

Understanding the effects of processing on fiber/MOF composites

Susan K. Kozawa^{1,2}, Laura Mundy^{1,3}, Greg Peterson¹

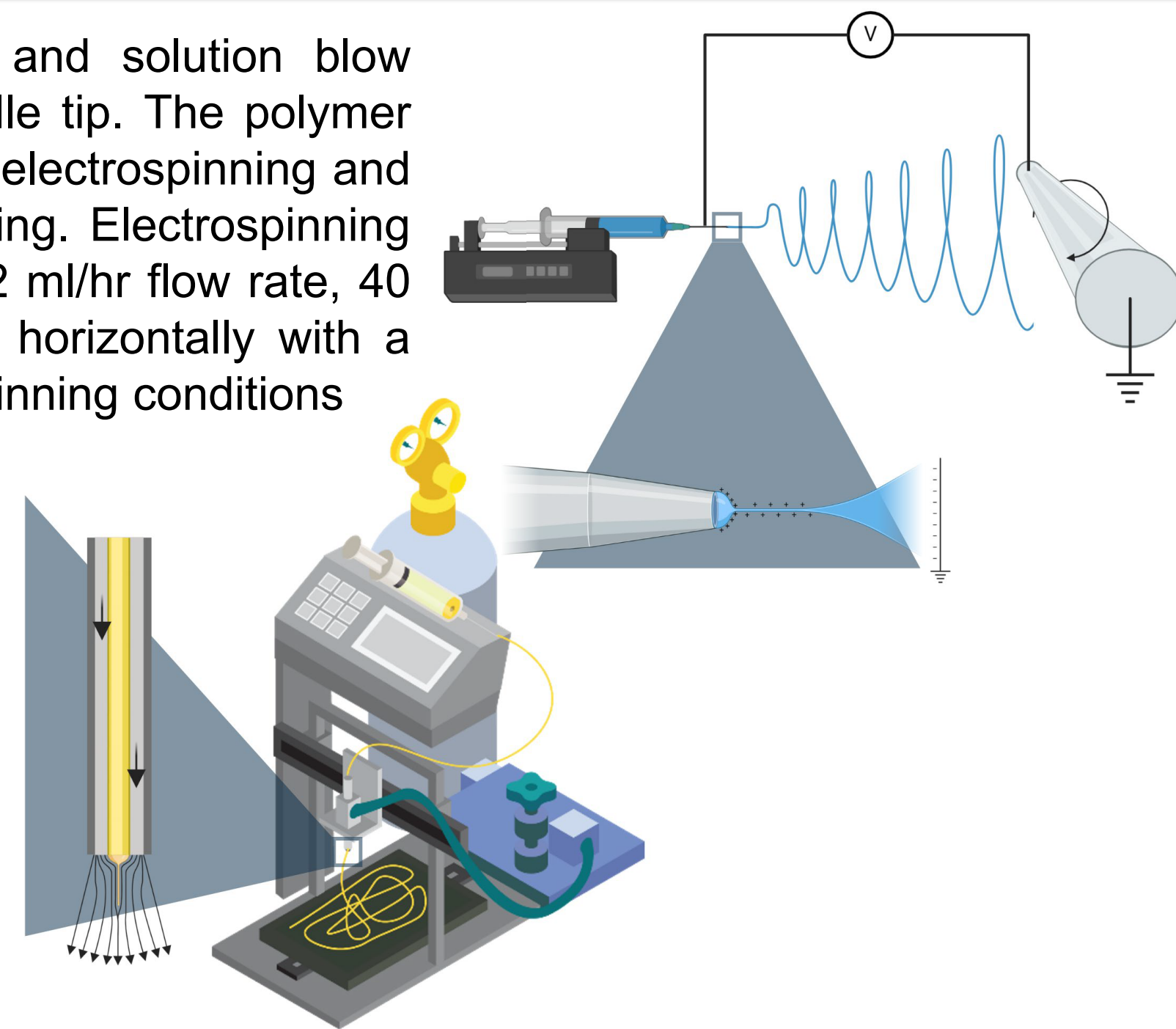
¹U.S. Army Combat Capabilities Development Command Chemical Biological Center, Aberdeen Proving Ground, MD, ²Oak Ridge Institute for Science and Education, Oak Ridge, TN, ³Leidos Inc. Reston, VA

