Preliminary experimental research of metal-organic frameworks (MOFs) for formaldehyde dynamic adsorption

Chen, Shan; Zu, Kan; Fang, Lei; Qin, Menghao

Published in:
Journal of Physics: Conference Series

Link to article, DOI:
10.1088/1742-6596/2069/1/012246

Publication date:
2021

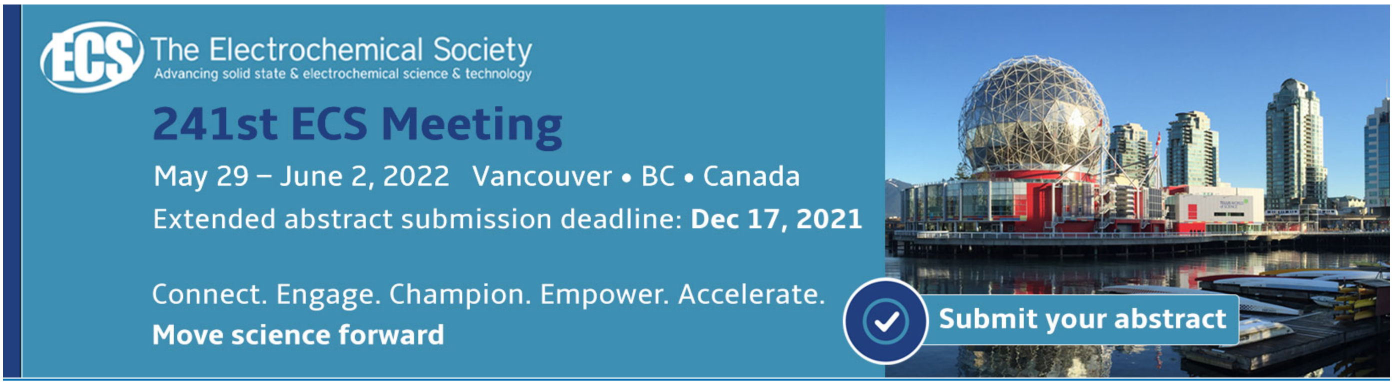
Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Chen, S., Zu, K., Fang, L., & Qin, M. (2021). Preliminary experimental research of metal-organic frameworks (MOFs) for formaldehyde dynamic adsorption. *Journal of Physics: Conference Series*, *2069*(1), Article 012246. https://doi.org/10.1088/1742-6596/2069/1/012246

Journal of Physics: Conference Series

Preliminary experimental research of metal-organic frameworks (MOFs) for formaldehyde dynamic adsorption

To cite this article: Shan Chen *et al* 2021 *J. Phys.: Conf. Ser.* **2069** 012246



Preliminary experimental research of metal-organic frameworks (MOFs) for formaldehyde dynamic adsorption

Shan Chen, Kan Zu, Lei Fang and Menghao Qin

Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark
Corresponding email: menqin@byg.dtu.dk

Abstract. Formaldehyde is a common emission from furniture and indoor decorations. Although the concentration of formaldehyde gas is not too high in the indoor environment, it is highly toxic and carcinogenic. The formaldehyde removal potential of a novel type of green and safe nano-porous materials, Metal-Organic Frameworks (MOFs), with a high surface-to-volume ratio, strong adsorption capacity, and low regeneration temperature was investigated. To date, researchers are mainly focusing on formaldehyde selectivity and detection using MOFs in low moisture circumstances. This study carried out a series of experiments to compare breakthrough curves of formaldehyde dynamic adsorption on MIL-100(Fe), MIL-160(Al), and aluminum fumarate with activated carbon. In experiments, the formaldehyde was evaporated from diluted formalin solution, dried to 30±5 % RH, and driven through different adsorbents by nitrogen. The results indicated that MOFs showed great potential for indoor air formaldehyde removal.

1. Introduction

People spent roughly 90% of their time indoors in the 1960s [1] and tended to spend more time inside buildings with the process of urbanization. Especially during the COVID-19 pandemic, half of the world's population is under lockdown and works remotely [2]. Hence, the indoor environment quality plays a non-negligible role in people's modern life. Sick-building syndrome (SBS) occurs more frequently after long-term exposure to airtight and energy-efficient buildings[3]. More strict standards on airtightness performance are implemented worldwide [4] to accomplish the energy-saving buildings, leading to less air infiltration in buildings. To compensate for this amount of reduced natural ventilation, mechanical ventilation is needed to supply sufficient fresh air at the inevitable cost of energy consumption. Therefore, when mechanical ventilation is not used in buildings, the air changes per hour (ACH) declines, resulting in the accumulation of indoor pollutants. Many indoor air contaminants could be significant causes of SBS, comprised of volatile organic compounds (VOCs), dust/fibers, bioaerosols, entrapped outdoor sources, and contaminants generated by human activity[3].

