



Mitigating the relative humidity effects on the simultaneous removal of VOCs and PM_{2.5} of a metal–organic framework coated electret filter

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ABSTRACT

An electret filter media coated with highly porous metal–organic framework (MOF, i.e., MIL-125-NH₂ in this work) particles, called E-MOFilter, has been developed to remove fine particulate matters (PM_{2.5}, particulate matter less than 2.5 μm in diameter) and volatile organic compounds (VOCs, e.g., toluene) simultaneously. However, its adsorption efficiency and capacity of toluene was deteriorated at an elevated relative humidity (RH). This was due to the hydrophilic nature of MIL-125-NH₂ leading to competitive adsorption between toluene and water molecules. To address this issue, five modification methods were conducted to alter MIL-125-NH₂ from inherent hydrophilic into hydrophobic, which included the internal (alkylation method), external (coating with polydimethylsiloxane, PDMS), combined (alkylation plus PDMS coating), polyvinylpyrrolidone (PVP) surfactant, and N-coordination modifications. The new E-MOFilters were fabricated based on these modified MIL-125-NH₂ and then systematically compared for their toluene adsorption efficiency and capacity under various RH levels (from 10, 30, 40, 50 to 60%). In addition to toluene, the PM removal efficiency and PM_{2.5} holding capacity by the modified E-MOFilters were also evaluated. The toluene adsorption results revealed the PDMS-coated E-MOFilter outperformed all other modifications. The PM removal ability were retained for all modified E-MOFilters indicating the charge and structure of the electret media were not altered. This study is the first to combine the MOFs with electret filter media for a low pressure drop and simultaneous removal of PM and toluene under different RHs. The effectiveness and performance towards toluene adsorption under elevated RH conditions for E-MOFilters with various modifications were comprehensively evaluated and discussed.

1. Introduction

Indoor air quality (IAQ) has been becoming a major concern worldwide because statistical data showed that the indoor concentrations of gas pollutants, e.g., volatile organic compounds (VOCs) and particulate matters (PMs) are often 2–5 times higher than that of outdoors [1,2]. Especially, people spend 87% of their time indoors and increasing to more than 90% during COVID-19 pandemic [3–6]. The high concentration of these indoor air pollutants is mainly due to the reduced air change rate for the design of energy-efficient building construction and the increased usage of furnishings, glues, paints, furnaces, etc., leading to outgassing and particle emission [2]. Prolonged exposure to these pollutants can cause acute and chronic effects on respiratory and central nervous systems [7–10]. Therefore, it is urgent to effectively remove PMs and VOCs to improve the indoor air quality.

To mitigate indoor PMs, electret filters, with quasi-permanent electrical charges on the fibers have been widely used in the heating,

ventilation, and air conditioning (HVAC) systems and indoor air purifiers, which show a high initial PMs filtration efficiency and a much lower pressure drop (ΔP) compared to the mechanical filters [11]. To remove VOCs, gas adsorbents, e.g., activated carbon (AC) and zeolites, are usually used because of their high efficiency and relatively low price. However, low selectivity and weak affinity to polar pollutants of these adsorbents are of a great concern [12,20]. In addition to these common adsorbents, the metal–organic frameworks (MOFs), a type of novel porous materials, have been receiving increased attention due to their large surface area, tailorable particle size and tunable functionality, making them promising candidates for capturing gaseous pollutants [13–15]. To simultaneously remove PMs and VOCs, the MIL-125-NH₂ MOF was synthesized and successfully integrated into a commercially available electret filter with a minimum efficiency reporting value of 13 (MERV 13), named E-MOFilter [16]. This E-MOFilter demonstrated a low pressure drop (less than 15 Pa at 5 cm s^{−1} face velocity) and a high removal efficiency (~90%) for both PMs and toluene (C₆H₅CH₃) under a

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relative humidity (RH) less than 30%. However, the adsorption efficiency of toluene reduces with increasing RH levels [17–20]. This RH effect on VOC adsorption degradation is commonly seen in many traditional adsorbents, including AC and zeolites [21]. Because under high RH conditions the adsorption sites of the adsorbents are competitively occupied by the water molecules. This adverse RH effect is more significant for hydrophilic adsorbents, such as MIL-125-NH₂ where the adsorption sites have stronger affinity to water molecules than the less polar VOC molecules [22]. To address this issue [23], the adsorbents are often modified to increase their hydrophobicity to repel water molecules [20,24–30]. The water contact angle (WCA) tests are usually conducted to evaluate the hydrophobicity of the adsorbents. Typically, a WCA less than 90°, within 90°–150° and larger than 150° is considered to be hydrophilic, hydrophobic, and superhydrophobic, respectively [24].

The modifications can be categorized into three major methods, including internal, external and others. Internal modifications usually involve the reactions of ligand or metal cluster functionalization at the molecular level [24–27]. External modification is completely different, where a layer of hydrophobic materials is coated on the surface of adsorbents [19,28–31]. Other modifications mainly involve adding surfactants or nitrogenous compounds into the solution during MOFs synthesis [18,32–34]. The fundamental mechanisms, advantages and disadvantages of these modifications are compared in Table S1 of SI A (Synthesis and modification of MOFs). Besides, the details of these modifications are discussed in SI A. Basically, there exists an inherent tradeoff between the increase of hydrophobicity of MOFs for the water resistance and a reduction of surface area of MOFs due to the modification. Thus, it is important to conduct these modifications systematically to find the optimal condition and to compare their effectiveness on minimizing the RH effects.

In this study, the MIL-125-NH₂ MOF was synthesized and modified to increase its hydrophobicity in order to mitigate the adverse effects of RH on the removal efficiency towards toluene, a representative indoor VOC. Several modification methods, i.e., internal (alkylation method), external (PDMS-coating method), combined (alkylation plus PDMS-coating method), and other modifications (PVP and N-coordination methods) were conducted. The modified MIL-125-NH₂ MOFs were then transported to MERV13 electret filter media to form modified E-MOFilters. Systematic evaluations on the toluene removal efficiency by the original and modified E-MOFilters under different RHs (10–60%) were conducted. This study aims to compare and report the effectiveness of different modifications on mitigating the RH effects for both initial removal efficiency and adsorption capacity of toluene. As a simultaneous gas-particle removal filter, the modified E-MOFilters were also examined for their PM removal efficiency and PM_{2.5} (particulate matter less than 2.5 µm in diameter) holding capacity to confirm the modifications would not cause any degradation for PM removal performances. The ultimate goal of this study is to demonstrate the modified E-MOFilters not only have a high PMs filtration performance, but also an enhanced efficiency and adsorption capacity for toluene under elevated RH conditions.

2. Experimental

2.1. Modification of MOF MIL-125-NH₂ particles

MIL-125-NH₂ was synthesized according to our previous report [16] and the procedure is described in SI A. Then, the original MOFs MIL-125-NH₂ were undertaken alkylation, PDMS, surfactant and N-coordination modifications to obtain the modified MOFs.

For the alkylation modification, the MIL-125-NH₂ was grafted with long alkyl chains to yield MIL-125-R7 by following the procedures published elsewhere [25]. Briefly, the prepared MIL-125-NH₂ (49 mg) was activated at 200 °C for 2 h in air before the further modification. Then the MOF was dispersed in 5.0 mL of acetonitrile, to which 40 equivalent of n-octanoic anhydride was then added. The suspension was

stirred for 24 h at 80 °C. The final product was washed by CH₂Cl₂ three times.

In the PDMS coating method, a fresh PDMS stamp was placed inside a 100 mm glass petri dish [30] on the top with MIL-125-NH₂ particles uniformly spread on the bottom. The above glass petri dish containing both PDMS and MIL-125-NH₂ was sealed and kept in the oven at 235 °C for 6 h and then cooled down to room temperature [31,35]. The obtained products are named as PDMS@MIL-125-NH₂ and PDMS@MIL-125-R7 (combination of internal and external modification). It should be noted that the mass ratios of PDMS stamps to MOF particles were set from 3:1 to 400:1, for different coating amounts of PDMS on MOFs. The Energy Dispersive X-Ray (EDX, HITACHI SU-70, HITACHI Corp., Tokyo, Japan) analysis was conducted to determine the atomic ratio of Si and Ti and quantify the PDMS coated on the MOFs.

The PVP surfactant modification (MIL-125-NH₂/PVP) and N-coordination method (MIL-125-NH₂/N_x) were conducted according to Zhang et al. [18] and Hu et al. [34], respectively. Noteworthy, in addition to MIL-125-NH₂, the inherent hydrophobic MOF ZIF-8 was also synthesized for comparison [36]. The modification and synthesis procedures of these three MOFs are discussed in SI A.

2.2. Electret filter media and modified E-MOFilter

The 50 mm diameter flat sheets of the MERV 13 electret filter media were used for the deposition of modified (hydrophobicity) MOF particles to form modified E-MOFilter for the PM_{2.5} and toluene removal tests. Table S2 of SI B. (Specifications of the MERV 13) summarizes the specifications of the MERV 13. The experimental setup and parameters for the MOF coating onto electret filter media can be found in our previous work [16,37–39]. The coating level of differently modified MOFs was controlled at 10 wt% (MOFs/media). Two layers of MERV 13 flat sheet were used to enhance the removal efficiency of both PM_{2.5} and toluene. In total, there were seven kinds of E-MOFilters fabricated and tested, which were coated with MIL-125-NH₂, MIL-125-R7, PDMS@MIL-125-NH₂, PDMS@MIL-125-R7, MIL-125-NH₂/PVP, MIL-125-NH₂/N_x and ZIF-8 MOFs.

2.3. Characterization of MOF particles and E-MOFilters

The scanning electron microscopy (SEM, HITACHI SU-70, HITACHI Corp., Tokyo, Japan), x-ray diffraction (XRD, PANalytical X'Pert Pro, Malvern PANalytical Ltd., Malvern, UK) and fourier transform infrared spectroscopy (FT-IR, Nicolet iS50, Thermo Fisher Scientific, Waltham, MA), optical contact angle goniometer (OCA 15 goniometer, Data-Physics Instruments Corp., Charlotte, NC) were utilized to characterize the size and morphology, crystal structure, surface chemistry and WCA, respectively, of the modified MOF particles. The energy dispersive x-ray (EDX, HITACHI SU-70, HITACHI Corp., Tokyo, Japan) analysis were conducted to determine the atomic ratio of Si and Ti to confirm the quantity of PDMS coated on the MOFs. Besides, nitrogen adsorption-desorption isotherms were collected using a gas sorption analyzer (Autosorb iQ, Quantachrome Instruments Corp., Boynton Beach, FL) at 77 K to characterize the pore size distribution and Brunauer-Emmett-Teller (BET) surface area. The SEM analysis was also conducted for the modified E-MOFilters to evaluate if the MOF particles were coated uniformly on the filters.

2.4. Initial efficiency and holding capacity of modified E-MOFilters for PMs

After the characterization of the modified MOFs and E-MOFilters, the E-MOFilters were evaluated for their performance of PM and VOC removal under different test conditions. Table S3 of SI C. (Test conditions for the modified E-MOFilters against PM and VOC) summarizes the test conditions for the E-MOFilters against PM and VOC. Basically, the filtration face velocity for the PM tests was 5 cm s⁻¹. As demonstrated in

our previous work [16], the order of the PM filtration and VOCs removal tests would not cause different results. Therefore, this study conducted the PM initial efficiency and PM aging (size distribution close to ambient $PM_{2.5}$) tests first followed by the VOC removal and adsorption tests. The details of experiments for conducting PM removal performance tests and methods to determine the PM initial removal efficiency and holding capacity of E-MOFilters can be found elsewhere [11,16,40–44].

