

# HKUST-1 Synthesis in PET Track-Etched Membranes via Conversion of Deposited Cu for Carbon Dioxide Capture

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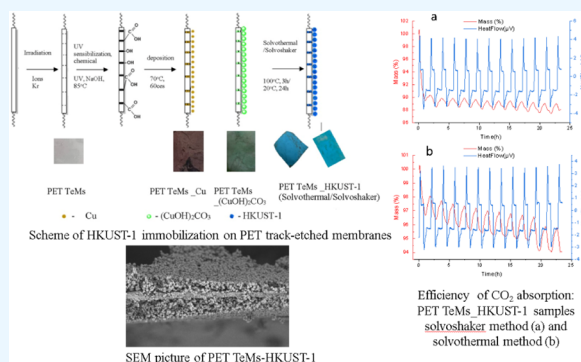
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**ABSTRACT:** Climate change remains one of the most critical global challenges, largely driven by the rise in atmospheric CO<sub>2</sub> levels. Effective strategies for capturing and utilizing CO<sub>2</sub> are crucial to mitigate its environmental impact. Metal–organic frameworks (MOFs), particularly HKUST-1 (MOF-199), are promising materials due to their high surface area, porosity, and tunable properties. In this study, HKUST-1 was successfully immobilized on polyethylene terephthalate (PET) track-etched membranes, leveraging the membranes' well-defined porosity and chemical stability. Membrane characterization via SEM revealed uniform coverage of octahedral HKUST-1 crystals with sizes ranging from 0.15  $\mu\text{m}$  (inside the pores) to 1.5–5  $\mu\text{m}$  (on the surface of the membrane). BET analysis of the PET TeMs-HKUST-1 composite membrane indicated a specific surface area of up to 382 m<sup>2</sup>/g. XRD confirmed the crystallinity of the HKUST-1 structure. The composite membranes exhibited CO<sub>2</sub> sorption capabilities, with an adsorption capacity of  $0.53 \pm 0.03$  mmol/g (after 1 h of adsorption) in the first cycle for the solvothermal method and  $0.31 \pm 0.02$  mmol/g (after 1 h of adsorption) for the solvoshaker method. Durability tests demonstrated a stable performance over 12 adsorption–desorption cycles. These results highlight the potential of PET TeMs-HKUST-1 composite membranes for scalable and efficient CO<sub>2</sub> capture, contributing to the development of sustainable solutions for addressing climate change.



## 1. INTRODUCTION

Climate change is one of the major environmental challenges of our time. The increasing levels of carbon dioxide (CO<sub>2</sub>) in the atmosphere, resulting from human activities, play a key role in intensifying the greenhouse effect and raising Earth's temperature, leading to climate changes and adverse consequences for natural ecosystems and society as a whole. Therefore, reducing CO<sub>2</sub> emissions has become a crucial task for ensuring stable and sustainable development.<sup>1–3</sup> The development of technologies to address this issue involves creating methods for capturing, storing, and using carbon dioxide. One of the most promising approaches is the use of sorption materials capable of efficiently capturing and separating CO<sub>2</sub> from other substances.<sup>4–6</sup> Among many such materials, metal–organic frameworks (MOFs) are of particular importance due to their unique properties. Metal–organic frameworks (MOFs) differ from other materials in their high adsorption capacity, attributed to their large surface area and porosity, enabling significant substance retention. Their chemical and thermal stabilities, as well as the ability to fine-tune their structure to enhance selectivity for CO<sub>2</sub>, make MOFs versatile and highly promising for use in carbon dioxide adsorption and storage systems. These advantages make MOFs key materials in developing new technologies to mitigate the

impacts of global climate change resulting from excessive release of CO<sub>2</sub> from anthropogenic sources.<sup>7–11</sup>

Metal–organic frameworks (MOFs) represent a class of crystalline porous materials composed of metal ions or clusters connected by organic ligands. This structure forms three-dimensional frameworks with highly organized pores whose size and properties can be tailored depending on the choice of components. The flexibility in selecting the geometry, size, and functionality of the components has enabled the creation of more than 20 000 different MOFs over the past decade.<sup>12–14</sup> The exponential growth of reticular chemistry research has led to challenges in extracting and synthesizing vast amounts of data from the literature. Zheng et al.<sup>15</sup> demonstrate how large language models (LLMs) can assist in streamlining this process by facilitating knowledge retrieval, synthesis optimization, and experimental automation. MOFs are formed from organic components, such as ditopic or polytopic organic carboxylates

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(and other negatively charged molecules), which bond with metal elements to create crystalline structures with a porosity exceeding 50% of their volume. The surface area of these MOFs typically ranges from 1000 to 10 000 m<sup>2</sup>/g, significantly surpassing that of traditional porous materials, including zeolites and carbon-based structures. Thanks to these properties, MOFs have become one of the best options for fuel storage and applications as catalysts.<sup>16,17</sup> Additionally, the pores of MOFs can capture and retain various molecules, making them effective sorbents for gases and liquids, including carbon dioxide capture. By modifying the pore sizes and the functional groups on the ligands, MOFs can be tailored for selective interactions with specific molecules, which is critical for separation and catalytic processes.<sup>18–20</sup>

HKUST-1 is one of the most extensively studied MOF structures. This structure features a secondary building unit with a distinctive paddlewheel-like configuration, where four carboxylate groups coordinate with two Cu<sup>2+</sup> ions and two solvent molecules, completing the coordination sphere. The labile solvent molecules can be removed, resulting in the formation of unsaturated metal centers. These open metal centers play a crucial role in adsorption, separation, and catalysis.<sup>21</sup>

Due to its porous structure, HKUST-1 possesses a significant specific surface area, making it an efficient sorbent for various molecules.<sup>9</sup> Additionally, HKUST-1 exhibits notable selectivity for carbon dioxide compared to other gases, such as methane or nitrogen.<sup>22</sup> These characteristics make HKUST-1 a promising material for applications in carbon capture and storage processes as well as in other fields requiring effective sorbents.

Track-etched membranes (TeMs) are characterized by a narrow pore size distribution, enhancing their selective properties and increasing the efficiency of separation processes. These membranes are produced from thin polymer films irradiated with heavy ions by using particle accelerators. A distinctive feature of TeMs is the regular pore structure, with the ability to adjust pore density per unit area by maintaining a narrow pore size range. This ensures high selectivity and specific operational efficiency of the membranes.<sup>23</sup> For instance, pore sizes can range from 50 nm to several tens of micrometers, with pore densities reaching from 10<sup>5</sup> to 10<sup>10</sup> per square centimeter. This structure allows for the tuning of membrane transport properties for various applications, including filtration and gas separation.<sup>24–26</sup> TeMs are typically fabricated from polymers such as poly(ethylene terephthalate) (PET) or polycarbonate (PC), which exhibit high mechanical strength and flexibility. When MOFs are deposited onto the surface of TeMs, a composite material is formed, where the robust polymer substrate supports the fragile crystalline MOF structure, preventing its degradation under external loads. It is well-known that track-etched membranes (TeMs) are used as templates for the formation of nanostructures.<sup>27–30</sup> The porous structure of TeMs, composed of channels, allows for precise control over the growth and morphology of structures to be synthesized inside the pores. A study on obtaining HKUST-1 inside the pores of TeMs using an automated LBL dip-coater has demonstrated promising results for gas separation.<sup>31</sup> We firmly believe that further research is essential to develop improved methods for synthesizing and securely anchoring HKUST-1 on PET TeMs, with a focus on enhancing its fixation and increasing its concentration to achieve a higher adsorption capacity.