As one of the common indoor VOCs, formaldehyde is released continually from the products processed with formaldehyde-based resins, such as furniture, artificial boards, carpets, clothing, and even the wall with paintings. Furthermore, formaldehyde is also an ingredient of numerous consumable household products, such as cosmetics, dishwashing liquids, carpet cleaners, shoe-care agents, fabric softeners, glues and adhesives, lacquers, antiseptics, and even medicines. Moreover, formaldehyde is classified as a human carcinogen. For example, short-term exposure to formaldehyde can irritate various body parts, and sustained exposure can possibly lead to nasopharyngeal cancer, leukemia, and asthma.[5] Three approaches to control indoor formaldehyde concentration are pollutant source control, ventilation, and introducing pollutant sink. Due to the ubiquitous existence of formaldehyde in the air, ventilation is the most used manner to lower the formaldehyde concentration. However, when sufficient ventilation cannot be guaranteed within the residence, introducing a pollutant sink is a meaningful way to remove the accumulated formaldehyde.

Activated carbon, clay, alumina, and zeolite are widely applied nano-porous materials to control the indoor formaldehyde concentration. However, their regeneration temperature usually is very high (>100 °C). In this situation, a new type of porous material, Metal-Organic Frameworks (MOFs), comes into view. The MOFs are constructed by forming strong-chemical bonds to bridge inorganic metal-related units with organic ligands, thus, creating open frameworks with ordered structures [6]. Due to the tunable structure and functional groups, many MOFs have a high surface-to-volume ratio, strong adsorption capacity, and low regeneration temperature. These characteristics give competitive advantages to MOFs over mentioned traditional materials. Furthermore, some applications of MOFs desiccants, like MOF-based precise humidity control material (MOF-PHCM), have been investigated to control indoor moisture[6]. Some MOFs' VOCs adsorption performance has been tested, such as cyclohexane adsorption by HSKUST-1 and zeolite ZSM-5 (ZSM = Zeolite Socony Mobil), benzene adsorption by HSKUST-1 and ZSM-5/HKUST-1 foam material, and toluene adsorption by HSKUST-1 and MIL-101. However, the concentration of tested toxic gases [7] is much higher than general residential indoor pollutants. Herein, some MOF materials were used to investigate the formaldehyde removal potential via physical adsorption.

2. Material and methods

The 4% formaldehyde aqueous solution, buffered, was diluted to 1/50 and then used as a formaldehyde source. Some absorbents such as MIL-100(Fe), MIL-160(Al), aluminum fumarate, and activated carbon were employed as formaldehyde sink in the experiments. The experiments were implemented at room temperature and atmospheric pressure. The Multi-gas Monitor Type 1302 with optical filter UA 0987 (toluene as the reference gas) was employed to monitor the total volatile organic compounds (TVOCs) concentration. The instrument was calibrated by nitrogen gas to set the zero point. The interference from water vapor is compensated by the automatic compensation function and the monitored pure water vapor TVOCs concentration . As shown in Figure 1, nitrogen was used as the carrier gas to evaporate the formaldehyde gas from the solution. A regulator controlled the outlet nitrogen gas at 1 bar, and the nitrogen flow was adjusted by the nitrogen flow meter at 1.2±0.2 L/min. The formaldehyde outflow of the washing bottle was driven through a drying barrel filled with calcium chloride to control the relative humidity to 30±5 %. 0.5±0.05 g tested sample powder was filled in the sample barrels. The formaldehyde concentration and absolute humidity of the flow were monitored at the inlet and the outlet of the sample barrels via Multi-gas Monitor Type 1302. After a 1-hour test, the sample powder was regenerated in a 105 °C oven, and after the temperature cooled down to room temperature, the sample barrels were reassembled.

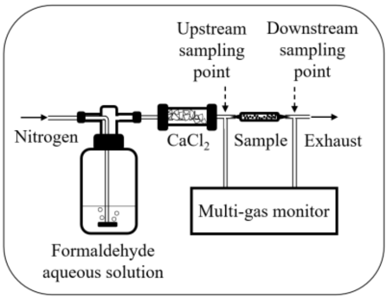


Figure 1. Experimental schematic diagram.