2.5. RH effects on the initial efficiency and adsorption capacity of the E-MOFilter for toluene

Toluene, a common and representative harmful indoor VOC, was selected to challenge the E-MOFilters [45–50]. Fig. 1 shows the experimental setup for investigating the RH effects on the toluene adsorption of the E-MOFilter. Different RHs were controlled by adjusting the flow rates of the compressed air ($\sim 5\%$ RH) and the water mists generated by the single jet atomizer (Model 9302, TSI Inc., Shoreview, MN). The toluene removal efficiency at 10% RH was first measured and the results were treated as dry condition and the baseline for examining the efficiency degradation at elevated RH values. The RH was raised to 30, 40, 50 and 60% and then followed by the efficiency measurement. Two face velocities, 0.5 and 5 $cm\ s^{-1}$, were applied to investigate their toluene removal efficiency. 5 $cm\ s^{-1}$ is commonly used in an HVAC application (velocity in pleated media) and 0.5 $cm\ s^{-1}$, a fairly low face velocity, is to simulate the relatively static flow condition that was often seen in the literature [51]. The toluene with 5 ppm concentration was prepared by adjusting the air and toluene flow rates via the mass flow controller (MFC, MKS Instruments Inc., Andover, MA) and confirmed by a gas chromatography (GC, Agilent 7890B, Agilent Technologies Inc., Santa Clara, CA) equipped with a flame ionization detector (FID, Agilent Technologies Inc., Santa Clara, CA) to challenge the E-MOFilters. The toluene removal efficiency, $\eta\%$, was calculated from the measured upstream (C_{up} , through the dummy holder) and downstream (C_{down} , through the filter holder) toluene concentration of the E-MOFilter as:

$$\eta\% = \left(1 - \frac{C_{down}}{C_{up}}\right) \times 100\% \quad (1)$$

When the toluene flow continued passing the E-MOFilter, the breakthrough curve, or the adsorption capacity, was determined. To obtain the representative results, measurements for both toluene and PM removal efficiency were repeated at least four times.

3. Results and discussion

3.1. Characterization of MOF particles

Fig. 2 summarizes the SEM images, XRD patterns, N_2 adsorption isotherms and FT-IR spectra for both original and modified MIL-125-NH₂ MOF particles. Fig. 2 (a)–(d) show the SEM images and WCAs of original MIL-125-NH₂, MIL-125-R7 (alkylated MIL-125-NH₂),

PDMS@MIL-125-NH₂ (PDMS-coated MIL-125-NH₂), and PDMS@MIL-125-R7 (alkylated and PDMS-coated MIL-125-NH₂) MOFs, respectively. The modified MIL-125-NH₂ particles have an almost identical tetragonal plate morphology as the original MOFs [49,52]. Besides, the WCAs were found to be 0°, 131.5°, 155.5° and 151.5° for the four MOFs, respectively. The SEM images and WCAs of other modified MOFs are shown in Fig. S1 of SI D. (Physical and chemical characterizations for other modified MOFs). According to the WCA results, the original MIL-125-NH₂ MOF was hydrophilic, and the PDMS-coated samples showed the best hydrophobicity amongst all modified MOFs, which should be a desired modification method for the current MIL-125-NH₂ as it was relatively simple and straightforward.

The mass ratio of PDMS to MIL-125-NH₂ was evaluated by determining the atomic ratios of Si/Ti using EDX, where Si and Ti were from PDMS and MIL-125-NH₂, respectively. As shown in Fig. S2 and SI D, the atomic ratios of Si/Ti were from 0.1 to 1.23, corresponding to the counterpart mass ratio of PDMS to MOF particles as desired. With various amounts of PDMS coating, the PDMS@MIL-125-NH₂ with a Si/Ti ratio of 0.43 and PDMS@MIL-125-R7 with a Si/Ti ratio of 0.22 showed the best toluene removal efficiency as compared to other ratios.

The XRD patterns of original MIL-125-NH₂, MIL-125-R7, PDMS@MIL-125-NH₂ and PDMS@MIL-125-R7 are shown in Fig. 2 (e) and that of other modified MOFs (not performing as well as aforementioned MOFs) are shown in Fig. S3. In Fig. 2 (e), it is seen the alkylated and PDMS-treated MOFs maintained their original crystal structures of MIL-125-NH₂. Similar results were also seen in the analysis of other modified MOFs (Fig. S3). It is concluded here that the crystal structure remained unchanged after the modification.

The FT-IR spectra shown in Fig. 2 (f) confirm that the major functional groups of modified MIL-125-NH₂ remained unchanged from the original MIL-125-NH₂ but some new peaks appeared. For MIL-125-R7, a new small peak at 3400–3500 cm^{-1} ascribed to the symmetric stretching vibration of the amino group disappeared after MIL-125-NH₂ was post-treated with n-octanoic anhydrides, indicating that the N-H band was replaced by other functional groups. A new small peak appeared at 1690 cm^{-1} due to the C=O stretching vibrations of the amide group [20], confirming the reaction between the amino group and anhydrides. For PDMS@MIL-125-NH₂, the appearing of peak at 1020–1074 cm^{-1} was assigned to the stretching mode of Si-O-Si bond [53], which can be a confirmation of a PDMS film coated on the external surface MOFs. To be noted, the Si/Ti here is 0.43, which is a relatively high ratio and thus the vibrations of Si-O-Si can be observed clearly. In comparison, there was a lower Si/Ti (0.22) for PDMS@MIL-125-R7, thus the absence of a peak appearing at 1690 cm^{-1} should be attributed to the low Si/Ti. This result was in agreement with that found by Zheng et al. [20] where no peak was seen at Si/Al = 0.2.

Fig. 2 (g) shows the N_2 adsorption/desorption isotherms of MIL-125-NH₂ and modified MIL-125-NH₂ MOFs. As expected, both original MIL-125-NH₂ and the modified MOFs exhibited type I adsorption isotherms at 77 K with no obvious hysteresis, which verified their microporous

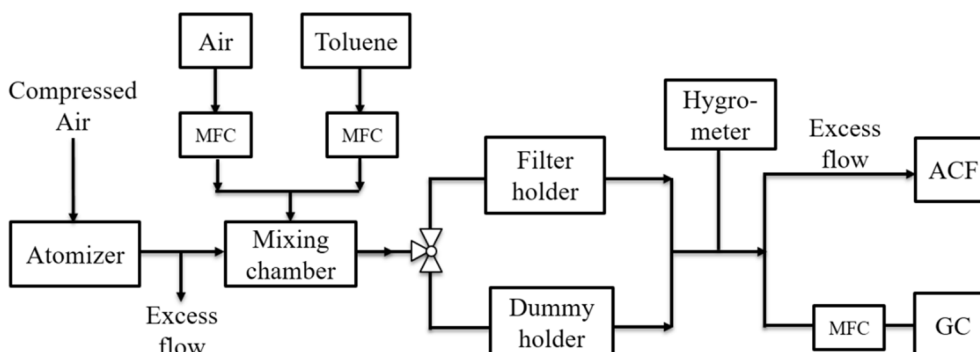


Fig. 1. Experimental setup for the initial removal efficiency and adsorption capacity of toluene by the E-MOFilters under different RHs.

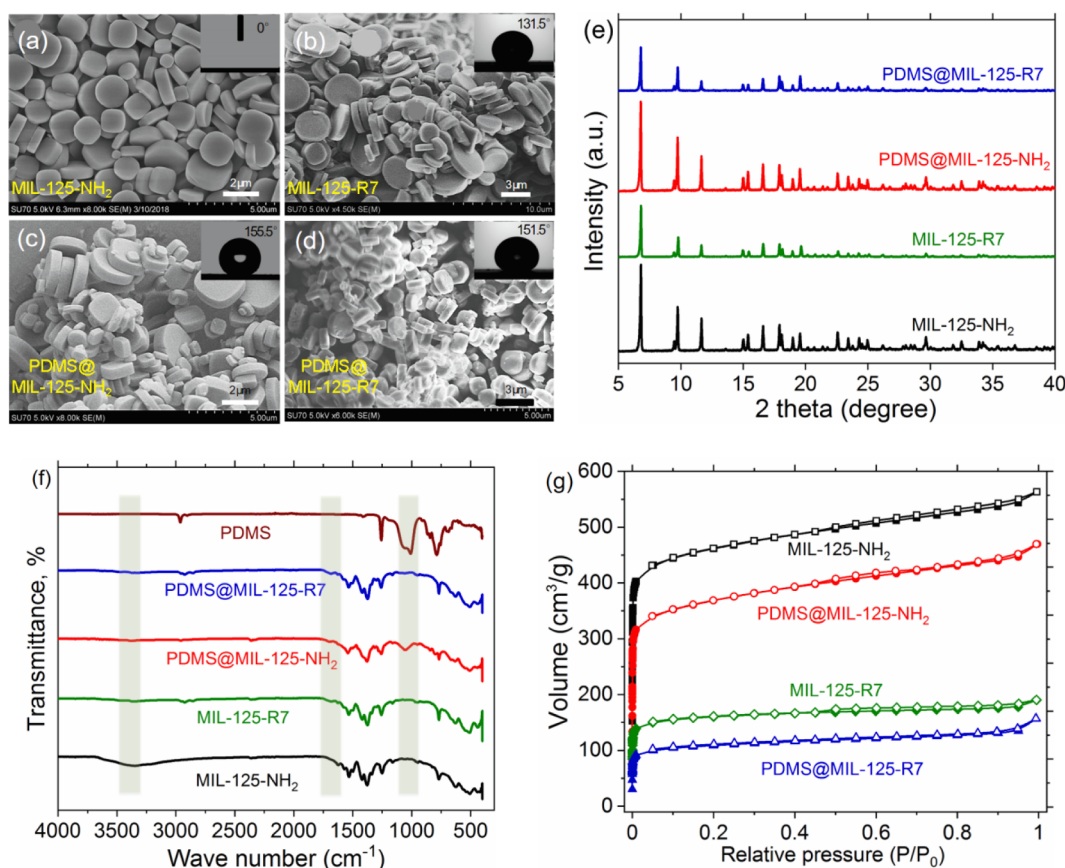


Fig. 2. Comparison of SEM images and WCAs (a: MIL-125-NH₂, b: MIL-125-R7, c: PDMS@MIL-125-NH₂, d: PDMS@MIL-125-R7), XRD patterns (e), FT-IR spectra (f) N₂ adsorption isotherms (g) between original and modified MIL-125-NH₂.

structure [49]. The BET specific surface area (SSA) and micropore volume of all modified MIL-125-NH₂ MOFs are summarized in Table 1. The SSA had an order of MIL-125-NH₂ > PDMS@MIL-125-NH₂ > MIL-125-R7 > PDMS@MIL-125-R7, which illustrated that PDMS@MIL-125-NH₂ has the largest SSA and micropore volume amongst the modified MOF. In addition, the results also indicated that both internal and external surface modification reduced the SSA and pore volume of MIL-125-NH₂ to some extent. That was because the pores were partially occupied by the long alkyl chains for the MIL-125-R7 [25] and PDMS would cover some of pores of MOFs, and the more PDMS coating there were lower

SSA, as shown in Fig. S4 and Table S4. For PDMS@MIL-125-R7, two factors as aforementioned, i.e., alkyl groups blockage and PDMS-coating, synergistically led to a significant decrease of its SSA and micropore volume. Therefore, based on the analysis above, it is of great importance to find out an optimal Si/Ti to not only enhance the hydrophobicity of PDMS-coated MOFs but also retain the toluene adsorption performance under humid conditions. In addition to SSA and micropore volume, the peak pore size of the PDMS@MIL-125-NH₂ were found to be 0.75 nm independent on Ti/Si as shown in Table S4. This value was in good agreement with that reported by Kim et al. [49]. The kinetic diameter of the toluene molecule is 5.85 Å (or 0.585 nm) [54–56], which is expected to be easily captured by the PDMS@MIL-125-NH₂ particles due to their suitable pore to molecule diameter ratio.

According to the results of WCA and BET analysis, the WCAs of PDMS coated MOFs remained ~ 150° without strong correlation of PDMS coating amount in the ranges of 0.1–1.23 of Si/Ti. However, SSA and micropore volume of PDMS coated MOFs exhibited a significant reduction with increasing PDMS coating as shown in Table S4 of SI D. In this study, it is found both PDMS@MIL-125-NH₂ (Si/Ti = 0.43) and PDMS@MIL-125-R7 (Si/Ti = 0.22) had better humidity resistance and remained acceptable SSA area and micropore volume. The lower PDMS coating for the latter was to compensate its already reduced SSA due to alkylation.

3.2. Characterization of modified E-MOFilters

The modified MIL-125-NH₂ MOFs were transported to MERV13 electret filter media to fabricate modified E-MOFilters. Fig. 3 (a) shows the SEM images of the depositions of modified MIL-125-NH₂ particles on the fibers of MERV13 electret filter. It is seen that the modified MOF particles were uniformly deposited on individual fibers and in-depth of

Table 1

BET analysis of original and modified MOF powders and E-MOFilters.

