapors.20 Zhang et al.21−24 found that modified UiO-66 materials exhibited enhanced adsorption performance of gaseous toluene. Moreover, Vellingiri et al.25 demonstrated that MOFs with −NH termination could be effectively applied in toluene capture.

Received: April 3, 2020
Accepted: June 3, 2020
Published: June 15, 2020

https://dx.doi.org/10.1021/acsomega.0c01504
ACS Omega 2020, 5, 15402−15408
© 2020 American Chemical Society
Recently, adenine-based MOFs, typically known as bio-MOFs, have been reported with their various applications concerning water treatment,26 drug delivery,27,28 fluorescent sensor,29 CO₂ capture,30 and gas separation.31−33 Adenine is a versatile biomolecular building block in view of its multiple Lewis-basic sites consisting of four heterocyclic N atoms and one exocyclic amino-N atom, which could facilitate the adsorption of VOC molecules.25,34,35 Interestingly, all the five N atoms can coordinate with metals and thereby form multiple binding modes. Moreover, the distinctive coordination mode of bio-MOF-11 contributes to more free Lewis-basic sites than other bio-MOFs36−38 and hence considerable potential for the removal of VOCs. However, this potential still lacks further exploration, as VOC adsorption on bio-MOFs has scarcely been involved in the available literature, let alone on bio-MOF-11. Therefore, related research is claimed.

In this context, bio-MOF-11, characterized here as Co₂(ad)₂(CH₃CO₂)₂·0.3EtOH·0.6H₂O (ad = adeninate), was developed via a facile solvothermal method, as shown in Figure 1. Subsequently, the synthesized bio-MOF-11 was employed as the adsorbent toward a series of VOCs with varying physicochemical properties. The adsorption behavior of targeted VOCs on bio-MOF-11 was analyzed in detail, and the results were correlated to their intrinsic characteristics such as the boiling point, polarity, and size of VOC molecules. In addition, the effect of temperature on adsorption was studied as well. This work aims to provide a fundamental understanding about VOC adsorption characteristics of bio-MOF-11.

### RESULTS AND DISCUSSION

#### Physicochemical Properties of Bio-MOF-11.

The crystallinity of synthesized bio-MOF-11 was examined by X-ray diffraction (XRD), as shown in Figure 2a, and the characteristic peaks are identical to the previously reported study.39 Besides, the Fourier transform infrared spectroscopy (FTIR) spectrum of bio-MOF-11 is shown in Figure 2b, and the linkage of Co nodes and adenine linkers could be clearly observed. As shown, the broad bands at 3337 and 3194 cm⁻¹ result from amino N–H stretching vibration in adeninate. The bands between 1650 and 1500 cm⁻¹ are ascribed to stretching and bending vibration of imidazole ring in adeninate, while the bands between 1450 and 1050 cm⁻¹ are ascribed to a complex of C–N stretching, C–H bending, and C–O stretching vibration in adeninate and acetate structures. Furthermore, the bands in the range of 800−500 cm⁻¹ are attributed to the stretching vibration of Co nodes.26,39

According to thermogravimetric (TG) and derivative thermogravimetry (DTG) curves in Figure 2c, bio-MOF-11
exhibited an initial weight loss below 470 K ascribed to the removal of EtOH and water guest molecules. Subsequently, the decomposition of the framework started from around 550 K. In addition, the microstructure of bio-MOF-11 was detected by scanning electron microscopy (SEM) and is shown in Figure 2d. Apparently, polyhedral crystals could be observed, and the particle size (200−300 nm) is smaller compared to the literature (10−35 μm),33 which might be caused by the difference in the synthesis process as this study adopted a simplified method.