A variety of synthesis methods have been explored to produce metal–organic frameworks (MOFs), each offering unique advantages and limitations.<sup>16</sup> In this study, solvothermal and solvoshaker methods were employed for the immobilization of HKUST-1 on PET TeMs. The solvothermal method, which involves high-temperature and high-pressure conditions in an autoclave, is well-known for yielding highly crystalline and well-defined MOF structures.<sup>32</sup> However, it requires long reaction times, precise temperature control, and specialized equipment, making large-scale production challenging.<sup>20</sup> On the other hand, the solvoshaker method involves room-temperature synthesis with continuous agitation, allowing for lower energy consumption, reduced synthesis time, and simplified scalability.<sup>33</sup> Despite these advantages, solvoshaker synthesis may result in lower crystallinity and weaker MOF adhesion to the membrane compared to the solvothermal approach.<sup>34</sup> By comparing these two methods, this study aims to determine the most effective strategy for fabricating PET TeMs-HKUST-1 composite membranes with optimal CO<sub>2</sub> adsorption properties.

The aim of this study is to develop and optimize methods for synthesizing HKUST-1 on PET TeMs to create composite materials with high sorption performance for carbon dioxide (CO<sub>2</sub>). HKUST-1 was immobilized on PET TeMs by first depositing copper microtubes in the channels, followed by their conversion into HKUST-1 using solvothermal and solvoshaker methods. These composites combine the high porosity and selectivity of MOFs with the mechanical strength and flexibility of polymer membranes, making them promising candidates for applications in gas separation and sorption systems.

## 2. EXPERIMENTAL PART

**2.1. Preparation of TeMs.** Track-etched membranes made of poly(ethylene terephthalate) (PET-TeMs) were prepared by irradiating 12 μm thick PET films (Mitsubishi Polyester Film) with <sup>84</sup>Kr<sup>15+</sup> ions using the DC-60 accelerator with an average energy of 1.75 MeV/nucleon and an ion density of 1 × 10<sup>8</sup> ions/cm<sup>2</sup>. The membranes were then subjected to photosensitization for 30 min on each side, followed by chemical treatment with 2.2 M NaOH at 85 °C for 180 s to produce membranes with pore sizes of approximately 300 nm.

**2.2. Oxidation of PET TeMs.** PET TeM samples measuring 5 × 7.5 cm were placed in a 100 mL dish, and hydrogen peroxide (37% v/v) was added to achieve the desired final concentration. The pH was maintained at 3.0 by adding a 3.0 M HCl solution.<sup>35,36</sup> The samples were kept in this solution for 5–10 s by occasional stirring.

**2.3. Chemical Deposition of Copper on PET TeMs.** The sensitization process involved immersing the samples in a solution containing 2 g of SnCl<sub>2</sub> and 2 mL of 37% HCl in 200 mL of water for 6 min, followed by thorough rinsing with hot water for 2–3 min. The samples were then activated by immersion in a solution of 0.1 g of PdCl<sub>2</sub> and 1 mL of 37% HCl in 100 mL of water for 6 min. The copper deposition was performed in a solution containing 7.63 g/L CuSO<sub>4</sub>·5H<sub>2</sub>O, 10.26 g/L EDTA, 5 mg/L sodium lauryl sulfate, and 8.14 g/L glyoxylic acid, adjusted to a pH of 12.65–13.49 with 12.0 M KOH. The reaction was conducted at a temperature of 70 °C for 60 s.<sup>37</sup>

**2.4. Synthesis of MOF-199 (HKUST-1) on PET TeMs.** The synthesis was based on the methodology developed by the

authors<sup>38</sup> with adaptations for PET TeMs-Cu. The copper-coated PET TeMs were immersed in a 0.1 M HCl solution to remove surface oxides and then rinsed with deionized water. The cleaned samples were pretreated in a solution of 2 mL NaHCO<sub>3</sub> (1 mol/L), 2 mL Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.05 mol/L), and 16 mL water for 24 h. Sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) acts as a strong oxidizing agent, introducing active functional groups (e.g., hydroxyl and carboxyl groups) on the PET surface to enhance the attachment of the MOF. Sodium bicarbonate (NaHCO<sub>3</sub>) maintains a mildly alkaline environment, promoting favorable conditions for surface oxidation. Next, the PET TeMs were soaked in a solution of 0.13 g trimesic acid, 23.5 mL ethanol, and 9 mL water for 24 h. The synthesis of HKUST-1 was then carried out using trimesic acid and copper nitrate in a molar ratio of 0.5:1, with DMF, ethanol, and water in a 1:1:1 volume ratio. The process was performed in an autoclave at 80–120 °C for 3–24 h (solvothetical method). Other samples of membranes were immersed in the reaction solution and agitated using a shaker for 24 h at 20 °C (solvothetical method). This approach allows for the formation of MOF crystals with a high degree of crystallinity and strong adhesion to the membrane surface.<sup>39</sup> Various synthesis parameters were investigated and are presented in Table 1.

**Table 1. Parameters Used in the Synthesis of Cu(NO<sub>3</sub>)<sub>2</sub>:H<sub>3</sub>BTC<sup>a</sup>**

| Number of recipes | Ratio Cu(NO <sub>3</sub> ) <sub>2</sub> :H <sub>3</sub> BTC | Time, h |
|-------------------|-------------------------------------------------------------|---------|
| 1                 | 0.2:0.1                                                     | 3       |
| 2                 | 0.2:0.1                                                     | 6       |
| 3                 | 0.2:0.1                                                     | 24      |
| 4                 | 0.05:0.025                                                  | 3       |
| 5                 | 0.05:0.025                                                  | 6       |
| 6                 | 0.05:0.025                                                  | 24      |

<sup>a</sup>Under each condition, the reaction was carried out at 100 °C (solvothetical) and 20 °C (solvothetical).

**2.5. CO<sub>2</sub> Capture by PET TeMs-HKUST-1.** Thermogravimetric analysis (TGA) was used to evaluate the amount of CO<sub>2</sub> adsorbed by the composite membranes containing HKUST-1. The adsorption test procedure consisted of three stages: degassing, adsorption, and desorption. The TeMs were placed in the sampler holder of the TGA. Degassing was performed at 150 °C for 60 min at a heating rate of 10 °C/min. The sample was then cooled to 25 °C, and the sample chamber was flushed with pure CO<sub>2</sub>, and CO<sub>2</sub> adsorption was conducted for 60 min. Following this, the temperature was increased to 150 °C to perform desorption, which lasted for 60 min.

**2.6. Characterization Methods.** Chemical changes before and after modification of the PET TeMs were measured by a Fourier Transform Infrared (FTIR) spectrometer (InfraLUM FT-08) with an ATR accessory (GradiATR, PIKE). Spectra recordings were conducted within the range of 400–4000 cm<sup>-1</sup>, utilizing 20 scans and a resolution of 2 cm<sup>-1</sup> at room temperature.

The study of the surface morphology as well as the elemental composition was carried out using scanning electron microscopy (SEM) on a Phenom ProX G6 scanning electron microscope (Thermo Fisher Scientific, Eindhoven, The Netherlands) with the possibility of energy-dispersive spectroscopy.

X-ray diffraction (XRD) patterns of the samples were recorded by using a Rigaku SmartLab diffractometer under standard conditions with a Cu K $\alpha$  radiation source ( $\lambda$  = 1.5406 Å). The diffraction patterns were recorded in Bragg–Brentano geometry ( $\theta$ – $\theta$  scan) with a step size of 0.025° and a scanning speed of 3°/min.

The water contact angle (CA) was measured by using a digital microscope with 1000 $\times$  magnification (Suzhou, China) at room temperature. The CA was evaluated by using the static drop method. The measurement was consecutively repeated three times at different positions. The CA was found using ImageJ 1.4.3.67 software with Drop Analysis/Drop Snake plugins.

Thermogravimetric analysis (TGA) of the samples was performed using a Themys One thermogravimetric analyzer (Setaram). The TGA was conducted in an argon atmosphere with a heating rate of 10 °C/min over a temperature range of 30–700 °C. Data analysis included recording sample mass changes (TGA) and thermal effects (HeatFlow), which were synchronously monitored. The results were used to study the thermal stability, decomposition processes, and adsorption–desorption behavior.

The surface area of the samples was measured based on N<sub>2</sub> adsorption isotherms using a V-Sorb 2800P BET surface area and porosity analyzer (Gold App Instruments Corp., China).