	Adsorbents	BET surface area (m ² /g)	Total /Micro pore volume (cm ³ /g)	Pore diameter (nm)
Original and modified MOF powder	MIL-125-NH ₂	1871	0.837/0.667	0.78
	MIL-125-R7	771	0.379/0.223	0.72
	PDMS@ MIL-125-NH ₂	1417	0.726/0.463	0.78
	PDMS@ MIL-125-R7	561	0.263/0.155	0.72
	MIL-125-NH ₂ /PVP	1580	0.744/0.544	0.75
	MIL-125-NH ₂ /N _x	1388	0.673/0.468	0.75
	ZIF-8	1357	0.735/0.627	1.08
Original and modified E-MOFilter	MIL-125-NH ₂	320	0.149/0.114	0.78
	MIL-125-R7	206	0.089/0.073	0.72
	PDMS@ MIL-125-NH ₂	301	0.135/0.105	0.78
	PDMS@ MIL-125-R7	181	0.071/0.063	0.72

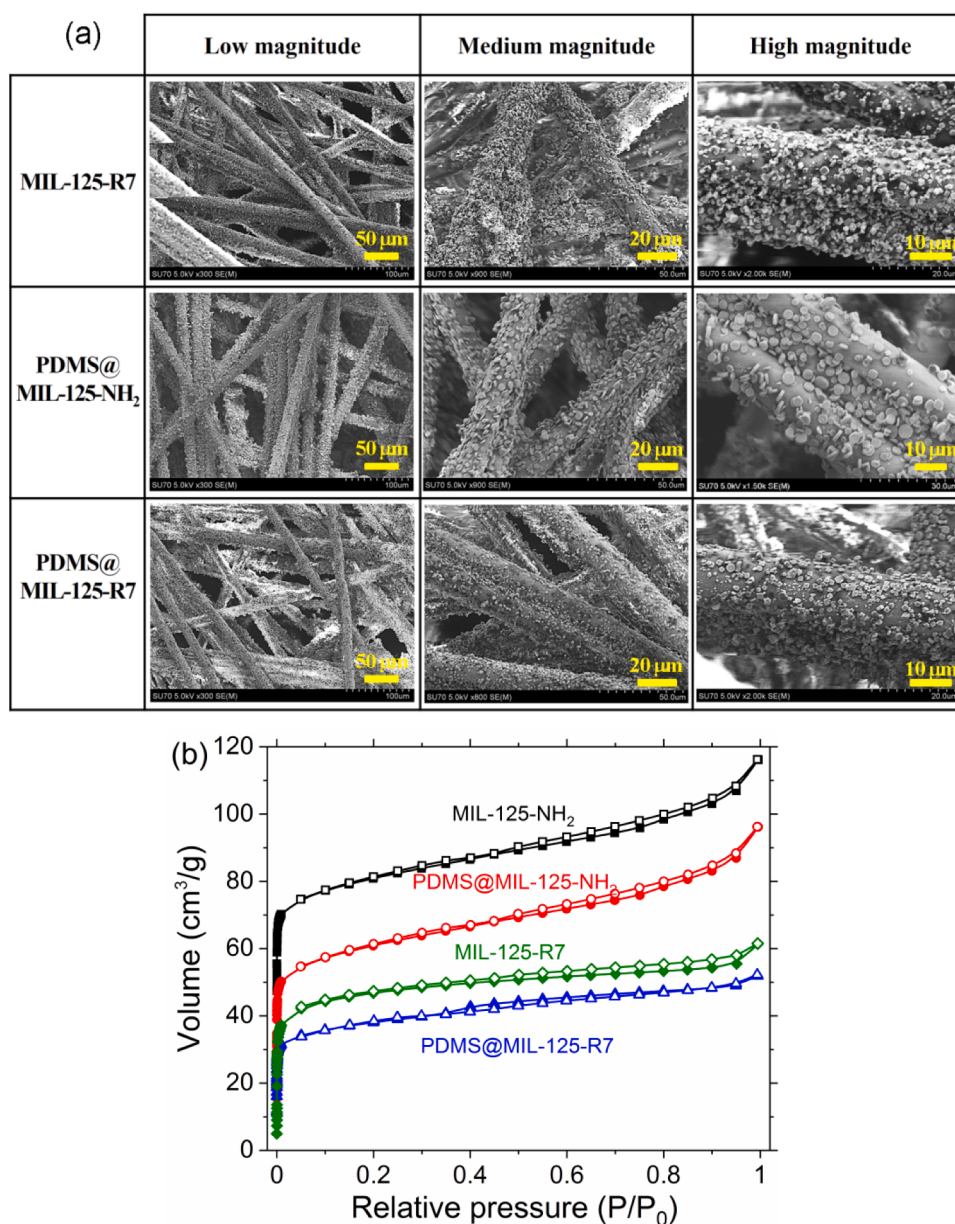


Fig. 3. SEM images of the depositions of modified MIL-125-NH₂ particles on the fibers of MERV13 electret filter (a) and N₂ adsorption isotherms of original and modified E-MOFilters (b).

the E-MOFilter, which again indicated that the liquid filtration coating method was feasible and effective in practice [16].

Fig. 3 (b) shows N₂ adsorption/desorption isotherms for the original and modified E-MOFilter. Table 1 summarizes the results of BET analysis, including SSA, pore volume, and peak pore diameter for the original and modified E-MOFilters. Compared with the MIL-125-NH₂ particles (1871 m² g⁻¹), the original E-MOFilter already had a significant SSA reduction to 320 m² g⁻¹. Nevertheless, this SSA is still higher than activated carbon fiber respirators used to protect welding workers [16]. The PDMS@MIL-125-NH₂ coated E-MOFilters has a similar SSA value compared to the original E-MOFilter. However, MIL-125-R7 and PDMS@MIL-125-R7 E-MOFilters had a SSA of only 206 and 181 m² g⁻¹, respectively. Nevertheless, they all maintain a peak pore diameter of ~0.75 nm. This is because the MIL-125-NH₂ particles rather than the coated polymers that contributed most of the microporous structures of the E-MOFilters. From above BET and SEM results, it is expected that the modified E-MOFilters would be capable of capturing toluene under different humidity due to their remained microporous structures,

successful in-depth hydrophobic MOF particles coating and acceptable SSA.

3.3. Initial efficiency of modified E-MOFilters for PMs

To investigate the effects of MOF coating (10 wt%) on the PM removal of fabricated E-MOFilters, the size-fractionated efficiencies of the MERV13 and original and modified E-MOFilters were measured (5 cm s⁻¹ face velocity) and compared. The efficiency of discharged MERV 13 (by isopropyl alcohol, IPA, vapor) was also compared to evaluate the efficiency decline due to charge degradation by the coated MOFs. As shown in Fig. 4, a decline of less than 10% of PM removal efficiency in all particle sizes was observed for the alkylated and PDMS modified E-MOFilters as compared to the original MERV 13. The substantial higher efficiency of all modified E-MOFilters than the discharged MERV 13 indicates a significant retention of fiber charges after the coating of MOFs. It is noted that the PM removal performance was not evaluated for other modified E-MOFilters due to their relatively poor VOCs

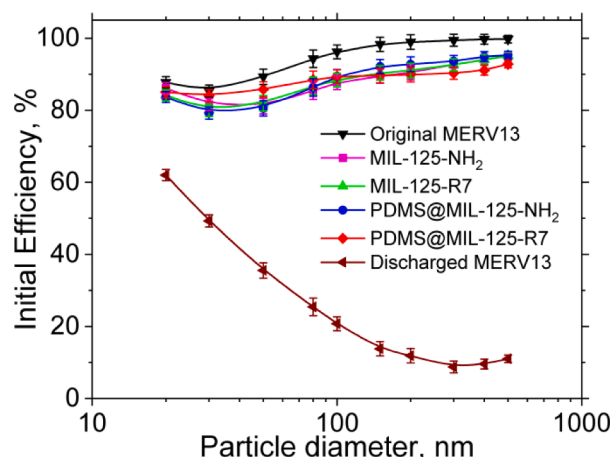


Fig. 4. Initial size-fractionated efficiency of MERV 13 E-MOFilters coated with MIL-125-NH₂, PDMS@MIL-125-NH₂, MIL-125-R7 and PDMS@MIL-125-R7 MOF particles.

removal performance compared to those shown in Fig. 4.

3.4. Performance of modified E-MOFilters on PM loading

In addition to the initial efficiency, the filtration performance of the filters over a period of operation, e.g., a few months, is of great concern. A common criterion is the PM holding capacity, i.e., the loaded PM mass versus the pressure drop growth which relates to the energy consumption in operating the filtration.

Table 2 summarizes the initial pressure drop and holding capacity of fabricated E-MOFilters. To be noted again that there were two layers of MERV 13 flat media used in each fabricated E-MOFilters. It was found that the increase of initial pressure drops was very minor with around 4 Pa for all the E-MOFilters. In the PM_{2.5} aging tests, the endpoint was set at 1.0 in-H₂O (250 Pa) and the more mass of PM_{2.5} can be collected the better the filter is. As shown in Table 2, the clean MERV 13 had the highest holding capacity (19.1 g m⁻²) and all fabricated E-MOFilters remained a decent holding capacity of ~14.2 g m⁻². Therefore, it can be concluded that, in terms of degradation of PM holding capacity, the alkylated and PDMS E-MOFilters should be acceptable. To be noted, the PM_{2.5} holding capacity tests were conducted at 30 ± 5% in this study and the RH effects on PM loading were discussed in our previous study [42].

3.5. RH effects on the initial efficiency and adsorption capacity of the E-MOFilters for toluene

3.5.1. Initial removal efficiency

In the previous section, the PM filtration performances of the modified E-MOFilters have been demonstrated to be comparable to that of the clean electret filters. In this section, the toluene removal performance will be quantitatively compared amongst different modified E-MOFilters under different RHs. Fig. 5 (a) and (b) compare the initial toluene (5 ppm) removal efficiency of original, alkylated and PDMS

Table 2

Initial pressure drops and holding capacities of fabricated E-MOFilters (2 layers of MERV13 as the substrate).

Type	Initial ΔP (Pa)	Holding capacity
MERV 13	8.8	19.1
MIL-125-NH ₂	12.5	14.3
MIL-125-R7	12.6	14.1
PDMS@ MIL-125-NH ₂	12.7	14.0
PDMS@ MIL-125-R7	12.4	14.5

coated E-MOFilters under different RH conditions (10–60%) at 5 cm s⁻¹ and 0.5 cm s⁻¹ face velocity, respectively. It is seen the initial removal efficiency was decreased with increasing RH and it was higher at reduced filtration face velocity. Under extremely dry condition of 10% RH, the efficiency of the four modified E-MOFilters was very close with an efficiency of about 80–85%. However, it is clearly seen the efficiency of original E-MOFilters (MIL-125-NH₂) decreases dramatically with increasing RH, especially when RH is higher than 30%, indicating the MIL-125-NH₂ does need a hydrophobic modification. At elevated RHs, the toluene removal efficiency had an order of PDMS@MIL-125-NH₂ > PDMS@MIL-125-R7 > MIL-125-R7 > MIL-125-NH₂. This is consistent with the order of the measured WCAs. However, from the results tested at 50 and 60% RH, only the PDMS@MIL-125-NH₂ could remain a fairly good initial toluene removal efficiency (56% and 41%, respectively). Its better toluene removal was attributed to its superhydrophobicity and larger surface area compared with the PDMS@MIL-125-R7 and MIL-125-R7.