The pore structure properties of bio-MOF-11 were characterized by N2 adsorption−desorption at 77 K. As shown in Figure 3a, the isotherm of type I−IV hybrid shape according to the IUPAC classification indicates a combined micro- and mesoporous structure of the adsorbent. The steep slope at low pressures is associated to pore filling in micropores, and the H4 hysteresis loop at higher pressures reveals the existence of slit-like mesopores,40 which is further verified by the pore size distribution (PSD) curve, as shown in Figure 3b.

For better understanding the hierarchically porous structure, the results of surface area analysis are summarized in Table S1. The specific surface area (S BET) of bio-MOF-11 reaches 580 m2/g. The values of total pore volume (V) and micropore volume (V micro) are 0.35 and 0.26 mL/g, respectively, with a V micro/V of 0.74, indicating a mainly microporous structure. Meanwhile, the most probable width of micro- and mesopores (Wp-micro and Wp-mesop, respectively) occurs at 0.53 and 3.77 nm, respectively, and pores of 0.53 nm demonstrate an overwhelming dominance, which could be clearly reflected by the PSD curve in Figure 3b. It is worthwhile to note that the theoretical diameter of cavities in periodically paddle-wheel cobalt–adeninate–acetate structure is 0.58 nm,39 in agreement with the measured value (Wp-micro: 0.53 nm).

**VOC Adsorption Isotherms on Bio-MOF-11.** Adsorption isotherms of methanol (polar VOC), acetone (polar VOC), benzene (nonpolar VOC), and toluene (weak polar VOC) on bio-MOF-11 at 288, 298, and 308 K are plotted in Figure 4. As shown, VOC adsorption isotherms belong to type I−IV that displays a rapid increase at the beginning and then forms a wide bend subsequently with steady adsorption at higher pressures, which is related to the micro- and mesoporosities of bio-MOF-11. With the same experimental conditions, the amount of VOCs adsorbed follows the sequence: toluene < benzene < acetone < methanol. For instance, under an equilibrium pressure of 1 kPa and 288 K, the uptake of methanol, acetone, benzene and toluene on bio-MOF-11 reached 2.65, 1.86, 1.17, and 0.79 mmol/g, respectively. For each VOC, adsorption declines with increasing adsorption temperature as adsorption is an...
toward targeted VOCs are summarized in Table S3. It is worth noting that the adsorption capacity values of various MOFs with adeninate linkers may provide diverse adsorption sites for polar VOCs. The adsorption capacity values of various MOFs are easier to access the intrapore of the adsorbent whereas competitive values appear after normalization by its moderate specific surface area compared with other MOFs, whereas competitive values appear after normalization with $S_{\text{BET}}$, which might be associated with the intrinsic structure of this material. Additionally, the reproducibility of bio-MOF-11 was evaluated by taking acetone adsorption as an exemplification. As shown in Figure S2, at 288 K and 18.1 kPa, the adsorption capacity of bio-MOF-11 toward acetone vapor is 2.72 mmol/g for the first cycle, which remains 98.2 and 94.5% for the second and third cycle respectively, indicating the good recycling performance and structural stability of bio-MOF-11. In addition, the XRD patterns after acetone adsorption (Figure S3) also verify that bio-MOF-11 remains structurally stable during the adsorption process.

**Effect of Adsorption Temperature on VOC Adsorption.** Temperature is a crucial determinant of adsorption. Hence, to explore the influence of adsorption temperature on the adsorption capacity of bio-MOF-11, adsorption tests were conducted under 288, 298, and 308 K. For comparison, Figure 5a depicts the $q_s$ for VOCs under these three temperatures, which is the fitting parameter of the Langmuir model that could represent the saturated adsorption capacity independent of equilibrium pressure.