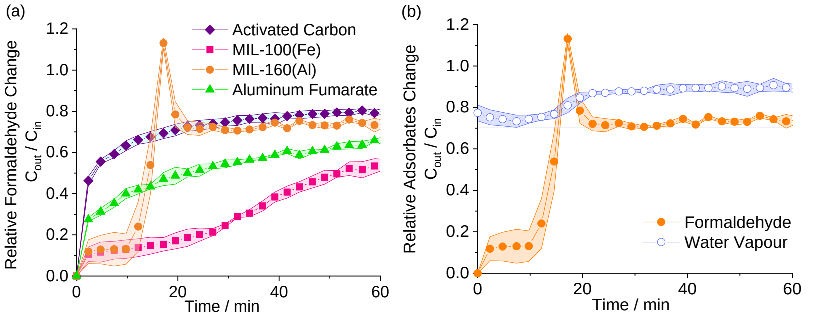


Figure 2. (a) Breakthrough curves of formaldehyde on different materials. (b) The breakthrough curve of formaldehyde and water vapor on MIL-160 (Al).

3. Results and discussions

The formaldehyde adsorption performance on different materials is presented in relative formaldehyde concentration in Figure 2 (a), which refers to the ratio of formaldehyde concentration at outlet and inlet.

During the first hour of adsorption, MIL-100(Fe) and aluminum fumarate showed higher formaldehyde harvest potential than activated carbon. The two stages of the MIL-100(Fe) breakthrough curve could be explained by two types of different cage sizes, whose diameter is 25Å with 4.7-5.5Å windows and 29Å with 8.6Å windows[8], respectively. This may explain that the smaller cages are gradually filled with formaldehyde molecules from 20 min to 55 min.

Figure 2 (b) reveals relative moisture change and formaldehyde concentration ratio during the MIL-160(Al) adsorption process. It is worth noticing that the formaldehyde breakthrough curve of MIL-160(Al) presents a roll-up effect (Figure 2 (b)), which was also observed in the binary adsorption on activated carbon[9], and the mixture adsorption on MOF-199(Cu) due to different molecular diffusion rate in pores structure [10]. MIL-160(Al) adsorbs water vapor under low RH (below 20%) [11]. The relative moisture change between outlet and inlet reached 76±2 % during the first 15 min and then increases to 89±1% within a short time. As the water vapor harvesting rate drops down, which is shown as an increase on the water vapor breakthrough curve in Figure 2 (b), the formaldehyde breakthrough curve of MIL-160(Al) goes up to 1. The adsorbed formaldehyde is eluted from the material corresponding to the concentration ratio points larger than 1 on the curve. It seems that water and formaldehyde molecules acted as competitive guests due to their similar molecular size and polarity . As the adsorption progresses , water molecules can substitute formaldehyde molecules because of the weaker intermolecular force.

4. Conclusions

In this preliminary experimental research, MOFs showed great potential for formaldehyde removal in indoor pollutants levels. Under the experimental conditions, 30±5 % RH and room temperature, the competitive adsorption of formaldehyde and moisture was observed on some MOFs. Formaldehyde adsorption stability and formaldehyde adsorption isotherm of three MOFs used in experiments is remained to be investigated further. To exclude the influence of moisture on indoor formaldehyde removal, novel MOFs materials that have a high affinity for formaldehyde while less interaction with water vapor is under development.

Acknowledgments

The authors thank J F Grigoncza, N Ziersen, X Fan and M Bivolarova for the help during the tests.

Reference

[1] Hinkle L E and Murray S H 1981 Bull. New. York. *Acad. Med.* **57** 827-44

[2] Kylili A et al 2020 The role of remote working in smart cities: lessons learnt from covid-19 pandemic Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

[3] Redlich C A, Sparer J and Cullen M R 1997 *Lancet* **349** 1013-6

[4] Feng X, Qin M, Cui S and Rode C 2018 Metal-organic framework MIL-100(Fe) as a novel moisture buffer material for energy-efficient indoor humidity control, *Build. Environ.* **145** 234-242

[5] Qu M, Lu J and He R 2017 Formaldehyde from environment Formaldehyde and Cognition ed R He (Netherlands: Springer Netherlands) chapter 1 pp 1-19

[6] Zu K, Qin M and Cui S 2020 Progress and potential of metal-organic frameworks (MOFs) as novel desiccants for built environment control: A review *Renew. Sust. Energ. Rev.* **133** 110246

[7] Woellner M et al 2018 *Adv. Mater.* **30** 1704679

[8] Horcajada P et al 2007 Synthesis and catalytic properties of MIL-100(Fe), an iron(III) carboxylate with large pores *Chem. Commun.* 2820-2

[9] Qiao S and Hu X 2000 *Stud. Surf. Sci. Catal.* **128** 401-10

[10] Chevalier V et al 2019 *J. Environ. Chem. Eng.* **7** 103131

[11] Zu K and Qin M 2021 Experimental and modeling investigation of water adsorption of hydrophilic carboxylate-based MOF for indoor moisture control *Energy* **228** 120654