In Fig. 5 (b), it is seen the initial toluene removal efficiency under 0.5 cm s⁻¹ face velocity amongst fabricated E-MOFilters were remained higher at elevated RHs than that under 5 cm s⁻¹. The higher toluene removal efficiency at dry conditions (RH ≤ 30%) was due to the longer residence time in the filtration. Again, a significant efficiency degradation is seen at elevated RH for the original MIL-125-NH₂ E-MOFilters, which was due to its inherent hydrophilicity. The higher efficiency for modified E-MOFilters at elevated RHs was due to the lower amount of water molecules at reduced flow velocity, which reduced their occupancy at the adsorption sites facilitating the adsorption of toluene. Similar to the results under 5 cm s⁻¹, the toluene removal efficiency had an order of PDMS@MIL-125-NH₂ > PDMS@MIL-125-R7 > MIL-125-R7 > MIL-125-NH₂ at elevated RHs. It is worth mentioning that PDMS@MIL-125-NH₂ E-MOFilters exhibited a decent toluene initial removal efficiency of 83% and 71%, respectively, at 50 and 60% RH. Besides, the toluene initial removal efficiencies by PDMS@MIL-125-R7 were of 63 and 45%, respectively, and that of MIL-125-R7 were 45 and 31%, respectively.

The toluene removal efficiencies of other modified E-MOFilters, i.e., PVP surfactant modified (MIL-125-NH₂/PVP) and N-coordination modified (MIL-125-NH₂/N_x), and hydrophobic ZIF-8 E-MOFilters were also investigated under different RHs at both 5 and 0.5 cm s⁻¹ face velocity. As expected, the efficiencies of these three filters were also decreased with increasing RH under both face velocities, as shown in Figs. S6 (a) and (b) of SI E. (Toluene removal efficiency at different RHs for other modified MOFs). The MIL-125-NH₂/N_x and MIL-125-NH₂/PVP E-MOFilters had a close performance for toluene removal and much better than the ZIF-8. The low efficiency of ZIF-8 E-MOFilters under any RH conditions was due to its smaller pore diameter (0.34 nm) than the size of toluene molecules (dynamic molecules length, 0.58 nm) causing obstacles for toluene molecules to diffuse into its pores [55,56]. Although MIL-125-NH₂/PVP and MIL-125-NH₂/N_x performed closely, a trend with the former performing better at low RH and the latter better at raised RH can be seen. This was because the MIL-125-NH₂/PVP had a higher surface area than that of MIL-125-NH₂/N_x (Table 1). In comparison, at raised RHs 30–60%, N groups in MIL-125-NH₂/N_x replaced part of oxygen in the metal clusters (Ti-O-Ti) to coordinate with Ti⁴⁺, which will weaken the interaction between hydrophilic metal sites and water molecules and promote the toluene adsorption [34]. Comparing the results shown in Fig. 5 and Fig. S7, it is concluded that the PDMS-coating E-MOFilters exhibited the best toluene removal efficiency amongst all the methods.

3.5.2. Toluene adsorption capacity

In previous section, the toluene initial removal efficiency of E-MOFilters under different RHs (10–60% RH) were systematically tested. In this section, toluene adsorption capacity of alkylated and PDMS modified E-MOFilters under 50% RH at 0.5 cm s⁻¹ face velocity was specially shown to illustrate the breakthrough curves of the fabricated E-

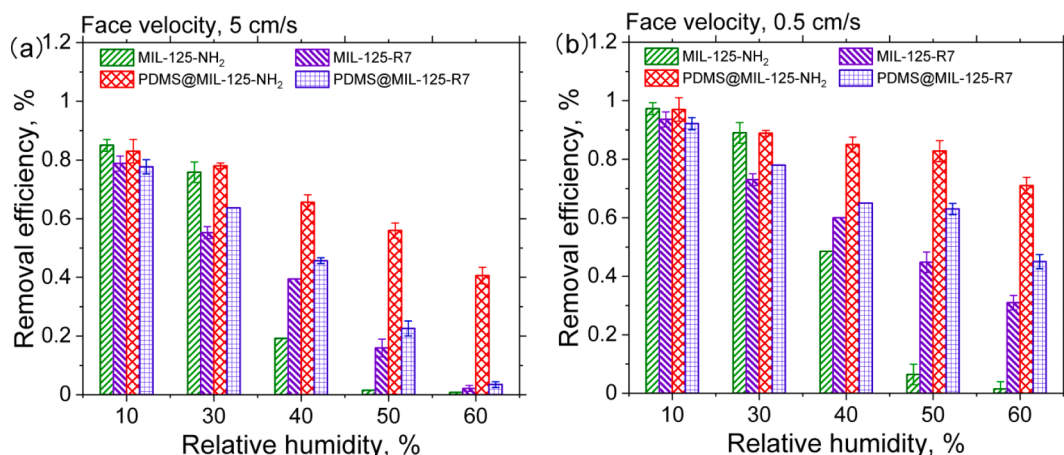


Fig. 5. Comparison of initial toluene removal efficiency of MERV 13 based E-MOFilters coated with alkylated and PDMS-treated MIL-125-NH₂ at 5 cm s⁻¹ (a) and 0.5 cm s⁻¹ (b).

MOFilters. The adsorption capacities for other E-MOFilters were not tested as their efficiency for toluene were not as good as the alkylated and PDMS modified E-MOFilters. In addition, the 50% RH is not only a typical indoor air RH, but also a recommended value for assessing the performance of air cleaning systems by ASHRAE 145.2.

Fig. 6 compares the toluene adsorption capacity, or breakthrough curves, between alkylated and PDMS modified E-MOFilters under 50% RH. As seen, the original MIL-125-NH₂ E-MOFilter did not show an obvious toluene adsorption capacity (shortest breakthrough time), due to water vapor competitive adsorption caused by its abundant metal sites and hydrophilic amine groups. In comparison, the PDMS@MIL-125-NH₂ showed the highest toluene adsorption capacity (longest breakthrough time) due to its superhydrophobic surface property demonstrated by the WCA results and its relatively high SSA, then followed by PDMS@MIL-125-R7 and MIL-125-R7. It is worth mentioning that the PDMS coated MIL-125-R7 showed a slightly higher toluene adsorption capacity than the MIL-125-R7. This could be again due to the higher hydrophobicity induced by PDMS coating, as evidenced by its higher WCA.

It was calculated that the adsorption capacity of PDMS@MIL-125-NH₂ E-MOFilter was 8 times of the original MIL-125-NH₂ E-MOFilter. Furthermore, it is also worth mentioning that the breakthrough time for PDMS@MIL-125-NH₂ E-MOFilter only lasted for ~ 1.5 h under current experiment conditions even if it showed the highest hydrophobicity and

surface area among all the modified E-MOFilters. This breakthrough time is fairly shorter than that reported by Zheng et al. [20]. This was because the current E-MOFilter coated relatively low quantity of MOFs (only ~ 30%) compared with that of Zheng et al. [20], besides, the toluene concentration in the challenge was five times higher in this study (5 vs. 1 ppm). Table S5 of SI E compares the challenging toluene concentration, filtration flow rate, removal efficiency, breakthrough time and adsorption capacity at RH = 50% amongst the current E-MOFilters with different modifications and the MOFs CAU-1 ([Al₄(O-H)₂(OCH₃)₄(H₂N-BDC)₃·xH₂O) tested by Zheng et al. [20]. It is observed the performance of the PDMS modified E-MOFilter is comparable with the MOF CAU-1 on the adsorption capacity. To be concluded, PDMS@MIL-125-NH₂ E-MOFilter was demonstrated to have the best toluene adsorption performance under 50% RH amongst all modified E-MOFilters. Besides, since this method is relatively facile and cost effective, it could be used in practical application to decrease the RH effects on the gas removal filter media.

To evaluate the mechanical stability of the modified E-MOFilter, we conducted the MOF shedding test using a ultrafine condensation particle counter according to [16] to realize whether MOFs would detect from the MERV13 fibers. Besides, morphologies and crystalline structures of PDMS modified E-MOFilter after toluene adsorption were compared with the untreated one using the SEM and XRD, respectively. A negligible MOF shedding under the filtration velocity of 5–30 cm s⁻¹ was obtained which concluded a good physical stability of the E-MOFilter. The SEM and XRD analysis results shown in Fig. S7 indicated the morphology and crystal structure of the modified E-MOFilter remained unchanged after adsorption tests.

4. Conclusion

In this study, a representative MOF (MIL-125-NH₂) was successfully synthesized and modified via internal, external and combined modifications, i.e., alkylation, PDMS and both. Then these modified MOFs were coated to a MERV 13 grade electret filter media to develop a water/moisture resistant E-MOFilter for a simultaneous removal of PM_{2.5} and volatile organic compounds (VOCs) under different humid conditions (10–60% RH). The modified MOFs were characterized by SEM, EDX, XRD, FTIR and WCA and BET analysis and demonstrated to be hydrophobic. A series of systematic experiments for the toluene removal by the original and modified E-MOFilter under different RHs were conducted. Results showed the toluene initial removal efficiency of the original E-MOFilter was decreased to almost below 10% when RH was increased to 60%. However, the hydrophobically modified E-MOFilters performed much better than the original filter. Amongst the modified filters, the PDMS modified MIL-125-NH₂ E-MOFilter outperformed all

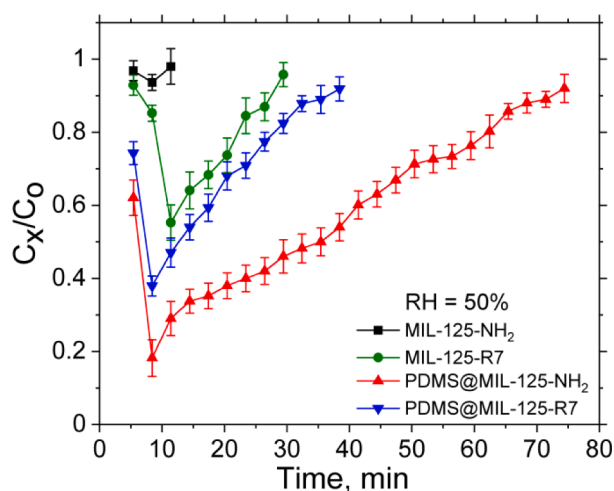


Fig. 6. Comparison of breakthrough curves amongst E-MOFilters coated with original and modified MOF particles under 0.5 cm s⁻¹ face velocity.

filters having a decent initial removal efficiency ($\sim 80\%$ at 0.5 cm s^{-1} face velocity and $\sim 60\%$ at 5 cm s^{-1} face velocity) and the longest breakthrough time for toluene under 50% RH. This was because of the high hydrophobicity and retaining high surface area and pore volume of the PDMS modified MIL-125-NH₂. Meanwhile, a series of measurements were conducted to test the PM removal performances, in terms of initial efficiency and holding capacity by the modified E-MOFilters. Results showed that the PM removal performance by the modified E-MOFilters were found to be comparable to the original MERV 13 filter. This indicates the modifications did not deteriorate the fiber charges and structures.

Comparing all the modifications in this work, it becomes clear that SSA, micropore volume and hydrophobicity are of great significance for achieving a good toluene removal efficiency under elevated humid conditions. Besides, regardless the hydrophobicity of the adsorbents, there is a prerequisite that the relative pore size of the MOFs and three-dimensional size of VOC molecules are crucial for achieving good toluene adsorption performance of the filters. It is not easy to fundamentally tackle with the water competitive adsorption issue and much more efforts should be made to extend the E-MOFilter applications in high humid conditions. Nevertheless, the systematic tests and the results from this study provided some new insights into the application of E-MOFilter under elevated RHs.

In conclusion, the significance and distinction of this study include: 1. The first to combine the MOF (MIL-125-NH₂) particles on electret filter media (as the E-MOFilter) for a low pressure drop and simultaneous removal of PM and VOC; 2. The E-MOFilter readily for both gas and particle purification towards a good indoor air quality. 3. Providing a series of modifications and optimization for the MIL-125-NH₂ MOFs and a systematic evaluation of the modified E-MOFilter against toluene under different RH levels. 4. Showing and ranking the effectiveness of the modifications on the mitigation of RH effects for the reference of future study.

CRediT authorship contribution statement

Yu Zhang: Data curation, Writing – original draft. **Zan Zhu:** Formal analysis, Writing – review & editing. **Wei-Ning Wang:** Resources, Writing – review & editing. **Sheng-Chieh Chen:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2021.120309>.