As summarized in Table S2, the $q_s$ was estimated to be 0.73–3.57 mmol/g. As expected, the $q_s$ for every targeted VOC falls as adsorption temperature increases because of the inhibition effect of temperature in view of physical exothermic adsorption. Taking methanol adsorption as an example, the $q_s$ is 3.57 mmol/g at 288 K, decreasing by 3.6 and 7.3% at 298 and 308 K, respectively. However, for acetone adsorption, the inhibition effect becomes much more marked that $q_s$ dropped by 25.1 and 35.6% from 288 to 298 and 308 K, respectively. Overall, the $q_s$ exhibits a linear correlation with the adsorption temperature, as shown in Figure 5b. A similar trend was observed by Wang et al. Note that the linearity for toluene adsorption is less obvious (Figure S3) also verify that bio-MOF-11 remains structurally stable during the adsorption process.

**Effect of Physicochemical Properties of Adsorbate on VOC Adsorption.** On the other hand, different adsorbates...
result in variations in adsorption behavior. Some basic properties of the four targeted VOCs are shown in Table S4. Considering the molecular mass ($M_r$) and molecular dynamics diameter ($D_m$) to be two representative parameters, respectively, for intrinsic static and dynamic characteristics of the adsorbates, the two parameters were adopted for further analysis to evaluate the impact of adsorbate properties on VOC adsorption by bio-MOF-11. Based on Figure 5a, a rough direction of the $q_e$ could be easily distinguished for all adsorption temperatures as toluene < benzene < acetone < methanol, which is exactly opposite to the sequence of the $M_r$ as well as the $D_m$ as listed in Table S4. Then, the $q_e$ was plotted respectively versus the $M_r$ and $D_m$ of different VOCs in Figure 6.

As shown in Figure 6a, the $q_e$ is almost inversely proportional to the $M_r$. With the $M_r$ increasing from 32 to 92, the $q_e$ sharply reduced by 70.6−77.9%. Such dependence of adsorption capacity and molecular weight has also been reported by Goto et al. In fact, there is an inherent connection between the $M_r$ and the $D_m$ that both account for molecule size. Likewise, the $q_e$ proves negatively correlated with the $D_m$ according to Figure 6b because larger molecules have difficulty in accessing narrow pores on account of molecular size exclusion characteristics of the adsorbent. It is well recognized that micropores especially narrow micropores of the adsorbent play a critical role in VOC adsorption. Considering the pore size of bio-MOF-11 ($W_{\text{p-mic}}$: 0.53 nm), it is understandable that methanol ($D_m$: 0.43 nm) adsorption is preferential to others, especially benzene ($D_m$: 0.65 nm) and toluene ($D_m$: 0.67 nm), which are hard to be accommodated by the cavities during host-guest interactions. Moreover, in terms of other VOC properties, adsorbates with strong polarity tend to be preferred on bio-MOF-11. This could be explained by the abundant exposed nitrogen atoms and amino groups in bio-MOF-11 cavities that facilitate the adsorption of polar VOC molecules. In summary, the correlation between adsorption and the molecule size of VOCs is more pronounced in this study.

### CONCLUSIONS

Herein, bio-MOF-11 (Co$_2$(ad)$_2$(CH$_3$CO$_2$)$_2$·0.3EtOH·0.6H$_2$O (ad = adeninate): C, 33.03; H, 3.61; N, 26.39. Found: C, 32.95; H, 3.11; N, 26.38 (Table S1)). Liquid methanol (≥99.5%), acetone (≥99.5%), benzene (≥99.5%), and toluene (≥99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

**Synthesis.** In this study, a facile method without the cryogenic process, simplified from the study of An et al., was adopted to synthesize bio-MOF-11. Schematic illustration of the synthesis of bio-MOF-11 is shown in Figure 1. To be specific, 2.70 mmol adenine and 0.90 mmol cobalt acetate were dissolved in 54 and 18 mL EtOH, respectively, and stirred vigorously for 1 h. Subsequently, the two solutions and 0.25 mL ultrapure water were added to a 100 mL autoclave, heated at 393 K for 24 h, and then cooled to room temperature. The product was filtered, washed with 54 mL EtOH for three times, and dried at 373 K in vacuum overnight. Elemental analysis calculated for Co$_2$(ad)$_2$(CH$_3$CO$_2$)$_2$·0.3EtOH·0.6H$_2$O (ad = adeninate): C, 33.03; H, 3.61; N, 26.39. Found: C, 32.95; H, 3.11; N, 26.38 (Table S1).

