



A comparative study on metal organic frameworks for indoor environment application: Adsorption evaluation



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HIGHLIGHTS

- Three metal organic frameworks, MIL-101, MIL-53 and CPM-5, are used for VOCs adsorption.
- Adsorption isotherms and TGA indicates the physisorption of toluene and isobutanol on these MOFs.
- In dry air, MIL-101 shows the highest adsorption capacity for one ppm of toluene and isobutanol.
- At 30% relative humidity, MIL-53 demonstrates the highest adsorption capacity of toluene.
- CPM-5 shows the least adsorption capacity for toluene and isobutanol in both dry and humid air.

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ABSTRACT

In this study, three metal organic frameworks (MOFs), MIL-101, MIL-53 and CPM-5 are synthesized and characterized. Adsorption isotherms and breakthrough behaviors of these MOFs are studied for two volatile organic compounds: toluene and isobutanol. Also, the effect of the presence of relative humidity on the adsorption capacity of one (1) ppm toluene and isobutanol on each MOF is investigated. Results demonstrate a superior capacity of MIL-101 for adsorption of these organic compounds in dry air. The presence of relative humidity (30%), however, decreases this adsorption capacity by 80%. MIL-53 shows the highest adsorption capacity of toluene and isobutanol at this level of humidity, while CPM-5 shows the least adsorption capacity for both toluene and isobutanol at both dry and humid air.

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1. Introduction

Volatile organic compounds (VOCs) are a group of biogenic and/or anthropogenic compounds that are emitted from several sources in indoor environment [1,2]. The negative effect of these compounds is proven for various health problems [3–5]. To eliminate VOCs from indoor environment, different physical and chemical

methods have been developed. For instance, adsorption is a physical phenomenon in which the removal of VOCs is performed in the presence of an appropriate adsorbent like activated carbon (AC) and zeolites [6–9]. Photocatalytic oxidation (PCO) and non-thermal plasma (NTP) methods, on the other hand, are two proposed chemical methods for the removal of VOCs from indoor air environment [10,11].

Although the ability of VOCs degradation using chemical techniques provides many advantages compared to adsorption, the application of chemical techniques alone in indoor environment is not cost effective due to very low concentration of VOCs [12]. Therefore, developing reactive adsorption processes has become a new approach to improve VOCs removal efficiency of air purification systems [13]. In a reactive adsorption process, a combination of chemical reactions coupled with the adsorption process is performed simultaneously, in a single unit operation [12,14].

Abbreviations: AC, activated carbon; BDDT, Brunauer, Deming, Deming, and Teller; BET, Brunauer-Emmett-Teller; CPM-5, crystalline porous material; DFA/C, dual functional adsorbent/catalyst; DMF, dimethylformamide; DVS, dynamic vapor sorption; DW, distilled water; MIL-101, Materials of Institute Lavoisier-101; MIL-53, Materials of Institute Lavoisier-53; MOF, metal organic framework; MW, microwave; NTP, non-thermal plasma; PCO, photocatalytic oxidation; RH, relative humidity; TGA, thermo-gravimetric analysis; VOC, Volatile organic compound; XRD, X-ray diffraction.

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Utilizing such an adsorber-reactor is not only favorable from an economic point of view, but it is also advantageous due to higher removal efficiency of the reactor [12].

When a reactive adsorption process is considered for indoor air treatment, selecting an appropriate dual functional adsorbent/catalyst (DFA/C) becomes a challenge. This is because the employed DFA/C should not only possess high oxidation capability, but it should also have a high adsorption capacity. Furthermore, due to the presence of humidity in the indoor environment and the competition between VOCs and water molecules for adsorption on DFA/C, hydrophobicity of the media is a crucial factor, especially at very low levels of VOCs (ppb range) [15]. Another important aspect in selecting an appropriate DFA/C is the ability to regenerate the DFA/C after being saturated with adsorbate. Therefore, sorption of VOCs should be physisorption rather than chemisorption. Surface area, pore size and availability of pores are other determining factors in adsorbent efficiency [16]. Due to the structural and chemical diversities of VOCs, finding a suitable DFA/C with the ability of adsorbing and degrading these compounds is a challenging issue.

Hydrophobic zeolites are highly crystalline materials with extremely uniform frameworks [17,18]. These properties, along

with their stable structure in the presence of humidity, make zeolites excellent DFA/Cs. However, the hardly tunable and relatively small size of zeolite micropores (<2 nm) inhibit their application for removal of large size VOCs [19].