References

- [1] P. Gustafson, C. Östman, G. Sällsten, Indoor levels of polycyclic aromatic hydrocarbons in homes with or without wood burning for heating, *Environ. Sci. Technol.* 42 (14) (2008) 5074–5080.
- [2] EPA, <https://www.epa.gov/report-environment/indoor-air-quality>.
- [3] N.E. Klepeis, W.C. Nelson, W.R. Ott, J.P. Robinson, A.M. Tsang, P. Switzer, J. V. Behar, S.C. Hern, W.H. Engelmann, The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants, *J. Expo. Anal. Environ. Epidemiol.* 11 (2001) 231–252.
- [4] S. Brasche, W. Bischof, Daily time spent indoors in German homes – Baseline data for the assessment of indoor exposure of German occupants, *Int. J. Hyg. Environ. Health.* 208 (4) (2005) 247–253.
- [5] C. Schweizer, R.D. Edwards, L. Bayer-Oglesby, W.J. Gauderman, V. Ilacqua, M. Juhani Jantunen, H.K. Lai, M. Nieuwenhuijsen, N. Künzli, Indoor time-microenvironment-activity patterns in seven regions of Europe, *J. Expo. Sci. Environ. Epidemiol.* 17 (2) (2007) 170–181.
- [6] M. Awada, B. Becerik-Gerber, S. Hoque, Z. O'Neill, G. Pedrielli, J. Wen, T. Wu, Ten questions concerning occupant health in buildings during normal operations and extreme events including the COVID-19 pandemic, *Build. Environ.* 188 (2021), 107480.
- [7] Q.i. Chen, H. Sun, J. Zhang, Y. Xu, Z. Ding, The hematologic effects of BTEX exposure among elderly residents in Nanjing: a cross-sectional study, *Environ. Sci. Pollut. Res.* 26 (11) (2019) 10552–10561.
- [8] D.Y.H. Pui, S.-C. Chen, Z. Zuo, PM_{2.5} in China: Measurements, sources, visibility and health effects, and mitigation, *Particuology.* 13 (2014) 1–26.
- [9] D.A. Sarigiannis, S.P. Karakitsios, A. Gotti, I.L. Liakos, A. Katsoyiannis, Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk, *Environ. Int.* 37 (4) (2011) 743–765.
- [10] Y. Du, X. Xu, M. Chu, Y. Guo, J. Wang, Air particulate matter and cardiovascular disease: the epidemiological, biomedical and clinical evidence, *J. Thorac. Dis.* 8 (2016) E8–E19.
- [11] M. Tang, D. Thompson, D.-Q. Chang, S.-C. Chen, D.Y.H. Pui, Filtration efficiency and loading characteristics of PM_{2.5} through commercial electret filter media, *Sep. Purif. Technol.* 195 (2018) 101–109.
- [12] J.B. DeCoste, G.W. Peterson, Metal-Organic Frameworks for Air Purification of Toxic Chemicals, *Chem. Rev.* 114 (11) (2014) 5695–5727.
- [13] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The Chemistry and Applications of Metal-Organic Frameworks, *Science* 341 (6149) (2013), <https://doi.org/10.1126/science.1230444>.
- [14] N.S. Bobbitt, M.L. Mendonca, A.J. Howarth, T. Islamoglu, J.T. Hupp, O.K. Farha, R. Q. Snurr, Metal-organic frameworks for the removal of toxic industrial chemicals and chemical warfare agents, *Chem. Soc. Rev.* 46 (11) (2017) 3357–3385.
- [15] D.W. Wang, Z.W. Li, J. Zhou, H. Fang, X. He, P.R. Jena, J.B. Zeng, W.N. Wang, Simultaneous Detection and Removal of Formaldehyde at Room Temperature: Janus Au@ZnO@ZIF-8 Nanoparticles, *Nano-Micro Letters* 10 (2018) 4.
- [16] Y. Zhang, X. He, Z. Zhu, W.-N. Wang, S.-C. Chen, Simultaneous removal of VOCs and PM_{2.5} by metal-organic framework coated electret filter media, *J. Membr. Sci.* 618 (2021), 118629.
- [17] J. Pei, J.S. Zhang, Determination of adsorption isotherm and diffusion coefficient of toluene on activated carbon at low concentrations, *Build. Environ.* 48 (2012) 66–76.
- [18] X. Zhang, X. Lv, X. Shi, Y. Yang, Y. Yang, 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.* 539 (2019) 152–160.
- [19] X. Li, L. Zhang, Z. Yang, Z. He, P. Wang, Y. Yan, J. Ran, Hydrophobic modified activated carbon using PDMS for the adsorption of VOCs in humid condition, *Sep. Purif. Technol.* 239 (2020), 116517.
- [20] X. Zheng, S. Liu, S. Rehman, Z. Li, P. Zhang, Highly improved adsorption performance of metal-organic frameworks CAU-1 for trace toluene in humid air via sequential internal and external surface modification, *Chem. Eng. J.* 389 (2020), 123424.
- [21] L. Zhu, D. Shen, K.H. Luo, A critical review on VOCs adsorption by different porous materials: Species, mechanisms and modification methods, *J. Hazard. Mater.* 389 (2020), 122102.
- [22] M. Zhu, P. Hu, Z. Tong, Z. Zhao, Z. Zhao, Enhanced hydrophobic MIL(Cr) metal-organic framework with high capacity and selectivity for benzene VOCs capture from high humid air, *Chem. Eng. J.* 313 (2017) 1122–1131.
- [23] EPA, <https://www.epa.gov/mold/brief-guide-mold-moisture-and-your-home>.
- [24] J.G. Nguyen, S.M. Cohen, Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification, *J. Am. Chem. Soc.* 132 (13) (2010) 4560–4561.
- [25] Y. Isaka, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, Two-Phase System Utilizing Hydrophobic Metal-Organic Frameworks (MOFs) for Photocatalytic Synthesis of Hydrogen Peroxide, *Angew. Chem.* 131 (16) (2019) 5456–5460.
- [26] Y. Sun, Q.i. Sun, H. Huang, B. Aguila, Z. Niu, J.A. Perman, S. Ma, A molecular-level superhydrophobic external surface to improve the stability of metal-organic frameworks, *J. Mater. Chem. A.* 5 (35) (2017) 18770–18776.
- [27] Y. Kawase, Y. Isaka, Y. Kuwahara, K. Mori, H. Yamashita, Ti cluster-alkylated hydrophobic MOFs for photocatalytic production of hydrogen peroxide in two-phase systems, *Chem. Commun.* 55 (47) (2019) 6743–6746.
- [28] K.-D. Kim, E.J. Park, H.O. Seo, M.-G. Jeong, Y.D. Kim, D.C. Lim, Effect of thin hydrophobic films for toluene adsorption and desorption behavior on activated carbon fiber under dry and humid conditions, *Chem. Eng. J.* 200–202 (2012) 133–139.

- [29] H.-B. Liu, B. Yang, N.-D. Xue, Enhanced adsorption of benzene vapor on granular activated carbon under humid conditions due to shifts in hydrophobicity and total micropore volume, *J. Hazard. Mater.* 318 (2016) 425–432.
- [30] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, A Facile and General Coating Approach to Moisture/Water-Resistant Metal-Organic Frameworks with Intact Porosity, *J. Am. Chem. Soc.* 136 (49) (2014) 16978–16981.
- [31] G. Wen, Z. Guo, Facile modification of NH₂-MIL-125(Ti) to enhance water stability for efficient adsorptive removal of crystal violet from aqueous solution, *Colloids Surf. Physicochem. Eng. Asp.* 541 (2018) 58–67.
- [32] X. Zhang, Y. Yang, L. Song, J. Chen, Y. Yang, Y. Wang, Enhanced adsorption performance of gaseous toluene on defective UiO-66 metal organic framework: Equilibrium and kinetic studies, *J. Hazard. Mater.* 365 (2019) 597–605.
- [33] X. Zhang, Y. Yang, X. Lv, Y. Wang, N. Liu, D. Chen, L. Cui, Adsorption/desorption kinetics and breakthrough of gaseous toluene for modified microporous-mesoporous UiO-66 metal organic framework, *J. Hazard. Mater.* 366 (2019) 140–150.
- [34] P. Hu, X. Liang, M. Yaseen, X. Sun, Z. Tong, Z. Zhao, Z. Zhao, Preparation of highly-hydrophobic novel N-coordinated UiO-66(Zr) with dopamine via fast mechano-chemical method for (CHO-/Cl-)-VOCs competitive adsorption in humid environment, *Chem. Eng. J.* 332 (2018) 608–618.
- [35] J. Yuan, X. Liu, O. Akbulut, J. Hu, S.L. Suib, J. Kong, F. Stellacci, Superwetting nanowire membranes for selective absorption, *Nat. Nanotechnol.* 3 (6) (2008) 332–336.
- [36] S. Jafari, F. Ghorbani-Shahna, A. Bahrami, H. Kazemian, Adsorptive removal of toluene and carbon tetrachloride from gas phase using Zeolitic Imidazolate Framework-8: Effects of synthesis method, particle size, and pretreatment of the adsorbent, *Microporous Mesoporous Mater.* 268 (2018) 58–68.
- [37] D.-Q. Chang, C.-Y. Tien, C.-Y. Peng, M. Tang, S.-C. Chen, Development of composite filters with high efficiency, low pressure drop, and high holding capacity PM2.5 filtration, *Sep. Purif. Technol.* 212 (2019) 699–708.
- [38] S.-C. Chen, D. Segets, T.-Y. Ling, W. Peukert, D.Y.H. Pui, An experimental study of ultrafiltration for sub-10nm quantum dots and sub-150 nm nanoparticles through PTFE membrane and Nuclepore filters, *J. Membr. Sci.* 497 (2016) 153–161.
- [39] Z. Fan, P. Ji, J. Zhang, D. Segets, D.-R. Chen, S.-C. Chen, Wavelet neural network modeling for the retention efficiency of sub-15 nm nanoparticles in ultrafiltration under small particle to pore diameter ratio, *J. Membr. Sci.* 635 (2021), 119503.
- [40] M. Tang, S.-C. Chen, D.-Q. Chang, X. Xie, J. Sun, D.Y.H. Pui, Filtration efficiency and loading characteristics of PM2.5 through composite filter media consisting of commercial HVAC electret media and nanofiber layer, *Sep. Purif. Technol.* 198 (2018) 137–145.
- [41] M. Tang, D. Thompson, S.-C. Chen, Y. Liang, D.Y.H. Pui, Evaluation of different discharging methods on HVAC electret filter media, *Build. Environ.* 141 (2018) 206–214.
- [42] S. Li, D.-R. Chen, F. Zhou, S.-C. Chen, Effects of relative humidity and particle hygroscopicity on the initial efficiency and aging characteristics of electret HVAC filter media, *Build. Environ.* 171 (2020), 106669.
- [43] C.-Y. Tien, J.-P. Chen, S. Li, Z. Li, Y.-M. Zheng, A.S. Peng, F. Zhou, C.-J. Tsai, S.-C. Chen, Experimental and theoretical analysis of loading characteristics of different electret media with various properties toward the design of ideal depth filtration for nanoparticles and fine particles, *Sep. Purif. Technol.* 233 (2020), 116002.
- [44] Z. Zhu, Y.u. Zhang, L. Bao, J. Chen, S. Duan, S.-C. Chen, P. Xu, W.-N. Wang, Self-decontaminating nanofibrous filters for efficient particulate matter removal and airborne bacteria inactivation, *Environ. Sci. Nano.* 8 (4) (2021) 1081–1095.
- [45] F. Rezaei, G. Moussavi, A.R. Bakhtiari, Y. Yamini, Toluene removal from waste air stream by the catalytic ozonation process with MgO/GAC composite as catalyst, *J. Hazard. Mater.* 306 (2016) 348–358.
- [46] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations, *Carbon.* 43 (8) (2005) 1758–1767.
- [47] J.M. Kim, J.H. Kim, C.Y. Lee, D.W. Jerng, H.S. Ahn, Toluene and acetaldehyde removal from air on to graphene-based adsorbents with micro-sized pores, *J. Hazard. Mater.* 344 (2018) 458–465.
- [48] J. Mohammed, N.S. Nasri, M.A. Ahmad Zaini, U.D. Hamza, F.N. Ani, Adsorption of benzene and toluene onto KOH activated coconut shell based carbon treated with NH₃, *Int. Biodeterior. Biodegrad.* 102 (2015) 245–255.
- [49] B. Kim, Y.-R. Lee, H.-Y. Kim, W.-S. Ahn, Adsorption of volatile organic compounds over MIL-125-NH₂, *Polyhedron.* 154 (2018) 343–349.
- [50] K. Vellingiri, P. Kumar, A. Deep, K.-H. Kim, Metal-organic frameworks for the adsorption of gaseous toluene under ambient temperature and pressure, *Chem. Eng. J.* 307 (2017) 1116–1126.
- [51] X. Zheng, Z. Wu, J. Yang, S. Rehman, R. Cao, P. Zhang, Metal-Organic Gel Derived N-Doped Granular Carbon: Remarkable Toluene Uptake and Rapid Regeneration, *ACS Appl. Mater. Interfaces.* 13 (2021) 17543–17553.
- [52] S.-N. Kim, J. Kim, H.-Y. Kim, H.-Y. Cho, W.-S. Ahn, Adsorption/catalytic properties of MIL-125 and NH₂-MIL-125, *Catal. Today.* 204 (2013) 85–93.
- [53] D. Bodas, C. Khan-Malek, Formation of more stable hydrophilic surfaces of PDMS by plasma and chemical treatments, *Microelectron. Eng.* 83 (4-9) (2006) 1277–1279.
- [54] Y. Zhang, H. Chi, W. Zhang, Y. Sun, Q. Liang, Y.u. Gu, R. Jing, Highly Efficient Adsorption of Copper Ions by a PVP-Reduced Graphene Oxide Based On a New Adsorptions Mechanism, *Nano-Micro Lett.* 6 (1) (2014) 80–87.
- [55] M. Jahandar Lashaki, M. Fayaz, S. Niknaddaf, Z. Hashisho, 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.* 241–242 (2012) 154–163.
- [56] C.E. Webster, R.S. Drago, M.C. Zerner, Molecular Dimensions for Adsorptives, *J. Am. Chem. Soc.* 120 (22) (1998) 5509–5516.