Abstract

Metal-organic frameworks (MOFs) are porous solids that are capable of effectively and efficiently ab/adsorbing and detoxifying dangerous chemicals. In recent years, the manufacturing of MOFs has been successfully scaled up such that they are economically positioned to be utilized in commercial goods. While this has proved an exciting opportunity for the CBRN protective research, a challenge still exists in translating MOFs to protective gear due to their form factor as a powder. Polymer nanofibers provide for an interesting opportunity to embed these brittle materials into a viable form factor that has an inertly high surface area and tunable properties. This high surface area ensures for the maximum interface between a threat and the selected MOF, and the tunability of the fiber properties allows for the inclusion of elasticity and inherent properties of certain polymers such as a voltage response that can be utilized for sensing or energy storage. Electrospinning is a nano/microfiber production technique that uses a voltage to drive fibers out of polymer solution. This method requires a conducting and volatile solution that produces fibers at ml/hr rates. Solution blow spinning is also a nano/microfiber production technique that uses compressed air as a driving force to pull fibers out of polymer solution. This method utilizes heat, air pressure, and volatility of the solvent to produce fibers at a highly scalable level in ml/min. Here, we compared electrospinning and solution blow spinning in creating poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP fibers) with the MOF UiO-66-NH₂. We find that even though varying processing methods produce similar fiber structures visually, they have different polymer properties and MOF loading. The crystalline structures due to processing method directly impacts attractive properties such as elasticity and energy storage. This effort highlights that processing conditions can dictate fiber morphology and reactive particle loading and describes a potentially commercially relevant route into manufacturing protective fibers.

Processing Methods

Figure 1. Schematic of electrospinning and solution blow spinning with a focused view on the needle tip. The polymer solution is drawn into a fiber via current in electrospinning and via compressed air in solution blow spinning. Electrospinning conditions include a 20 G needle, 15 kV, 2 ml/hr flow rate, 40 in distance between needle and mandrel horizontally with a 300 rpm mandrel rotation. Solution blow spinning conditions include an 18 G needle, 40 psi, 0.3 ml/min flow rate, 150 mm vertical distance between needle and collection plate.