**Characterization.** The crystal structure of synthesized bio-MOF-11 was characterized by XRD (D8 ADVANCE, Bruker AXS GmbH, Germany). The morphology was observed through SEM (Verios XHR 460, FEI Co., USA). The chemical composition of bio-MOF-11 was determined via elemental analysis for C, H, and N (2400 Series II CHNS/O Analyzer, PerkinElmer Inc., USA) and the surface chemistry via FTIR analysis (Spectrum 100 FTIR Spectrometer, PerkinElmer Inc., USA).

### EXPERIMENTAL SECTION

**Materials.** Cobalt acetate (≥99.995%), adenine (≥99%), and ethanol (EtOH, ≥ 99.5%) were purchased from Sigma-Aldrich, Inc. (Australia) and used without further purification. Ultrapure water (15 MΩ·cm) was produced by the water purification system [Agilent Technologies Pty. Ltd. (Australia)]. Liquid methanol (≥99.5%), acetone (≥99.5%), benzene (≥99.5%), and toluene (≥99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

**Synthesis.** In this study, a facile method without the cryogenic process, simplified from the study of An et al., was adopted to synthesize bio-MOF-11. Schematic illustration of the synthesis of bio-MOF-11 is shown in Figure 1. To be specific, 2.70 mmol adenine and 0.90 mmol cobalt acetate were dissolved in 54 and 18 mL EtOH, respectively, and stirred vigorously for 1 h. Subsequently, the two solutions and 0.25 mL ultrapure water were added to a 100 mL autoclave, heated at 393 K for 24 h, and then cooled to room temperature. The product was filtered, washed with 54 mL EtOH for three times, and dried at 373 K in vacuum overnight. Elemental analysis calculated for Co$_2$(ad)$_2$(CH$_3$CO$_2$)$_2$·0.3EtOH·0.6H$_2$O (ad = adeninate): C, 33.03; H, 3.61; N, 26.39. Found: C, 32.95; H, 3.11; N, 26.38 (Table S1).

**Characterization.** The crystal structure of synthesized bio-MOF-11 was characterized by XRD (D8 ADVANCE, Bruker AXS GmbH, Germany). The morphology was observed through SEM (Verios XHR 460, FEI Co., USA). The chemical composition of bio-MOF-11 was determined via elemental analysis for C, H, and N (2400 Series II CHNS/O Analyzer, PerkinElmer Inc., USA) and the surface chemistry via FTIR analysis (Spectrum 100 FTIR Spectrometer, PerkinElmer Inc., USA).

The textural properties of bio-MOF-11 were estimated by N$_2$ adsorption−desorption at 77 K with a gas adsorption analyzer (JW-BK132Z, JWGB SCI. & TECH. Inc., China). Based on the isotherm, the specific surface area ($S_{\text{BET}}$), total pore volume $(V)$, and micropore volume $(V_{\text{mic}})$ were calculated via methods as described in our previous work. The micro- and meso-PSD curves were estimated from the desorption data with density functional theory and the Barrett−Joyner−Halenda method, respectively. Thermal characteristics were obtained using a TG analyzer (SDT Q600, Waters Corp., USA) under Ar flow (20 mL/min) at 10 K/min, with the DTG curve obtained simultaneously.