Metal organic frameworks (MOFs), on the other hand, are a new class of porous materials with large pore volume and uniform structures [20,21]. These materials possess a diverse structure, high to extra high porosity and surface area, tunable pore size, and very low density of framework [22,23]. The flexible framework of these porous materials causes some unusual patterns in their adsorption isotherms for small inorganic molecules (i.e., H₂O, N₂, O₂, Ar, CO₂, CH₄), as well as larger organic compounds (i.e., ethylene oxide, acetonitrile, benzene, xylene isomers, tetrahydrothiophene, cyclohexane and thiophene etc.) [24,25]. Furthermore, high adsorption capacity, fast kinetics and high reversibility of MOFs suggest that these materials can be applied as DFA/Cs in a reactive adsorption process [26]. Thus far, the application of MOFs has been studied in many areas including catalysis, ion exchange, gas storage, molecular sieves, size-selective separation, etc. [27–30]. Several studies have also reported adsorption of some VOCs on MOFs [20,31–33]. However, very few have discussed the effect of relative humidity (RH) on the adsorption behavior of

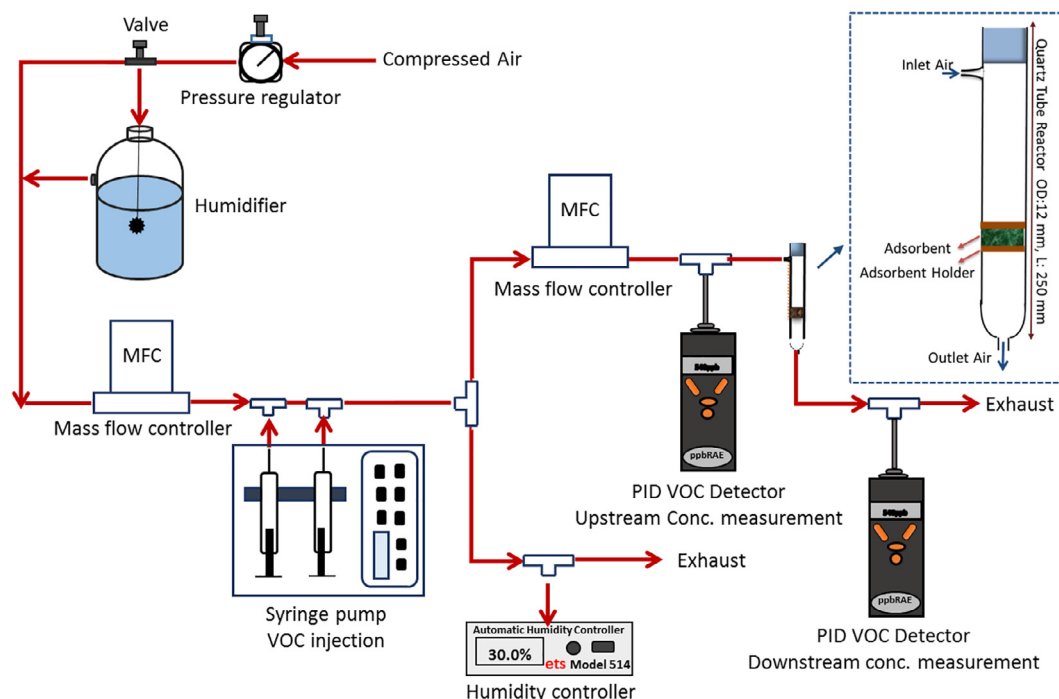


Fig. 1. Schematic diagram of the adsorption apparatus.

Table 1
Some physicochemical properties of the selected VOCs.

Compound	Supplier	Category	Formula	Molar mass (g/mol)	Boiling point (°C)	Polarity	Kinetic diameter (Å)	Dipolar moment (D)
Toluene	Fisher Scientific 99.9%	Aromatic	C ₇ H ₈	92.14	110.6	Non-polar	5.8	0.36
Isobutanol	Fisher Scientific 99.9%	Alcohol	C ₄ H ₁₀ O	74.12	80.2	Polar	5.4	1.79

Table 2
Experimental parameters of the adsorption tests.

Compound	Concentration (ppm)	Flow rate (mL min ⁻¹)	Temperature (°C)	Relative humidity (%)
Toluene	1	600 ± 2%	23 ± 1	0 and 30% ± 1
Isobutanol	1	600 ± 2%	23 ± 1	0 and 30% ± 1

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