The pore size of TeMs was measured by the gas flow rate method at a pressure of 20 kPa.

### 3. RESULTS AND DISCUSSION

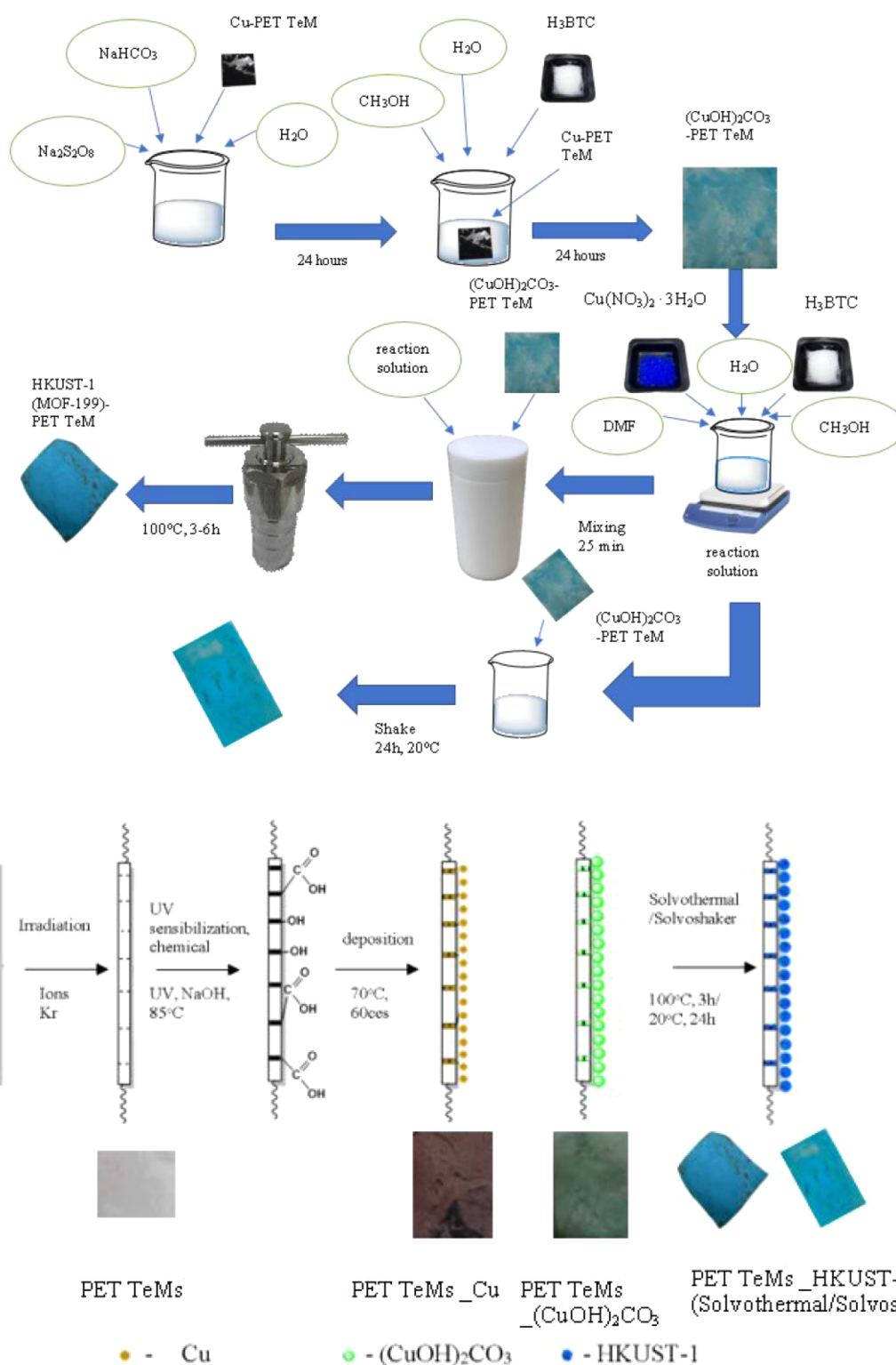
**3.1. Synthesis of HKUST-1 on PET TeMs.** A schematic representation of the synthesis of HKUST-1 on PET TeMs is shown in the scheme below and in Figure 1 following the experimental procedure outlined before.

Initially, the pore diameter of PET TeMs before and after copper deposition and its conversion to malachite and HKUST-1 was controlled by the gas permeability method. Thus, for the initial membranes, the pore diameter was 300 nm; after copper deposition, it decreased to 195 nm; after conversion to malachite, it was 93 nm; after the solvothetical method (HKUST-1), it was 89 nm; and after solvothetical (HKUST-1), it was 86 nm. A decrease in gas permeability indicates a gradual filling of the pores, but nevertheless, such membranes are capable of passing gas and can be used in further applications. The slight difference between the solvothetical and solvothetical methods indicates a thicker layer formed inside the channels for the solvothetical method.

Figure 2 shows the FTIR spectra after the process of converting copper microtubes into malachite and HKUST-1 under different conditions.

In the FTIR spectra of PET TeMs and PET TeMs-Cu and after its conversion to malachite (Figure 2a), the appearance of Cu–O absorption bands in the modified membranes indicates the formation of coordination bonds between copper ions and the functional groups of the polymer. The presence of the CO<sub>3</sub><sup>2-</sup> absorption band in the spectrum of the membrane after conversion to malachite confirms the presence of this compound in the composite.

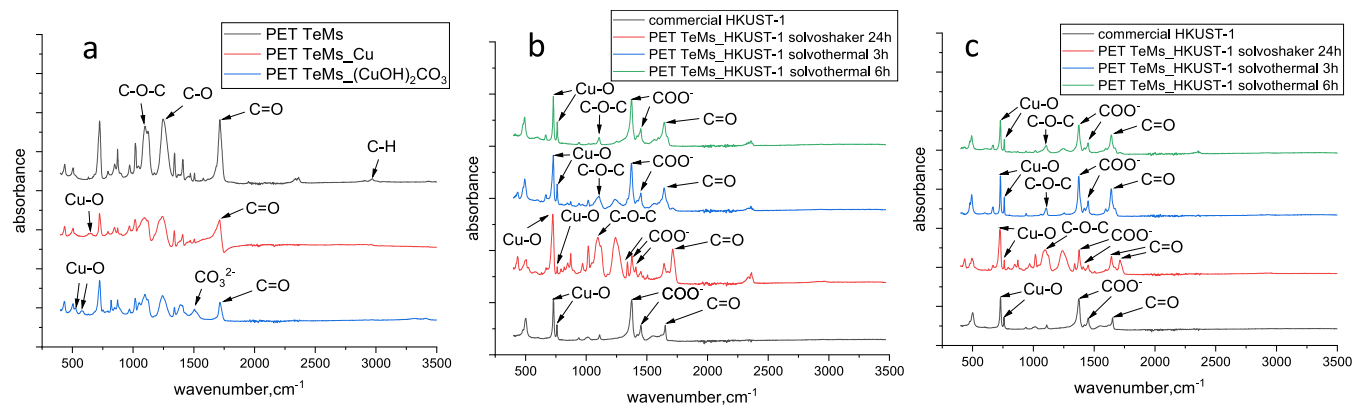
Figure 2b,c presents the FTIR spectra of four HKUST-1 samples synthesized using different methods and processing durations and also the spectrum of commercial HKUST-1 for comparison. All spectra exhibit characteristic bands indicative of the presence of a metal–organic framework structure. In the 500–700 cm<sup>-1</sup> region, bands corresponding to Cu–O



**Figure 1.** Scheme of synthesis of HKUST-1 by solvothermal/solvoshaker methods\*. \*Photograph of samples courtesy of Dias D. Omertassov. Copyright 2025.

vibrations are observed, confirming the presence of metallic centers within the framework. The 1400–1600  $\text{cm}^{-1}$  range is characterized by bands associated with vibrations of  $\text{COO}^-$  groups interacting with copper, indicating the successful formation of coordination bonds with trimesic acid. These bands are present in all samples, but their intensity varies, depending on the synthesis method and processing time. The