**Gas Adsorption Tests.** Adsorption isotherms of selected VOCs including methanol, acetone, benzene, and toluene vapor on bio-MOF-11 were obtained at 288, 298, and 308 K respectively using the JW-BK132Z adsorption instrument via a standard static volumetric method. To be specific, bio-MOF-11 (around 100 mg) was outgassed at 393 K for 6 h prior to every adsorption test. Purification of VOCs was conducted by repeating the freezing-liquefaction process for three times using liquid nitrogen. During the adsorption test, a thermostat water bath was adopted to achieve the required adsorption temperature for the sample tube. The adsorption capacity was calculated based on the corresponding volume of VOC adsorbed by bio-MOF-11 under standard conditions. All of the adsorption tests were carried out with the same procedure.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01504. VOC adsorption isotherms on bio-MOF-11 at 288, 298, and 308 K; reproducibility of bio-MOF-11; physico-chemical properties of bio-MOF-11; fitting parameters of the Freundlich model and Langmuir model for VOC adsorption.
adsorption on bio-MOF-11; adsorption capacity of different MOFs toward VOCs; and physicochemical properties of selected VOCs (PDF)

Author Information

Corresponding Authors
Liqing Li — School of Energy Science and Engineering, Central South University, Changsha, Hunan 410083, China; orcid.org/0000-0001-8297-309X; Email: liqingli@hotmail.com

Shaobin Wang — WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia; School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia; orcid.org/0000-0002-1751-9162; Email: shaobin.wang@adelaide.edu.au

Authors
Ruofei Chen — School of Energy Science and Engineering, Central South University, Changsha, Hunan 410083, China; WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia
Zhengxin Yao — WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia
Ning Han — WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia
Xiancheng Ma — School of Energy Science and Engineering, Central South University, Changsha, Hunan 410083, China
Shaomin Liu — WA School of Mines: Minerals, Energy and Chemical Engineering (WASM-MECE), Curtin University, Perth, Western Australia 6845, Australia
Hongqi Sun — School of Engineering, Edith Cowan University, Joondalup, Western Australia 6027, Australia; orcid.org/0000-0003-0907-5626

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01504

Author Contributions
R.C. and Z.Y. contributed equally. Ruofei Chen: conceptualization, data curation, formal analysis, investigation, methodology, and writing—original draft. Zhengxin Yao: formal analysis and investigation. Ning Han: writing—review and editing. Xiancheng Ma: investigation. Liqing Li: funding acquisition, resources, and supervision. Shaomin Liu and Hongqi Sun: supervision. Shaobin Wang: conceptualization, resources, and supervision.

Notes
The authors declare no competing financial interest.

Acknowledgments
We acknowledge the financial support from National Natural Science Foundation of China [grant number 21878338] and China Scholarship Council [grant number 201706370064].