Supporting Information

Relative humidity (RH) effects on simultaneous removal of VOCs and PM_{2.5} by metal-organic framework coated electret filter media

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SI A. Synthesis and modification of MOFs

Table S1. Comparison of existing modification methods towards the mitigation of RH effects on VOCs adsorption.

Category	Mechanisms	Advantages	Disadvantages	Ref.
Internal	Grafting hydrophobic alkyl chains through ligand or metal cluster functionalization	Molecular level grafting and hydrophobic functional group introduction achieving a better stability	Long alkyl chains block the pore of the MOFs; relatively complex preparation procedures	[1-5]
External	Coating hydrophobic materials (e.g., PDMS) on the MOFs surface	Simple procedures, relatively higher hydrophobicity and higher surface area remained after the modification	Excessive coating would block the pore of MOFs	[1, 6-10]
Others	Surfactants (PVP, CTAB, P123, etc.) incorporation; N-coordination	Simple procedures, higher surface area remained after modification	Lower hydrophobicity after modification	[11-14]

Nguyen et al. [2] reported that amine-contained MOFs, such as MIL-53(Al)-NH₂, would readily undergo modification to form amide-functionalized MOFs to improve its moisture resistance. Specifically, the authors added hydrophobic alkyl chains to the linkers of MIL-53(Al)-NH₂ to form MIL-53(Al)-AMn (-AMn: “amide” with a n-carbon chain). The results showed that MIL-53(Al)-AMn (n ≥ 4) had a > 150° WCA, while the original MIL-53(Al)-NH₂ was ~ 0° WCA, which means the modified MIL-53(Al)-AMn demonstrated a superhydrophobic property. It is

worth mentioning that whether the modification could cause a decrease in the surface area of the MOFs was not reported. Similarly, Isaka et al. [3] reported that by the alkylation of the linkers of MIL-125(Ti)-NH₂, the amino groups of MIL-125-NH₂ were transformed into hydrophobic groups via amide reaction. After modification, the WCA of MIL-125-R7 (n=7) showed a significant increase from 30° to 124° compared with that of pristine MIL-125-NH₂. However, with this alkylation method, a significant decrease of surface area of the MOFs was observed [3]. To keep a high surface area of MOFs when they are imparted with hydrophobic character, Sun et al. [4] developed a facile strategy of grafting alkylphosphonic acid molecules on the outer surface of MOFs. This was based on the fact that alkylphosphonic acids with a long alkyl chain end [CH₃(CH₂)_nP(O)(OH)₂] (n > 6) can be coordinated to metals (Ti, Zr, Zn, Al, etc.) with strong M–O–P bonds. Results showed that the octylphosphonic acid (OPA, an alkylphosphonic acid) modified MOFs (Zr-based MOFs) retained their high surface area (1068 m² g⁻¹) while obtained a superhydrophobicity (WCA = 160°). However, OPA is too expensive to be widely applied.

External modification, is completely different from that of internal, where a layer of hydrophobic materials is coated on the surface of adsorbents [1, 6-10]. For instance, Li et al. [6] used a chemical vapor deposition (CVD) method to coat a thin layer of hydrophobic polydimethylsiloxane (PDMS) film on the surface of AC in the form of Si-O-Si group at 200 °C. Their results showed that the VOCs adsorption capacity of hydrophilic bare-AC decreased by 55.9% when RH increased from 0 to 90%. However, the AC modified with PDMS had only a reduction of 19.3% [6]. Again, this was because the introduction of hydrophobicity on the surface of adsorbents, which made them to remain more adsorption sites readily for VOC adsorption. However, their results also demonstrated that the surface areas of PDMS/ACs were decreased with increasing coating amount of PDMS. Besides, PDMS could fill some pores of ACs, which degraded the VOCs adsorption capacity. Similarly, Liu et al. [8] observed PDMS-coated ACs at 250 °C (PDMS/ACs-250) had a superhydrophobicity property and a significant increase in benzene adsorption capacities compared to bare AC at elevated (0-90%) RHs. In addition to ACs, Zhang et al. [9] applied PDMS to hydrophilic MOFs (MOF-5, HKUST-1, and ZnBT) and found the modified MOFs exhibited highly hydrophobic feature, excellent moisture/water tolerance and remained a high surface area. In addition to CVD method, Wen et al. [10] reported a facile chemical immersion method to impart superhydrophobicity on hydrophilic MIL-125(Ti)-NH₂.

Their results demonstrated a superhydrophobic character after the treatment, meanwhile, this PDMS-treated MOF retained high crystallinity and porosity.

Zheng et al. [1] tried to apply both internal and external modification methods and found the hydrophobicity of the modified MOF, P_{0.5}-CAU-1-val, was significantly enhanced and the toluene adsorption capacity was also significantly increased from 0.89 to 6.82 mg/g under 50% RH. However, the application of both internal and external modifications increases the complexity. In addition to internal and external modification techniques, adding surfactants, e.g., polyvinylpyrrolidone (PVP), Cetyltrimethylammonium bromide (CTAB), P123 (EO₂₀PO₇₀EO₂₀), etc., during the synthesis of MOFs, were reported to be able to increase the VOCs adsorption in elevated RH conditions [11-13]. Besides, Hu et al. [14] reported that MOF UiO-66(Zr) modified with dopamine (DA) demonstrated a significantly enhanced chlorobenzene (ClB)/H₂O competitive adsorption. Although there have been many techniques reported to improve the gas adsorption in elevated RH, there is a lack of systematic study that compares the effectiveness of different hydrophobicity modifications for MOF particles. Thus, it is very important to conduct a systematic experiment to determine the RH effects on the PM and VOC removal for the original and modified E-MOFilters.

Synthesis of original and modified MIL-125-NH₂

MIL-125-NH₂ [15]: 0.797 mL titanium tetraisopropoxide (TTIP) and 0.651 g 2-aminoterephthalic acid (BDC-NH₂) were dissolved in the mixture of dimethylformamide (DMF)/methanol (15 mL/15 mL). Then, the mixture was transferred to a Teflon-lined steel autoclave reactor and placed in an oven at 150 °C for 15 hours. The obtained yellow products were isolated by centrifugation and washed by 30 mL DMF and 30 mL methanol, respectively, for three times. Finally, the samples were dried under 50 °C overnight in vacuum.

MIL-125-NH₂/PVP [11]: Briefly, 0.797 mL titanium tetraisopropoxide (TTIP), 0.651 g 2-aminoterephthalic acid (BDC-NH₂) and 1.046 g PVP (M_w = 55000 g mol⁻¹) were dissolved in the mixture of dimethylformamide (DMF)/methanol (15 mL/15 mL). Then, the mixture was transferred to a Teflon-lined steel autoclave reactor and placed in an oven at 150 °C for 15 hours. The obtained yellow products were isolated by centrifugation and washed by 30 mL DMF and 30

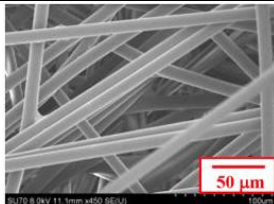
mL methanol, respectively, for three times. Finally, the samples were dried under 50 °C overnight in vacuum.

MIL-125-NH₂/N_x [14]: A total of 0.797 mL titanium tetraisopropoxide (TTIP) and 0.651 g 2-aminoterephthalic acid (BDC-NH₂) and 0.0149 g dopamine hydrochloride (DA) were dissolved in the mixture of dimethylformamide (DMF)/methanol (15 mL/15 mL). Thereafter, the mixture is heated for 15 h at 150 °C in a Teflon lined autoclave. After the reaction, the autoclave is cooled down to normal temperature, and resulting product is filtered and washed three times with 30 mL DMF and 30 mL methanol, respectively, for three times. Finally, the yellow powder is dried at 50 °C overnight in vacuum.

ZIF-8 [16]: Briefly, 1.188 g of Zn(NO₃)₂·6H₂O was dissolved in 6 mL of DI water (precursor I), and 0.656 g of 2-methylimidazole was dissolved in 7.52 g of an ammonium hydroxide solution (precursor II). The precursor I was added to the precursor II while mixing. The white products were collected by centrifugation and washed by DI water for three times. The final product was dried in oven at 60 °C overnight.

SI B. Specifications of the MERV 13

Table S2. Specification of the MERV 13 electret media (1 layer) for the MOF coating.

Grade	Fiber diameter (μm)	Thickness (mm)	Basic weight (g/m^2)	Solidity (α)	Charging density ($\mu\text{C}/\text{m}^2$)	Initial pressure drop at 5 cm/s (Pa)	Initial efficiency for 0.3 μm particles at 5 cm/s (%)	SEM images
MERV 13	13.1 ± 0.9	0.47 ± 0.02	75 ± 2	0.104	~ 50	4.5 ± 0.1	91.1 ± 0.2	

SI C. Test conditions for the modified E-MOFilters against PM and VOC

Table S3. Experimental conditions for PM and toluene removal tests of modified E-MOFilters.