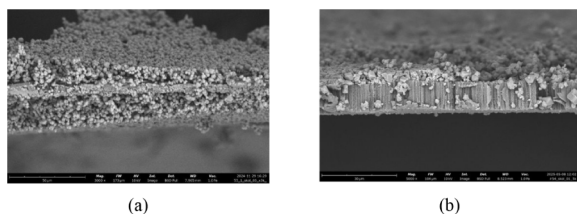
FTIR spectra obtained in our study were analyzed and compared to previously published data for HKUST-1 (MOF-199). The presence of strong stretching vibrations of carboxylate groups around 1400–1600  $\text{cm}^{-1}$ , as observed in our spectra, is consistent with the characteristic  $\text{COO}^-$  vibrations reported in the literature,<sup>40,41</sup> confirming the coordination between copper ions and the carboxylic groups



**Figure 2.** FTIR of PET TeMs, PET TeMs-Cu, and after conversion to malachite (a), and after synthesis of HKUST-1 under different conditions, obtained at a ratio of Cu(NO<sub>3</sub>)<sub>2</sub>:H<sub>3</sub>BTC = 0.2:0.1 g (b) and 0.05:0.025 g (c).

of trimesic acid. It is also clearly seen that when using the solvothermal method, compared with solvoshaking, the peaks related to the PET TeMs (such as the bands around  $\sim 1710$  cm<sup>-1</sup> and  $\sim 1100$ – $1250$  cm<sup>-1</sup>) become less intense, while the peaks related to HKUST-1 (Cu–O and COO<sup>-</sup> groups) exhibit higher intensity. This observation suggests that the PET substrate is more extensively covered by the HKUST-1 phase when the solvothermal method is applied, resulting in attenuation of the polymer's characteristic signals and enhancement of MOF-related features. These spectral differences indicate the formation of a thicker and more uniform HKUST-1 layer on the membrane surface under solvothermal conditions, which aligns with expectations based on synthesis duration and conditions. The difference in the thickness of the deposited layer is also confirmed by SEM.

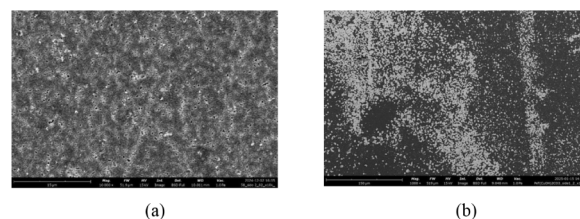
The SEM cross-section images in Figure 3 of the PET membrane–HKUST-1 obtained by solvothermal and solvosh-



**Figure 3.** SEM images of the cross-section of PET TeMs\_HKUST-1 solvothermal method (a) and solvoshaker method (b).

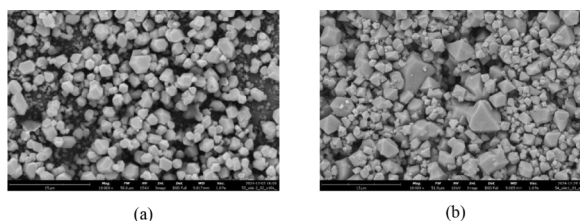
aker methods show the presence of a layered substrate structure. On the membrane surface, octahedral crystals corresponding to the HKUST-1 structure are visible, attached to the substrate with the average crystal size being  $2.6 \mu\text{m}$  for the solvothermal method. The octahedral crystals exhibit well-defined facets, indicating high crystallinity. For the solvoshaker method, the formation of both small and large particles with a wide range of sizes from  $1.5$  to  $5 \mu\text{m}$  is observed. Additionally, the average crystal size inside the pores is  $0.15 \mu\text{m}$ , indicating that HKUST-1 crystals are present inside the pores of PET TeMs as shown in Figure 3 for both the solvoshaker and solvothermal methods. Also, the difference between these two methods is the thickness of the HKUST-1 layer formed on the membrane surface: solvoshaker method: around  $5 \mu\text{m}$ ; solvothermal method:  $11 \mu\text{m}$ . This also confirms the observations obtained with ATR-FTIR.

The SEM images in Figure 4 show the PET TeMs-Cu surface and after conversion to PET TeMs-(CuOH)<sub>2</sub>CO<sub>3</sub>. A



**Figure 4.** SEM analysis of the PET TeMs\_Cu surface (a) and PET TeMs-(CuOH)<sub>2</sub>CO<sub>3</sub> surface (b).

change in the surface morphology and the formation of fluffy malachite crystals of various sizes, which are both on the surface and clogging the pores of the membrane, are clearly visible. The SEM images in Figure 5 show characteristic

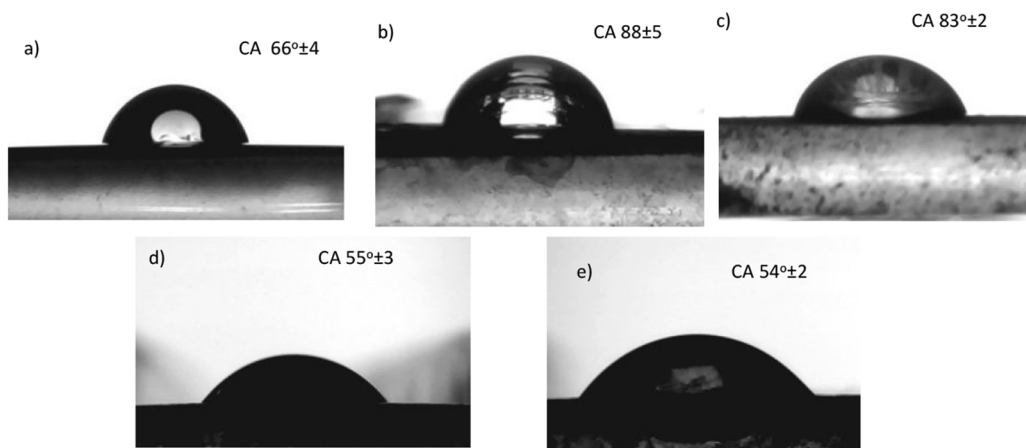


**Figure 5.** SEM image of the PET TeM\_HKUST-1 surface solvothermal method (a) and solvoshaker method (b).

octahedral crystals typical of the HKUST-1 MOF structure on the surface of PET TeMs.<sup>32</sup> The octahedral crystals are evenly distributed across the substrate surface, with some of them forming aggregates. The well-defined crystal facets reflect the high degree of crystallinity of the HKUST-1 material. The crystal sizes of HKUST-1 obtained by the solvothermal method are more uniform and are around  $2.6 \mu\text{m}$ , while HKUST-1 obtained by the solvoshaker method has a wider size distribution from  $1.5$  to  $5 \mu\text{m}$ . The SEM results obtained in our study (Figures 3–5) were compared with previously published data on the morphology and structure of HKUST-1 (MOF-199) materials.<sup>41–43</sup> The average crystal sizes observed in our samples ( $\sim 2.6 \mu\text{m}$  on the surface and  $\sim 0.15 \mu\text{m}$  inside the pores, solvothermal method) align well with those reported for HKUST-1 synthesized under comparable conditions.

Table 2. EDX Analysis of the Samples

| Sample                                        | Atomic concentration, % |              |              |              |
|-----------------------------------------------|-------------------------|--------------|--------------|--------------|
|                                               | C                       | O            | N            | Cu           |
| PET TeMs                                      | 80.24 ± 6.83            | 19.76 ± 3.21 | -            | -            |
| PET TeMs_Cu                                   | 56.17 ± 5.21            | 25.52 ± 3.10 | 6.11 ± 1.52  | 12.20 ± 1.41 |
| PET TeMs_-(CuOH) <sub>2</sub> CO <sub>3</sub> | 39.42 ± 4.42            | 45.92 ± 3.45 | -            | 14.66 ± 1.56 |
| PET TeMs_HKUST-1 (solvothral method)          | 56.02 ± 5.12            | 33.60 ± 3.54 | 4.46 ± 1.32  | 5.92 ± 0.56  |
| PET TeMs_HKUST-1 (solvoshaker method)         | 42.07 ± 4.56            | 33.33 ± 3.11 | 17.22 ± 3.51 | 7.38 ± 0.43  |



**Figure 6.** Contact angle (CA) of the original PET membrane (a), PET TeMs\_Cu (b), PET TeMs\_-(CuOH)<sub>2</sub>CO<sub>3</sub> (c), PET TeMs\_HKUST-1 (solvothral method) (d), and PET TeMs\_HKUST-1 (solvoshaker method) (e).