References
(1) Tong, R.; Zhang, L.; Yang, X.; Liu, J.; Zhou, P.; Li, J. Emission characteristics and probabilistic health risk of volatile organic compounds from solvents in wooden furniture manufacturing. J. Clean. Prod. 2019, 208, 1096–1108.
(2) Yang, C.; Miao, G.; Pi, Y.; Xia, Q.; Wu, J.; Li, Z.; Xiao, J. Abatement of various types of VOCs by adsorption/catalytic oxidation: A review. Chem. Eng. J. 2019, 370, 1128–1153.
(3) Zeng, K.; Li, X.; Wang, C.; Wang, Z.; Guo, P.; Yu, J.; Zhang, C.; Zhao, X. S. Three-dimensionally macroporous MnZrO catalysts for propane combustion: Synergistic structure and doping effects on physicochemical and catalytic properties. J. Colloid Interface Sci. 2020, 572, 281–296.
(4) Zhang, C.; Huang, H.; Li, G.; Wang, L.; Song, L.; Li, X. Zeolitic acidity as a promoter for the catalytic oxidation of toluene over MnO/HZSM-5 catalysts. Catal. Today 2019, 327, 374–381.
(5) Zhang, X.; Gao, B.; Creamer, A. E.; Cao, C.; Li, Y. Adsorption of VOCs onto engineered carbon materials: A review. J. Hazard. Mater. 2017, 338, 102–123.
(6) Li, X.; Zhang, L.; Yang, Z.; Wang, P.; Yan, Y.; Ran, J. Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review. Sep. Purif. Technol. 2020, 235, 116213.
(7) Szczesniak, B.; Choma, J.; Jaroniec, M. Gas adsorption properties of hybrid graphene-MOF materials. J. Colloid Interface Sci. 2018, 514, 801–813.
(8) Wang, H.; Zhu, T.; Fan, X.; Na, H. Adsorption and desorption of small molecule volatile organic compounds over carbide-derived carbon. Carbon 2014, 67, 712–720.
(9) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science 2002, 295, 469–472.
(10) Zheng, S.-T.; Wu, T.; Chou, C.; Fuhr, A.; Feng, P.; Bu, X. Development of composite inorganic building blocks for MOFs. J. Am. Chem. Soc. 2012, 134, 4517–4520.
(11) Lahoz-Martín, F. D.; Martin-Calvo, A.; Calero, S. Selective separation of BTX mixtures using metal–organic frameworks. J. Phys. Chem. C 2014, 118, 13126–13136.
(12) Bi, F.; Zhang, X.; Chen, J.; Yang, Y.; Wang, Y. Excellent catalytic activity and water resistance of UiO-66-supported highly dispersed Pd nanoparticles for toluene catalytic oxidation. Appl. Catal. B Environ. 2020, 269, 118767.
(13) Zhang, X.; Song, L.; Bi, F.; Zhang, D.; Wang, Y.; Cui, L. Catalytic oxidation of toluene using a facile synthesized Ag nanoparticle supported on UiO-66 derivative. J. Colloid Interface Sci. 2020, 571, 38–47.
(14) Zhang, X.; Li, H.; Lv, X.; Xu, J.; Wang, Y.; He, C.; Liu, N.; Yang, Y.; Wang, Y. Facile synthesis of highly efficient amorphous Mn-MIL-100 catalysts: Formation mechanism and structure changes during application in CO oxidation. Chem. - Eur. J. 2018, 24, 8822–8832.
(15) Zhang, X.; Yang, Y.; Huang, W.; Yang, Y.; Wang, Y.; He, C.; Liu, N.; Wu, M.; Tang, L. g-C3N4/Uio-66 nanohybrids with enhanced photocatalytic activities for the oxidation of dye under visible light irradiation. Mater. Res. Bull. 2018, 99, 349–358.
(16) Azhar, M. R.; Abid, H. R.; Tade, M. O.; Periasamy, V.; Sun, H.; Wang, S. Cascade applications of robust MIL-96 metal organic frameworks in environmental remediation: Proof of concept. Chem. Eng. J. 2018, 341, 262–271.
(17) Zhu, M.; Hu, P.; Tong, Z.; Zhao, Z.; Zhao, Z. Enhanced hydrophobic MIL(Cr) metal-organic framework with high capacity and selectivity for benzene VOCs capture from high humid air. Chem. Eng. J. 2017, 313, 1122–1131.
(18) Huang, C.-Y.; Song, M.; Gu, Z.-Y.; Wang, H.-F.; Yan, X.-P. Probing the adsorption characteristic of metal-organic framework MIL-101 for volatile organic compounds by quartz crystal microbalance. Environ. Sci. Technol. 2011, 45, 4490–4496.
(19) Yang, K.; Xue, F.; Sun, Q.; Yue, R.; Lin, D. Adsorption of volatile organic compounds by metal-organic frameworks MOF-177. J. Chem. Environ. Eng. 2013, 1, 713–718.
(20) Yang, C., Kaipa, U., Mather, Q. Z., Wang, X., Nesterov, V., Venero, A. F., Omary, M. A. Fluorous metal-organic frameworks with superior adsorption and hydrophobic properties toward oil spill cleanup and hydrocarbon storage. *J. Am. Chem. Soc.* 2011, 133, 18094–18097.