E-MOFilters	PM tests (5 cm s^{-1})		5 ppm toluene tests (5 cm s^{-1} & 0.5 cm s^{-1})	Other
	Initial efficiency	Aging test	RH (%) (10,30, 40, 50, 60)	
MIL-125-NH ₂	✓	✓	✓	-
MIL-125-R7	✓	✓	✓	59 % of linkers were alkylated [3]
PDMS@ MIL-125-NH ₂	✓	✓	✓	Si/Ti = 0.43
PDMS@ MIL-125-R7	✓	✓	✓	Si/Ti = 0.22
PVP/MIL-125-NH ₂	-	-	✓	-
MIL-125- NH ₂ -N _x	-	-	✓	-
ZIF-8	-	-	✓	-

SI D. Physical and chemical characterizations for other modified MOFs

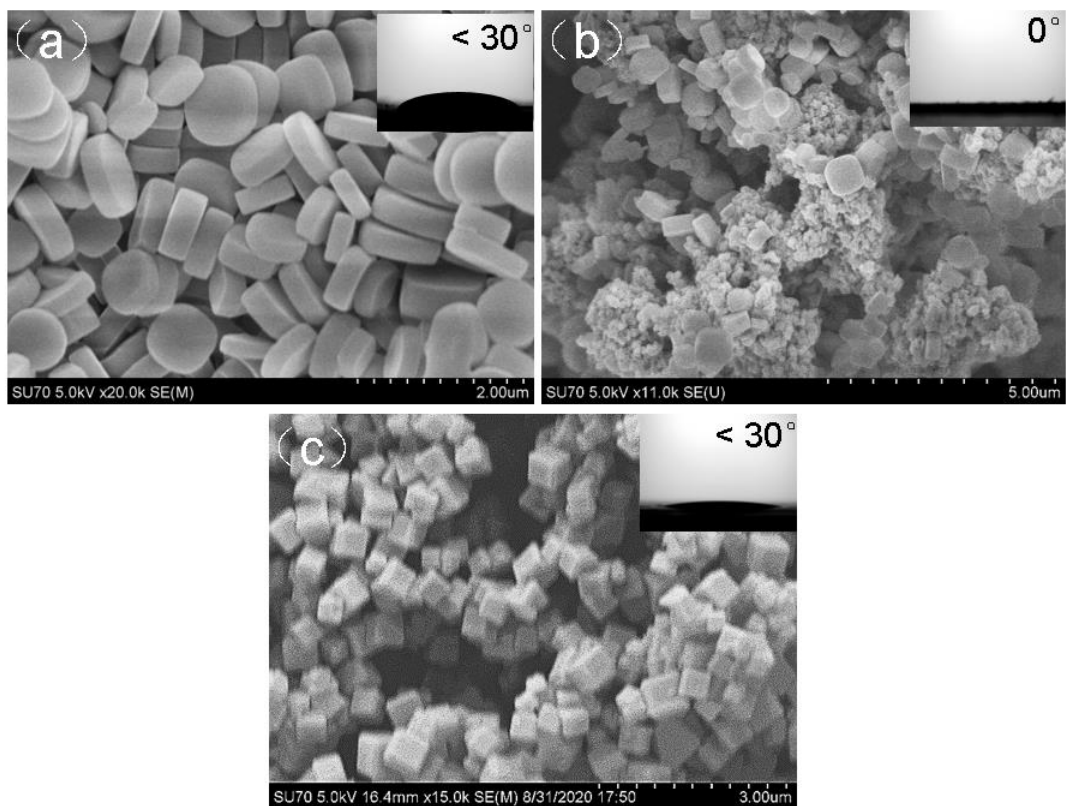


Fig. S1. SEM images and WCAs of (a) MIL-125-NH₂/PVP, (b) MIL-125-NH₂/Nx and (c) ZIF-8 MOF particles.

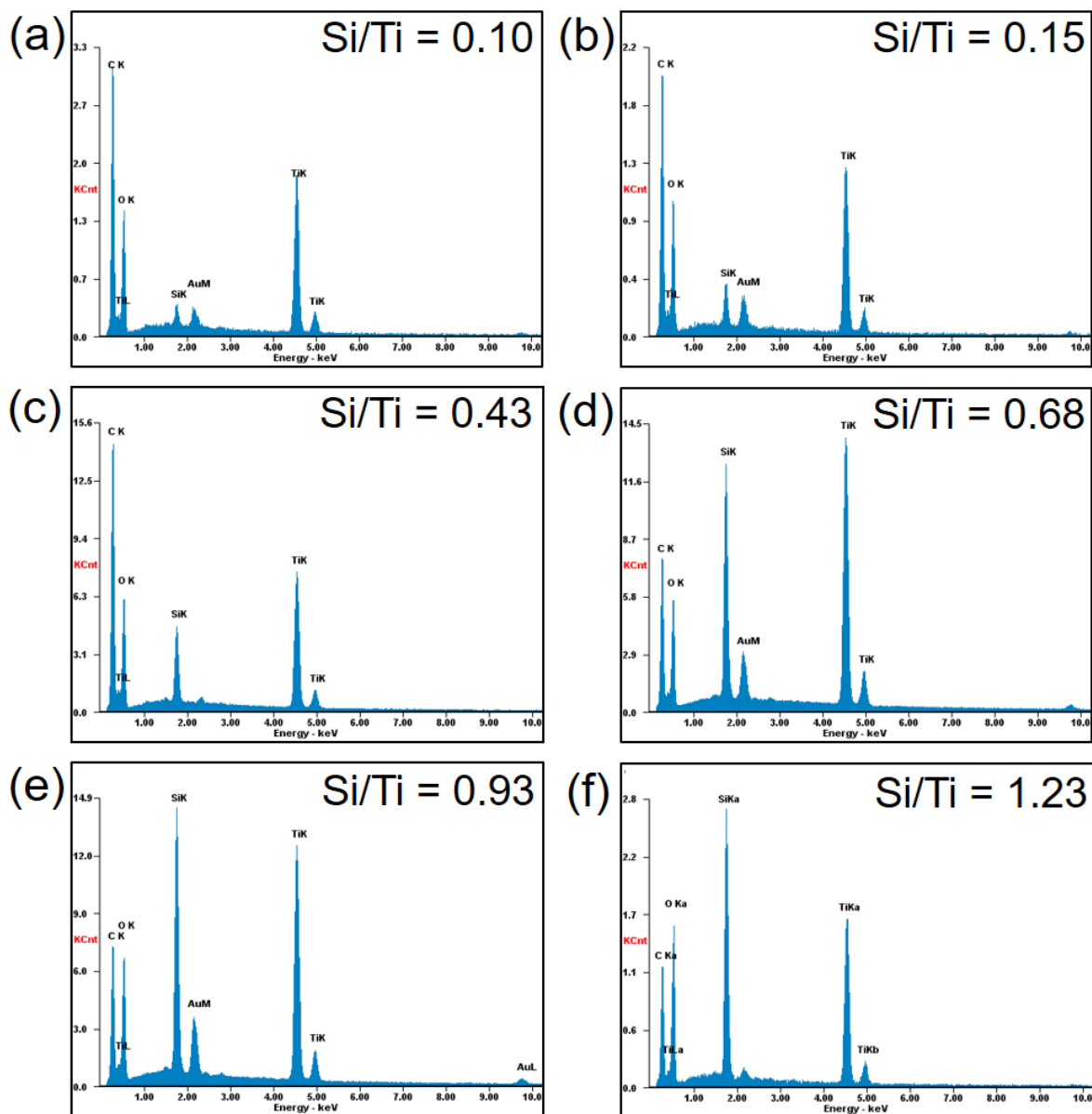


Fig. S2. The atomic ratios of Si and Ti (denoted as Si/Ti) obtained by EDS analysis of MIL-125-NH₂ treated with different quantities of PDMS (mass ratios of PDMS to MIL-125-NH₂ in (a-f) are 3:1, 10:1, 100:1, 200:1, 300:1 and 400:1, respectively).

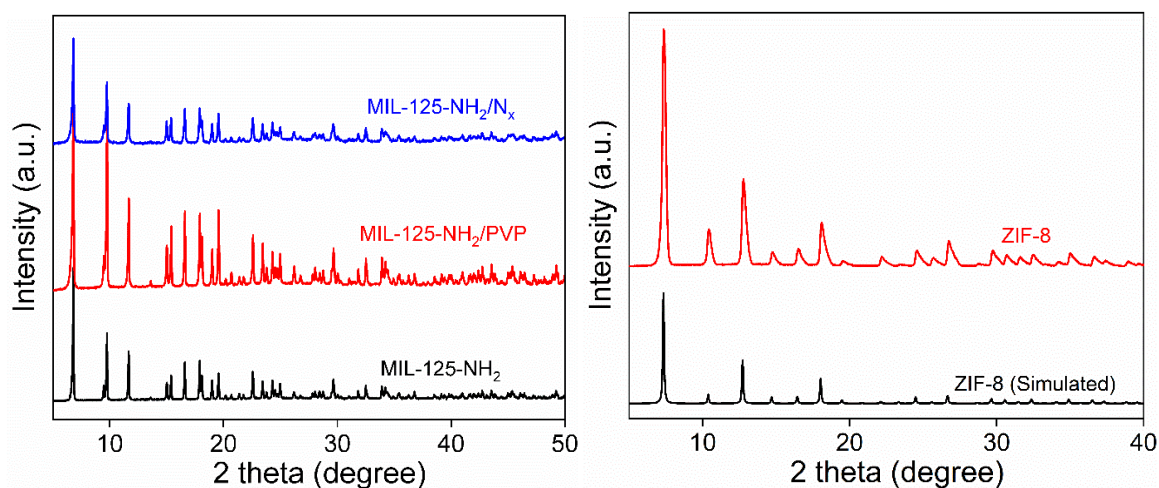


Fig. S3. XRD patterns of MIL-125-NH₂/PVP, MIL-125-NH₂/N_x and ZIF-8 MOF particles.

Table S4. BET analysis of PDMS@-MIL-125-NH₂ with different PDMS coating quantity.

Powder	Atomic ratio (Si/Ti)	BET surface area (m ² /g)	Total/Micropore volume (cm ³ /g)	Peak pore diameter (nm)	WCAs (°)
PDMS@ MIL-125- NH ₂	0.1	1790	0.871/0.602	0.78	150.5
	0.43	1417	0.726/0.463	0.78	155.5
	0.68	623	0.294/0.222	0.72	155.5
	1.23	582	0.195/0.009	0.72	155.5

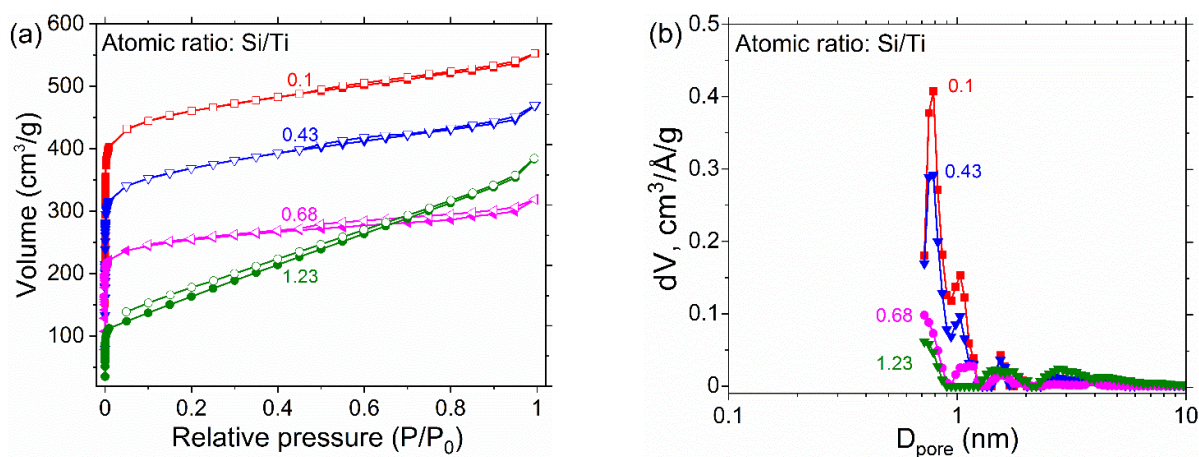


Fig. S4. Nitrogen adsorption isotherm (a) and pore size distribution (b) of PDMS-treated MIL-125-NH₂ with different PDMS coating amount at 77 K.