The surface elemental composition of the samples was evaluated using EDX, and the atomic percentages of carbon (C), oxygen (O), nitrogen (N), and copper (Cu) are summarized in Table 2 (EDX spectra are presented in Figure S1, mapping on Figure S2). The PET TeMs exhibited a typical elemental distribution: carbon (80.24%) and oxygen (19.76%). After copper deposition, the copper signal (12.21%) was observed, and nitrogen (6.11%) appeared due to the presence of EDTA during the reaction. After the conversion of Cu to malachite, nitrogen was removed. The samples functionalized with HKUST-1 showed nitrogen and copper peaks due to the use of copper(II) nitrate as the metal precursor in both solvothral and solvoshaker synthesis methods. Additionally, an unlabeled peak corresponding to gold (Au) was observed in all EDX spectra (at around 2.12 eV). This signal originates from the thin gold layer (~1.0–3.0 at. %) sputter-coated onto the membrane surfaces prior to analysis. The presence of gold was not quantified since it does not represent the actual membrane composition.

The contact angle (CA) was measured by using the static drop method, and the results are presented in Figure 6.

The oxidized surface of the PET TeMs exhibits a moderately hydrophobic character. CA of 66° indicates a certain degree of hydrophobicity. The deposited Cu (copper) coating demonstrates a CA of 88° higher than that of the oxidized PET membrane, indicating an increase in hydrophobicity. After treatment with (CuOH)<sub>2</sub>CO<sub>3</sub> (malachite), the surface shows an average CA of 83°. This suggests that the surface retains hydrophobic properties similar to those of the copper coating; however, the slight reduction in the contact angle is likely due to the presence of polar groups. The film coated with HKUST-1 exhibits the lowest CA, ranging between 54° and 55°, indicating significant hydrophilicity. This result aligns with previous reports on HKUST-1.<sup>44–46</sup> Although no direct

humidity tolerance tests were performed in this study, the observed contact angle suggests that the PET TeMs-HKUST-1 composite may exhibit reduced CO<sub>2</sub> sorption performance in high-humidity environments. Further studies are required to evaluate this behavior under the relevant operating conditions.

The surface area and pore size of the obtained samples were studied using nitrogen adsorption isotherms (77K). The results are presented in Table 3.

Table 3. Results of BET Analysis of the Samples

| Sample                                        | Specific area (m <sup>2</sup> /g) | Langmuir Square (m <sup>2</sup> /g) | Average pore size BJH, (nm) | Average pore volume BJH (cm <sup>3</sup> /g) |
|-----------------------------------------------|-----------------------------------|-------------------------------------|-----------------------------|----------------------------------------------|
| PET TeMs                                      | 1.73                              | 2.58                                | 30.85                       | 0.02                                         |
| PET TeMs_Cu                                   | 9.25                              | 17.68                               | 17.66                       | 0.07                                         |
| PET TeMs_-(CuOH) <sub>2</sub> CO <sub>3</sub> | 107.84                            | 118.06                              | 13.81                       | 0.09                                         |
| PET TeMs_HKUST-1 (solvothral method)          | 382.76                            | 517.98                              | 15.57                       | 0.37                                         |
| PET TeMs_HKUST-1 (solvoshaker method)         | 99.31                             | 142.68                              | 9.82                        | 0.04                                         |
| HKUST-1                                       | 813.12                            | 928.39                              | 11.23                       | 0.084                                        |

The BET analysis revealed a significant increase in specific surface area and pore volume as a result of the stepwise modification of PET TeMs. The pristine PET TeMs exhibited a low specific surface area of 1.73 m<sup>2</sup>/g. Upon modification with copper deposition (PET TeMs\_Cu) and subsequent conversion to the malachite phase (PET TeMs\_-(CuOH)<sub>2</sub>CO<sub>3</sub>), the surface area increased substantially to 107.84 m<sup>2</sup>/g. The growth of HKUST-1 on the membranes via

the solvothermal method resulted in a further increase in the surface area to 382.76 m<sup>2</sup>/g and a pore volume of 0.37 cm<sup>3</sup>/g. In contrast, the solvoshaker method led to a surface area of 99.31 m<sup>2</sup>/g suggesting that the solvothermal method is more effective for growing a thick (which also comes from SEM images and FTIR-ATR) MOF layer under elevated temperature and pressure conditions. These differences may be attributed to the improved nucleation and crystallinity of HKUST-1 in solvothermal conditions compared to the less intense solvoshaker approach. Regarding initial HKUST-1 powder, surface area of 813.12 m<sup>2</sup>/g can be compared previously reported data in the literature,<sup>47,48</sup> where HKUST-1 surface areas typically range from 700 to over 1200 m<sup>2</sup>/g, depending on synthesis conditions, solvent system, activation method, and crystallinity.

Figure 8 presents the XRD patterns of the studied samples obtained at room temperature. A powder diffractogram of the HKUST-1 material, previously synthesized by the hydrothermal method in powder form, was used as a reference. The phase composition was determined using the PDF database. For comparison purposes, the PDF card of the HKUST-1 material (PDF 00-065-1028, space group *Fm*3̄*m*) is also provided. Phase analysis based on the recorded diffractograms for the PET membrane samples with HKUST-1 (solvoshaker, solvothermal) shows that the films contain phases of PET and HKUST-1. This is evidenced by the intense reflections of PET (100), (110), (2–30) and the reflections of HKUST-1 (222), (220), (111), (400), and others. The positions of the reflections in the composite samples and the powder phase of HKUST-1 remain unchanged, indicating identical lattice parameters and interplanar spacings. For the PET membrane sample with copper (Cu), the presence of a (111) reflection from the copper phase with a face-centered cubic lattice is noted.

The XRD results presented in Figure 7 were compared with the published XRD patterns of MOF-199 and HKUST-1, as shown in the studies.<sup>41,43,49</sup> The characteristic diffraction peaks observed in our samples (including the PET\_TeMs\_HKUST-1 samples synthesized via solvoshaker and solvothermal

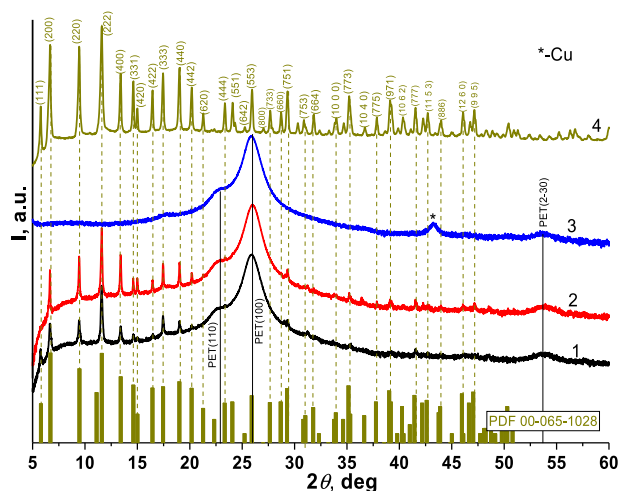
methods) match well with those of the hydrothermally synthesized HKUST-1 powder and the reference PDF card. This confirms the successful formation of the HKUST-1 phase with consistent lattice parameters and interplanar spacings across all synthesized materials. In addition, the PET\_TeMs\_Cu sample exhibits a peak corresponding to the (111) reflection of metallic copper, consistent with standard copper XRD patterns, which is also compared with previous studies.<sup>50,51</sup> These comparisons further validate the structural identity and crystalline quality of the synthesized HKUST-1.