(21) Zhang, X., Lv, X., Shi, X., Yang, Y., Yang, Y. Enhanced hydrophobic UiO-66 (University of Oslo 66) metal-organic framework with high capacity and selectivity for toluene capture from high humid air. *J. Colloid Interface Sci.* 2019, 539, 152–160.

(22) Zhang, X.; Shi, X.; Chen, J.; Yang, Y.; Lu, G. The preparation of defective UiO-66 metal organic framework using MOF-5 as structural modifier with high sorption capacity for gaseous toluene. *J. Chem. Environ. Eng.* 2019, 7, 103405.

(23) Zhang, X.; Yang, Y.; Lv, X.; Wang, Y.; Liu, N.; Chen, D.; Cui, L. Adsorption/desorption kinetics and breakthrough of gaseous toluene for modified microporous-mesoporous UiO-66 metal organic framework. *J. Hazard. Mater.* 2019, 366, 140–150.

(24) Zhang, X.; Yang, Y.; Song, L.; Chen, J.; Yang, Y.; Wang, Y. Enhanced adsorption performance of gaseous toluene on defective UiO-66 metal organic framework: Equilibrium and kinetic studies. *J. Hazard. Mater.* 2019, 365, 597–605.

(25) Vellipindi, K.; Kumar, P.; Deep, A.; Kim, K.-H. Metal-organic frameworks for the adsorption of gaseous toluene under temperature and pressure. *Chem. Eng. J.* 2017, 307, 1116–1126.

(26) Azhar, M. R.; Vijay, P.; Tadé, M. O.; Sun, H.; Wang, S. Submonolayer sized water-stable metal organic bio-framework (bio-MOF-11) for catalytic degradation of pharmaceuticals and personal care products. *Chemosphere* 2017, 196, 105–114.

(27) Ercucar, I.; Keskin, S. Efficient storage of drug and cosmetic molecules in biocompatible metal organic frameworks: A molecular simulation study. *Ind. Eng. Chem. Res.* 2016, 55, 1929–1939.

(28) An, J.; Geib, S. J.; Rosi, N. L. Cation-triggered drug release from a porous zinc-adeninate metal-organic framework. *J. Am. Chem. Soc.* 2009, 131, 8376–8377.

(29) Shen, X.; Yan, B. A novel fluorescence probe for sensing organic amine vapors from a Eu5+/ β-diketonate functionalized bio-MOF-1 hybrid system. *J. Mater. Chem. C* 2015, 3, 7038–7044.

(30) An, J.; Rosi, N. L. Tuning MOF CO2 adsorption properties via cation exchange. *J. Am. Chem. Soc.* 2010, 132, 5578–5579.

(31) Ishaq, S.; Tamime, R.; Bilad, M. R.; Khan, A. L. Mixed matrix membranes comprising of polysulfone and microporous Bio-MOF-1: Preparation and gas separation properties. *Sep. Purif. Technol.* 2019, 210, 442–451.

(32) Huang, Y. L.; Qiu, P. L.; Zeng, H.; Liu, H.; Luo, D.; Li, Y. Y.; Lu, W.; Li, D. Tuning the C2/C1 hydrocarbon separation performance in a bioMOF by surface functionalization. *Eur. J. Inorg. Chem.* 2020, 17, 1683–1689.

(33) Li, T.; Sullivan, J. E.; Rosi, N. L. Design and preparation of a core-shell metal-organic framework for selective CO2 capture. *J. Am. Chem. Soc.* 2013, 135, 9984–9987.

(34) Guo, Y.; Zeng, Z.; Li, L.; Su, C.; Chen, R.; Wang, C.; Zhou, K.; Xu, X.; Li, H. Competitive adsorption of methanol-acetone on surface functionalization (-COOH, -OH, -NH2, and -SO3H): Grand canonical Monte Carlo and density functional theory simulations. *ACS Appl. Mater. Interfaces* 2019, 11, 34241–34250.