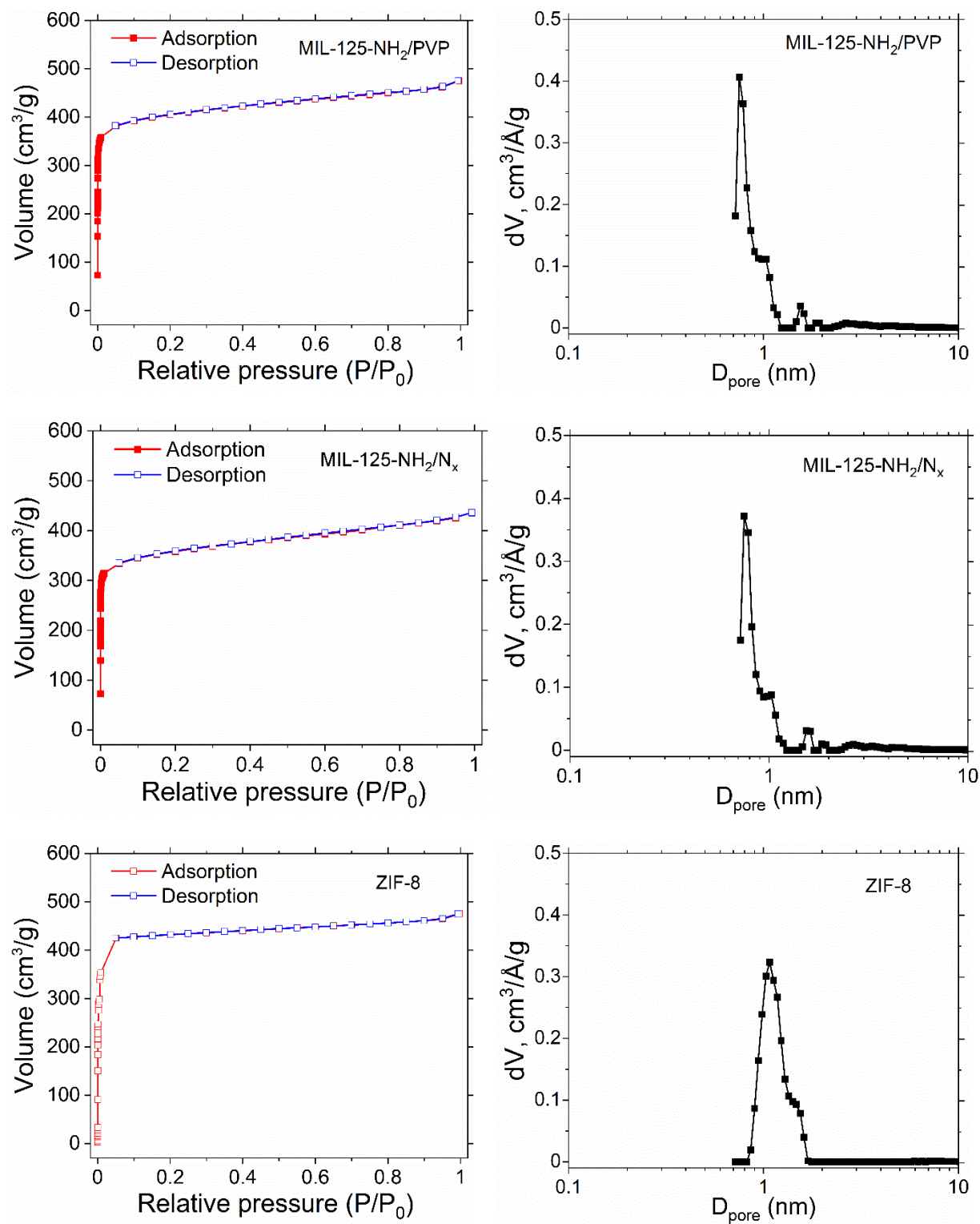


Fig. S5. Nitrogen adsorption isotherm and pore size distribution of MIL-125-NH₂/PVP, MIL-125-NH₂/N_x and ZIF-8 MOF particles at 77 K.

SI E. Toluene removal efficiency at different RHs for other modified MOFs

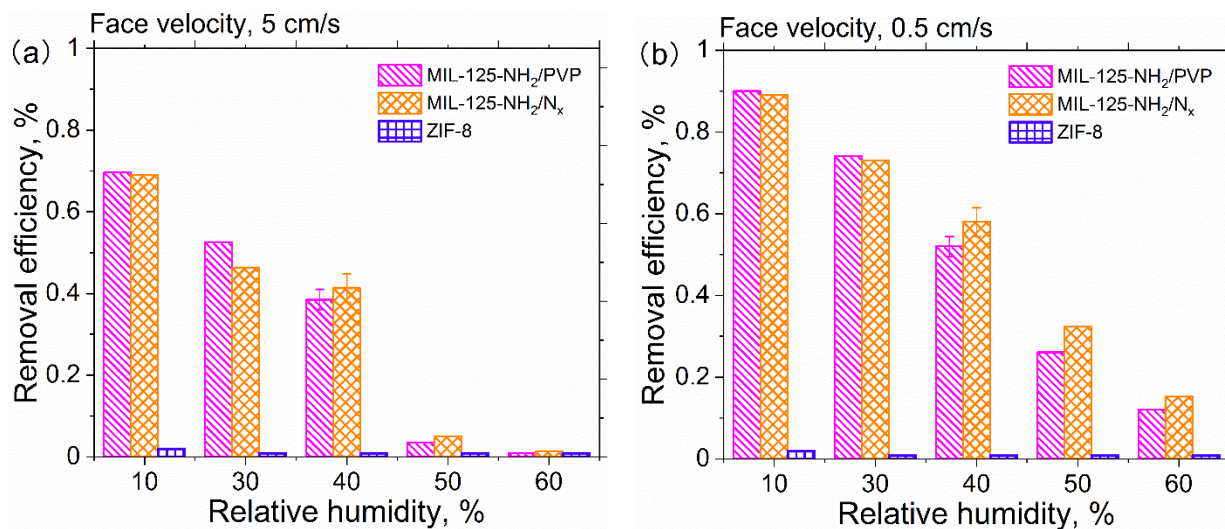


Fig. S6. Comparison of initial toluene removal efficiency of E-MOFilters coated with ZIF-8, MIL-125-NH₂/PVP and MIL-125-NH₂/N_x MOFs at 5 cm s⁻¹ (a) and 0.5 cm s⁻¹ (b).

Table S5. Comparison of VOCs adsorption performance of the modified E-MOFilters and MOF CAU [1] under RH=50%.

E-MOFilters	C ₀ (ppm)	Flow rate (mL/min)	Initial removal efficiency (%)	90% breakthrough time (min)	Adsorption capacity (mg/g)	Ref.
MIL-125-NH ₂	5	435	8.3	9	0.90	This work
MIL-125-R7	5	435	44.8	30	2.7	This work
PDMS@ MIL-125-NH ₂	5	435	82.7	81	8.11	This work
PDMS@ MIL-125-R7	5	435	63.0	45	3.04	This work
MIL-125-NH ₂ /PVP	5	435	26.1	15	1.29	This work
MIL-125- NH ₂ /N _x	5	435	32.3	18	1.97	This work
CAU-1-vale	1	200	100	650	3.29	[1]
p _{0.5} -CAU-1	1	200	100	350	1.55	[1]
p _{0.5} -CAU-1-vale	1	200	100	800	6.82	[1]

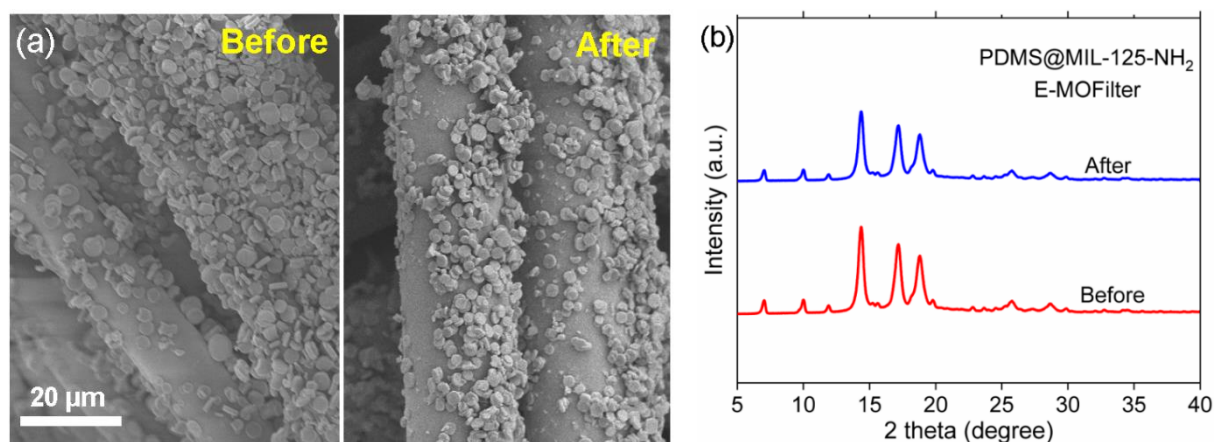


Fig. S7. Comparison of SEM images (a) and XRD patterns before and after the toluene adsorption tests on PDMS@MIL-125-NH₂ E-MOFilter (b).

References

- [1] X. Zheng, S. Liu, S. Rehman, Z. Li, P. Zhang, Highly improved adsorption performance of metal-organic frameworks CAU-1 for trace toluene in humid air via sequential internal and external surface modification, *Chem. Eng. J.* 389 (2020) 123424.
- [2] J.G. Nguyen, S.M. Cohen, Moisture-Resistant and Superhydrophobic Metal–Organic Frameworks Obtained via Postsynthetic Modification, *J. Am. Chem. Soc.* 132 (2010) 4560–4561.
- [3] Y. Isaka, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, Two-Phase System Utilizing Hydrophobic Metal–Organic Frameworks (MOFs) for Photocatalytic Synthesis of Hydrogen Peroxide, *Angew. Chem.* 131 (2019) 5456–5460.
- [4] Y. Sun, Q. Sun, H. Huang, B. Aguila, Z. Niu, J.A. Perman, S. Ma, A molecular-level superhydrophobic external surface to improve the stability of metal–organic frameworks, *J. Mater. Chem. A* 5 (2017) 18770–18776.
- [5] Y. Kawase, Y. Isaka, Y. Kuwahara, K. Mori, H. Yamashita, Ti cluster-alkylated hydrophobic MOFs for photocatalytic production of hydrogen peroxide in two-phase systems, *Chem. Commun.* 55 (2019) 6743–6746.
- [6] X. Li, L. Zhang, Z. Yang, Z. He, P. Wang, Y. Yan, J. Ran, Hydrophobic modified activated carbon using PDMS for the adsorption of VOCs in humid condition, *Sep. Purif. Technol.* 239 (2020) 116517.
- [7] K.-D. Kim, E.J. Park, H.O. Seo, M.-G. Jeong, Y.D. Kim, D.C. Lim, Effect of thin hydrophobic films for toluene adsorption and desorption behavior on activated carbon fiber under dry and humid conditions, *Chem. Eng. J.* 200–202 (2012) 133–139.

- [8] H.-B. Liu, B. Yang, N.-D. Xue, Enhanced adsorption of benzene vapor on granular activated carbon under humid conditions due to shifts in hydrophobicity and total micropore volume, *J. Hazard. Mater.* 318 (2016) 425–432.
- [9] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, A Facile and General Coating Approach to Moisture/Water-Resistant Metal–Organic Frameworks with Intact Porosity, *J. Am. Chem. Soc.* 136 (2014) 16978–16981.
- [10] G. Wen, Z. Guo, Facile modification of NH₂-MIL-125(Ti) to enhance water stability for efficient adsorptive removal of crystal violet from aqueous solution, *Colloids Surf. Physicochem. Eng. Asp.* 541 (2018) 58–67.
- [11] X. Zhang, X. Lv, X. Shi, Y. Yang, Y. Yang, 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.* 539 (2019) 152–160.
- [12] X. Zhang, Y. Yang, L. Song, J. Chen, Y. Yang, Y. Wang, Enhanced adsorption performance of gaseous toluene on defective UiO-66 metal organic framework: Equilibrium and kinetic studies, *J. Hazard. Mater.* 365 (2019) 597–605.
- [13] X. Zhang, Y. Yang, X. Lv, Y. Wang, N. Liu, D. Chen, L. Cui, Adsorption/desorption kinetics and breakthrough of gaseous toluene for modified microporous-mesoporous UiO-66 metal organic framework, *J. Hazard. Mater.* 366 (2019) 140–150.
- [14] P. Hu, X. Liang, M. Yaseen, X. Sun, Z. Tong, Z. Zhao, Z. Zhao, Preparation of highly-hydrophobic novel N-coordinated UiO-66(Zr) with dopamine via fast mechano-chemical method for (CHO-/Cl-)-VOCs competitive adsorption in humid environment, *Chem. Eng. J.* 332 (2018) 608–618.
- [15] Y. Zhang, X. He, Z. Zhu, W.-N. Wang, S.-C. Chen, Simultaneous removal of VOCs and PM_{2.5} by metal-organic framework coated electret filter media, *J. Membr. Sci.* 618 (2021) 118629.
- [16] S. Jafari, F. Ghorbani-Shahna, A. Bahrami, H. Kazemian, Adsorptive removal of toluene and carbon tetrachloride from gas phase using Zeolitic Imidazolate Framework-8: Effects of synthesis method, particle size, and pretreatment of the adsorbent, *Microporous Mesoporous Mater.* 268 (2018) 58–68.