Figure 8a–f presents the thermograms of PET TeMs, HKUST-1, membranes with Cu, (CuOH)<sub>2</sub>CO<sub>3</sub>, and HKUST-1 synthesized using solvothermal and solvoshaker methods. The single-stage weight loss of copper containing samples shows multistage degradation upon the inclusion of MOFs.

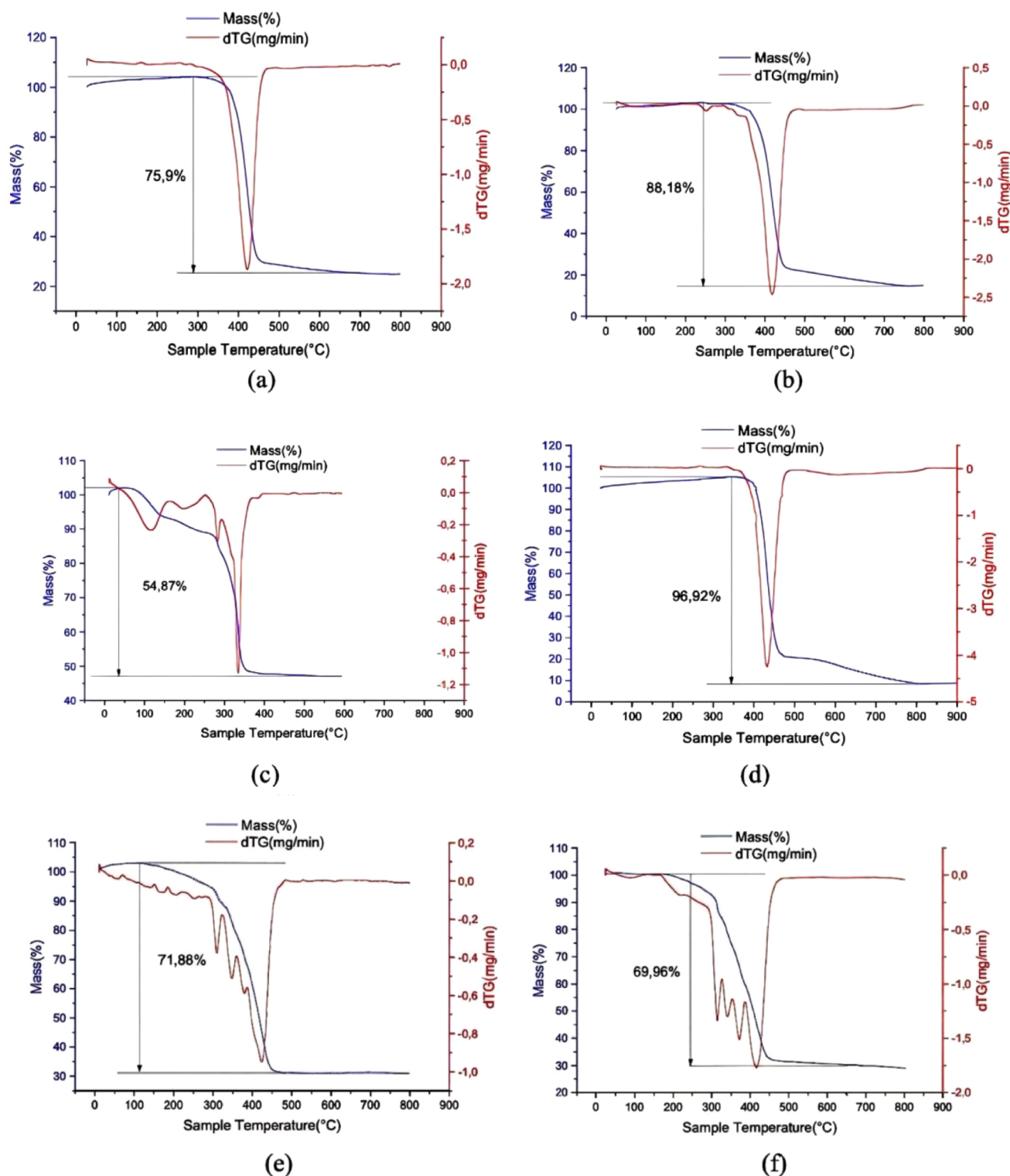
In Figure 8a, the sample's mass remains stable up to 300 °C, indicating the absence of significant decomposition processes. Between 300 and 400 °C, a decrease in mass is observed on the TG curve, marking the initial stage of polymer (PET) thermal decomposition. Between 400 and 500 °C, a sharp mass loss of 79.9% occurs, indicating active decomposition of organic components. From 500 to 800 °C, the mass remains nearly constant after the decomposition is complete. The residual mass (~25–30%) is attributed to the presence of inorganic remnants, in this case, copper (Cu) or its oxides (CuO). The single-step nature of the decomposition curve indicates that the main decomposition process occurs within a relatively narrow temperature range. A very similar behavior has been observed for PET TeMs containing (CuOH)<sub>2</sub>CO<sub>3</sub> as indicated in Figure 8b. While the thermograms of the PET TeMs-Cu and PET TeMs-malachite samples are very similar, they show significant changes for the PET TeMs-HKUST-1 samples.

In Figure 8c,e,f, all samples exhibit a multistep decomposition occurring in the range of 250–400 °C, which are quite similar to those of HKUST-1. The first mass loss is associated with the removal of physically adsorbed water and part of the solvent from the pores. The second and third mass losses correspond to the step destruction of the organic ligand (trimesic acid). Finally, the last mass loss corresponds to the breaking of PET polymer chains, as shown in Figure 9d, which shows the typical mass loss of PET\_TeMs after 400 °C.<sup>52</sup> The differences between the synthesis methods (solvoshaker and solvothermal) are reflected in the intensity and overall mass loss.

**3.2. CO<sub>2</sub> Capture by PET TeMs-HKUST-1.** Uptake and release of CO<sub>2</sub> by the composite membranes were performed by following the procedure described in Section 2.5. Membranes with immobilized HKUST-1 were used for CO<sub>2</sub> sorption/desorption analysis via TGA.<sup>53,54</sup> The graph in Figure 9 demonstrates 12 distinct cycles of CO<sub>2</sub> sorption–desorption that was performed during more than 20 h. The amplitude of the mass change remains stable, confirming the sustainability of the sorbent material over multiple uses. The CO<sub>2</sub> absorption process, which took 60 min, is accompanied by an increase in mass. After absorption was completed, heating of the samples to 150 °C started, and a decrease in mass was observed, indicating CO<sub>2</sub> desorption in 60 min. The mass changes fluctuate between 97–118% (solvothermal) and 92–118% (solvoshaker) relative to the first cycle, demonstrating the reproducibility of the sorption–desorption cycles and the stability of the membranes with HKUST-1.



**Figure 7.** Comparison of XRD of representative samples and the PDF card of the HKUST-1 crystalline phase. 1: PET TeMs\_HKUST-1 sample (solvoshaker method), 2: PET TeMs\_HKUST-1 sample (solvothermal method), 3: PET TeMs\_Cu sample, and 4: HKUST-1 synthesized by the hydrothermal method in powder form.



**Figure 8.** Thermogravimetric analysis results of the samples: (a) PET TeMs\_Cu, (b) PET TeMs\_(CuOH)<sub>2</sub>CO<sub>3</sub>, (c) HKUST-1, (d) PET\_TeMs, (e) PET TeMs\_HKUST-1 (solvo-shaker method), and (f) PET TeMs\_HKUST-1 (solvo-thermal method).