(35) Ma, X.; Li, L.; Zeng, Z.; Chen, R.; Wang, C.; Zhou, K.; Su, C.; Li, H. Synthesis of nitrogen-rich nanoporous carbon materials with C3N-type from ZIF-8 for methanol adsorption. *Chem. Eng. J.* 2019, 363, 49–56.

(36) Li, T.; Chen, D.-L.; Sullivan, J. E.; Kozlowski, M. T.; Johnson, J. K.; Rosi, N. L. Systematic modulation and enhancement of CO2:N2 selectivity and water stability in an isoreticular series of bio-MOF-11 analogues. *Chem. Sci.* 2013, 4, 1746–1755.

(37) An, J.; Farha, O. K.; Hupp, J. T.; Pohl, E.; Yeh, J. I.; Rosi, N. L. Metal-adeninate vertices for the construction of an exceptionally porous metal-organic framework. *Nat. Commun.* 2012, 3, 604.

(38) An, J.; Shade, C. M.; Chengelis-Czeged, D. A.; Petoud, S.; Rosi, N. L. Zinc-adeninate metal-organic framework for aqueous encapsulation and sensitization of near-infrared and visible emitting lanthanide cations. *J. Am. Chem. Soc.* 2011, 133, 1220–1223.

(39) An, J.; Geib, S. J.; Rosi, N. L. High and selective CO2 uptake in a cobalt adeninate metal-organic framework exhibiting pyrimidine- and amino-decorated pores. *J. Am. Chem. Soc.* 2010, 132, 38–39.

(40) Shen, Y.; Zhou, Y.; Fu, Y.; Zhang, N. Activated carbons synthesized from unaltered and pelletized biomass wastes for bio-tar adsorption in different phases. *Renewable Energy* 2020, 146, 1700–1709.

(41) Chen, R.; Han, N.; Li, L.; Wang, S.; Ma, X.; Wang, C.; Li, H.; Li, H.; Zeng, L. Fundamental understanding of oxygen content in activated carbon on acetone adsorption desorption. *Appl. Surf. Sci.* 2020, 508, 145211.

(42) Wang, H.; Wang, B.; Li, J.; Zhu, T. Adsorption equilibrium and thermodynamics of acetaldehyde/acetone on activated carbon. *Sep. Purif. Technol.* 2019, 209, 535–541.

(43) Zhang, X.; Xiang, W.; Wang, B.; Fang, J.; Zou, W.; He, F.; Li, Y.; Tsang, D. C. W.; Ok, Y. S.; Gao, B. Adsorption of acetone and cyclohexane onto CO2 activated hydrochars. *Chemosphere* 2020, 245, 125664.

(44) Chiang, Y.-C.; Chiang, P.-C.; Huang, C.-P. Effects of pore structure and temperature on VOC adsorption on activated carbon. *Carbon* 2001, 39, 523–534.

(45) Goto, M.; Sasaki, M.; Kawahara, S.; Hirose, T. Adsorption behavior of dioxin model compounds on activated carbon in supercritical carbon dioxide. *Adsorption* 2005, 11, 157–161.

(46) Jahandar Lashaki, M.; Fayaz, M.; Niknaddaf, S.; Hashisho, Z. Effect of the adsorbate kinetic diameter on the accuracy of the Dubinin-Radushkevich equation for modeling adsorption of organic vapors on activated carbon. *J. Hazard. Mater.* 2012, 241–242, 154–163.

(47) Lillo-Rodenas, M. A.; Cazorla-Amorós, D.; Linares-Solano, A. Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations. *Carbon* 2005, 43, 1758–1767.

(48) Chen, R.; Li, L.; Liu, Z.; Lu, M.; Wang, C.; Li, H.; Ma, W.; Wang, S. Preparation and characterization of activated carbons from tobacco stem by chemical activation. *J. Air Waste Manage. Assoc.* 2017, 67, 713–724.