The adsorption capacity (AC) was calculated by using the following equation:

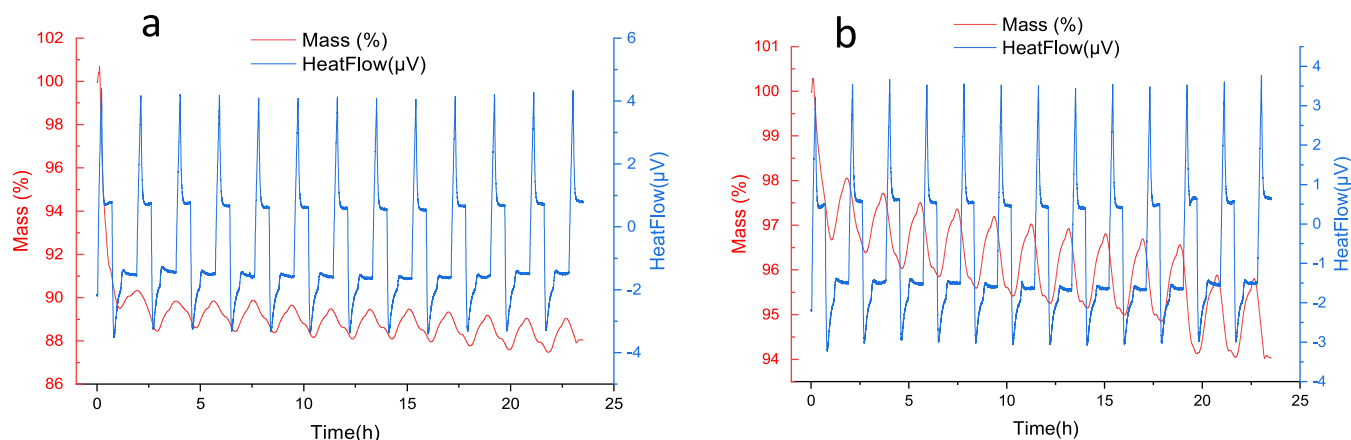
$$AC = \frac{m_1/44.009}{m_0}$$

AC — adsorption capacity, mmol/g  
 $m_0$  — mass of the membrane, g

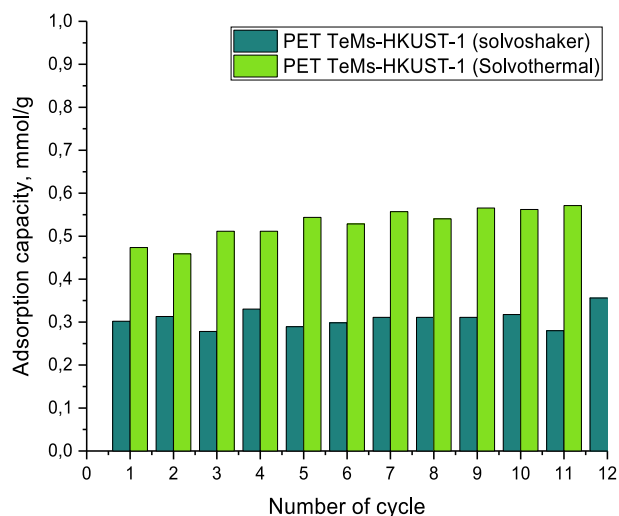
44.009 — molar mass of CO<sub>2</sub>, mg/mmol

$m_1$  — mass of adsorbed CO<sub>2</sub>, mg

Figure 10 illustrates the adsorption capacity of PET TeMs-HKUST-1 materials synthesized using two different methods: solvo-shaker (black bars) and solvo-thermal (red bars) over 12 adsorption–desorption cycles. The average adsorption capacity for PET TeMs-HKUST-1 prepared using the



**Figure 9.** Results of 12 sorption-desorption cycles of PET TeMs\_HKUST-1 samples: solvoshaker method (a) and solvothermal method (b).



**Figure 10.** Results of the adsorption capacity of PET membranes with HKUST-1 obtained by solvoshaker method and solvothermal method at 12 cycles.

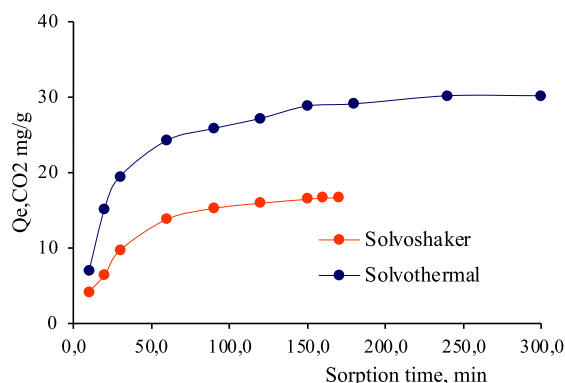
solvothermal method is  $0.53 \pm 0.03$  mmol/g, while that obtained via the solvoshaker method is  $0.31 \pm 0.02$  mmol/g. Throughout the 12 cycles, both samples maintain relatively stable performance, with fluctuations in adsorption capacity remaining within 97–118% (solvothermal) and 92–117%

(solvoshaker) relative to the first cycle. This indicates good reusability and structural stability of the composites under repeated use conditions.

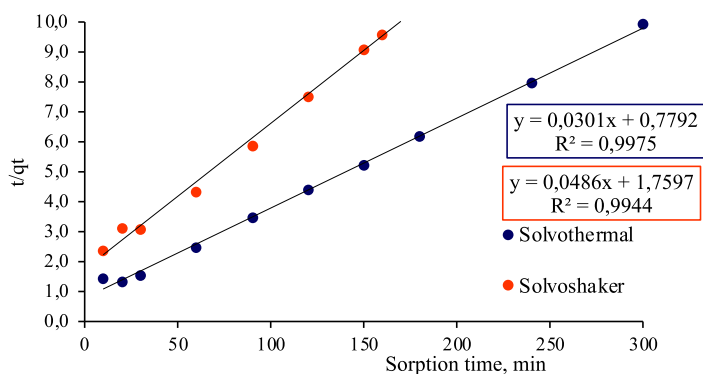
The observed differences between the synthesis methods suggest a more efficient sorption-desorption performance for the samples obtained via the solvothermal method. This enhanced efficiency can be attributed to their larger specific surface area, as confirmed by BET analysis, and the greater thickness of the HKUST-1 layer, as revealed by SEM imaging.

In order to evaluate the selectivity of the  $\text{CO}_2$  sorption in relation to the  $\text{N}_2$  sorption, gravimetric TGA was also estimated. The adsorption capacity of PET TeMs-HKUST-1 (solvoshaker methods) is  $0.099 \pm 0.015$  mmol/g (1 h of adsorption), while that of PET TeMs-HKUST-1 (solvothermal methods) is  $0.102 \pm 0.012$  mmol/g (1 h of adsorption). Thus, the ratio of the adsorption capacity of  $\text{CO}_2$  to the adsorption capacity of  $\text{N}_2$  is 3.1 for the solvoshaker method and 5.2 for the solvothermal method, which demonstrates the dominant sorption of carbon dioxide compared to nitrogen. However, it should be noted that more accurate measurements of selectivity on real gas mixtures or using the IAST theory are required.

The  $\text{CO}_2$  adsorption performance of PET TeMs-HKUST-1 is influenced by the method of HKUST-1 synthesis. The method of synthesis affects both the morphology of HKUST-1 and its concentration on the surface and inside the pores of



(a)



(b)

**Figure 11.** Adsorption kinetic for  $\text{CO}_2$  for PET TeMs-HKUST-1 solvoshaker and solvothermal methods (a) and linearized pseudo-second-order kinetic model for  $\text{CO}_2$  adsorption (b).

Table 4. The CO<sub>2</sub> Adsorption Capacities Obtained in Our Study and in Selected Works

| Study                                 | Pressure (bar) | Temperature (°C) | Material                               | Adsorption capacity (mmol/g) | Regeneration | Notes                                                                    |
|---------------------------------------|----------------|------------------|----------------------------------------|------------------------------|--------------|--------------------------------------------------------------------------|
| This study (solvoshaker method)       | 1              | 25               | PET TeMs-HKUST-1                       | 0.31 (1 h)<br>0.38 (5 h)     | 12 cycles    | High cycling stability                                                   |
| This study (solvothermal method)      | 1              | 25               | PET TeMs-HKUST-1                       | 0.53 (1 h)<br>0.69 (5 h)     | 12 cycles    | High cycling stability                                                   |
| Shang et al. (2020) <sup>58</sup>     | 1              | 25               | GO/HKUST-1 composite                   | 1.526                        | Not reported | Graphene oxide-based material                                            |
| Zhao et al. (2014) <sup>59</sup>      | 5              | 32               | HKUST-1 at atmospheric pressure        | 1.8                          | Not reported | Moderate adsorption at 32 °C                                             |
| Mu et al. (2018) <sup>34</sup>        | 1              | 27               | HKUST-1 1 (nanoscale, mild conditions) | 1.84                         | Not reported | Smaller particle size improves performance                               |
| Ho et al. (2022) <sup>33</sup>        | 1              | 30               | Solvent-free HKUST-1                   | 1.7                          | 5 cycles     | Green synthesis approach                                                 |
| Mu et al. (2018) <sup>34</sup>        | 1              | 27               | GO/HKUST-1 composite                   | 2.5                          | Not reported | increased surface area and improved hydrophilicity                       |
| Girimonte et al. (2024) <sup>60</sup> | 1              | -                | Ceramic foams/HKUST-1                  | 0.4                          | Not reported | Sustainability, regenerative cycling, scalability                        |
| Fateminia et al. (2023) <sup>61</sup> | 0.82           | 27               | core/shell Nylon 6,6/La-TMA            | 0.219                        | Not reported | MOF-shell nanocomposite fiber obtained by coaxial electrospinning        |
| Sneddon et al. (2017) <sup>62</sup>   | Not reported   | 30               | EDA-PVC/SBA-15                         | 0.54                         | Not reported | 1:1 CO <sub>2</sub> /N <sub>2</sub> mixtures; full regeneration at 75 °C |

PET TeMs. From the SEM images presented in Figures 3 and 5, it is seen that the solvoshaker method led to the presence of smaller crystals (and also together with large ones) in comparison to the solvothermal method. Moreover, a key morphological factor affecting the CO<sub>2</sub> sorption is crystal coverage. As seen in the SEM images, solvothermal synthesis produces a more continuous thick HKUST-1 layer (mass increase is 18.56%), potentially reducing accessibility to deeper sorption sites within the membrane. In contrast, solvoshaker synthesis results in a thinner layer of HKUST-1 (mass increase is 7.75%). These differences explain why solvothermal-synthesized membranes exhibited a higher initial CO<sub>2</sub> adsorption capacity (0.53 mmol/g) compared to solvoshaker samples (0.31 mmol/g) after 1 h of adsorption.

Figure 11a illustrates the kinetic profiles of CO<sub>2</sub> adsorption on PET TeMs-HKUST-1 composites synthesized by using solvothermal and solvoshaker methods. The adsorption capacity is plotted as a function of contact time up to 300 min for the solvothermal method and up to 170 min for the solvoshaker method (since above 170 min saturation occurred and the adsorption capacity did not increase up to 300 min). Both materials exhibit a typical two-phase kinetic behavior: a rapid initial uptake followed by a slower approach to equilibrium.

The solvothermal sample demonstrates a significantly higher adsorption capacity, reaching approximately 30.2 mg/g (0.69 mmol/g) after 5 h of sorption, while the solvoshaker sample plateaus at around 16.7 mg/g (0.38 mmol/g). Figure 11b presents the linearized form of the pseudo-second-order kinetic model for the adsorption of CO<sub>2</sub> for both samples. The plots display the relationship between  $t/q_t$  and sorption time  $t$ , allowing the determination of kinetic parameters.

Both methods show a strong linear correlation with high regression coefficients:  $R^2 = 0.9975$  for the solvothermal sample and  $R^2 = 0.9944$  for the solvoshaker sample, confirming the applicability of the pseudo-second-order model. The slope and intercept of the fitted lines were used to calculate the equilibrium adsorption capacity  $q_e$  and the pseudo-second-order rate constant  $k_2$ . The solvothermal method showed an adsorption capacity  $q_e = 33.22$  mg/g and a rate constant  $k_2 =$

$1.16 \times 10^{-3}$  g/(mg·min). The solvoshaker sample yielded a lower capacity ( $q_e = 20.58$  mg/g) and a higher rate constant ( $k_2 = 1.34 \times 10^{-3}$  g/(mg·min)) in comparison with the solvothermal method. These findings indicate that while the solvoshaker method provides a little faster kinetics, the solvothermal approach ensures a higher sorption capacity, due to the improved structural properties of the composite, as was mentioned above.

Recent studies have explored various strategies to enhance the CO<sub>2</sub> sorption capacity and stability of HKUST-1-based materials. For example, HKUST-1 composites incorporating pyrolyzed byproducts demonstrated improved water stability and CO<sub>2</sub> adsorption efficiency.<sup>55</sup> Similarly, graphene oxide (GO)-modified HKUST-1 exhibited enhanced CO<sub>2</sub> uptake due to increased surface area and improved hydrophilicity.<sup>56</sup> Another study focused on HKUST-1 templated with polyethylene glycol, leading to an unusually large microporous structure that enhanced CO<sub>2</sub> and CH<sub>4</sub> separation performance.<sup>9,57</sup> Additionally, a one-step hydrothermal synthesis of monolithic HKUST-1 was developed to simplify the fabrication process while maintaining high adsorption efficiency.<sup>57</sup> To evaluate the efficiency of the synthesized PET TeMs-HKUST-1 composites, we compared our results to previously reported CO<sub>2</sub> adsorption capacities of similar MOF-based materials (Table 4).

These findings suggest that PET TeMs-HKUST-1 composite membranes synthesized via the solvoshaker method offer a competitive alternative to existing MOF-based materials, combining high adsorption efficiency, scalability, and energy efficiency. Future research should focus on optimizing reaction conditions to further enhance MOF adhesion and crystallinity, thereby improving material performance, as well as conducting research on the selectivity of CO<sub>2</sub> separation in relation to other gases.

#### 4. CONCLUSIONS

This study successfully demonstrates the synthesis of HKUST-1 on PET track-etched membranes by using solvothermal and solvoshaker methods. The immobilization of HKUST-1 on PET membranes resulted in composite materials with high

crystallinity and good sorption properties. SEM analysis confirmed the formation of uniform octahedral HKUST-1 crystals, evenly distributed across the membrane surface as well as inside the channels of the membrane. XRD analysis further validated the integrity of the crystalline structure, while BET measurements revealed a significant surface area enhancement compared with uncoated PET membranes.

In this work, sorption studies highlighted the CO<sub>2</sub> adsorption and regeneration performance of these composites. The solvoshaker method achieved stable adsorption capacities at  $0.31 \pm 0.02$  mmol/g (1 h of adsorption), and the solvothermal method exhibited an adsorption capacity of  $0.53 \pm 0.03$  mmol/g (1 h of adsorption) with high regeneration efficiency after 12 cycles of sorption–desorption, indicating excellent cycling stability. These results underscore the material's durability and effectiveness in repeated CO<sub>2</sub> capture cycles. Overall, the synthesized PET TeMs–HKUST-1 composites represent a promising solution for scalable CO<sub>2</sub> capture, combining the advantages of metal–organic frameworks with the structural flexibility and stability of polymer membranes.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.5c01493>.

EDX spectra of the samples and mapping from EDX analysis (PDF)

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vision, writing—review and editing. I.V.K.: Conceptualization, supervision, writing—review and editing, project administration, funding acquisition.

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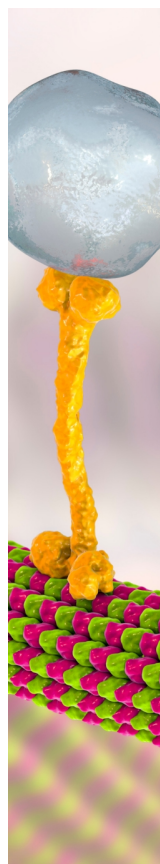
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