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Fiber Characterization

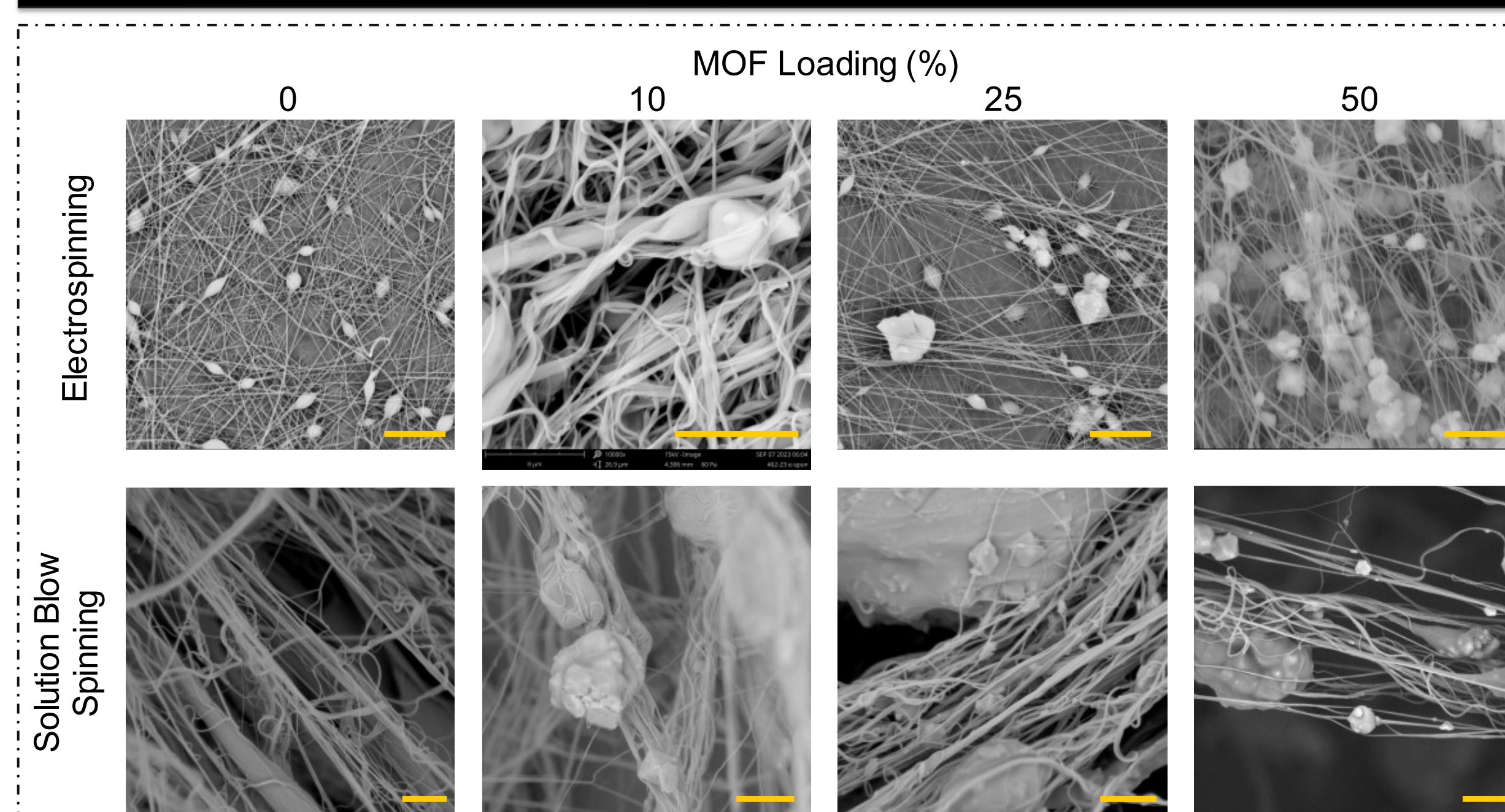


Figure 2. SEM images of fibers fabricated via electrospinning and solution blow spinning with 10 w/v polymer and increasing MOF weight percent relative to polymer in 4:1 acetone:DMF solution. Scale bar is 10 μ m.

Fibers from both processing methods yielded similar diameters, ranging from 4 — 15 μ m as seen in Figure 3. Chemical analysis using FT-IR spectroscopy revealed that the fibers have comparable piezoelectric properties, as demonstrated by the similar levels of β phases detected seen in Figure 3.

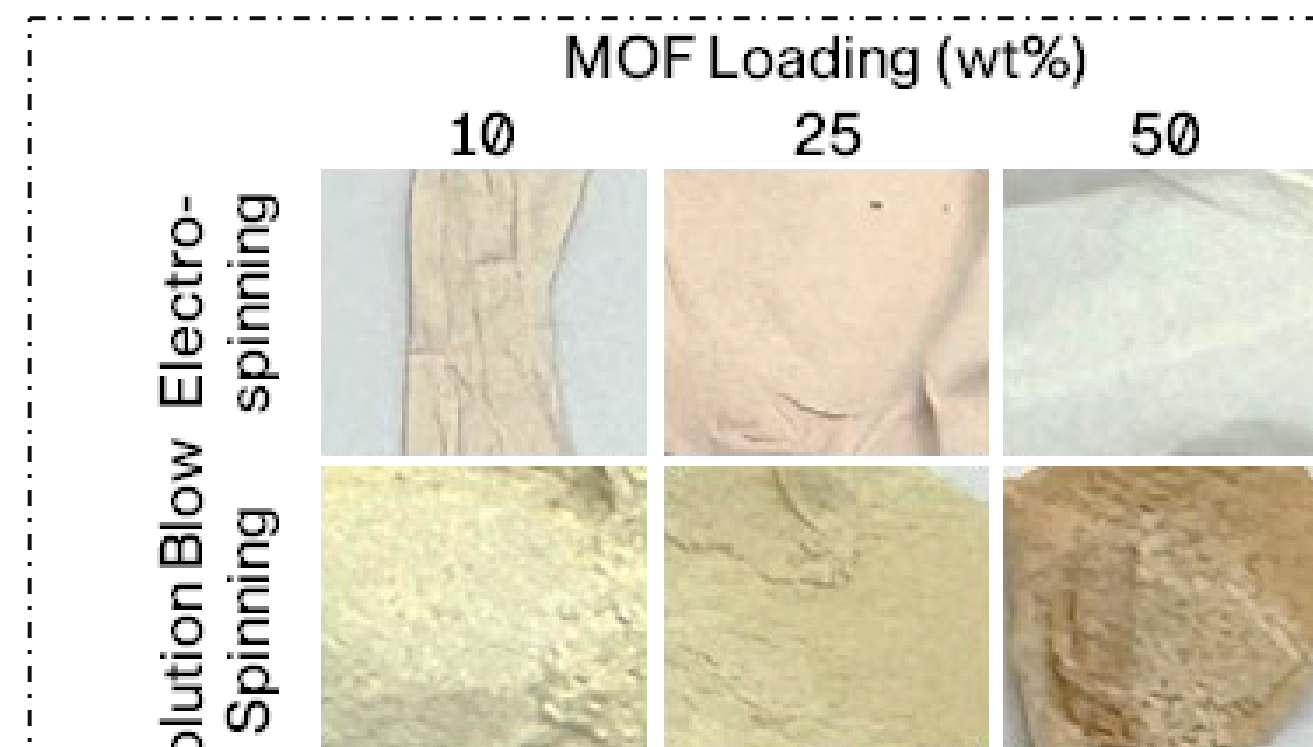


Figure 4. Optical images of fiber mats after significant periods of time. Exposure of MOF to ambient conditions results in a color change from yellow to brown.

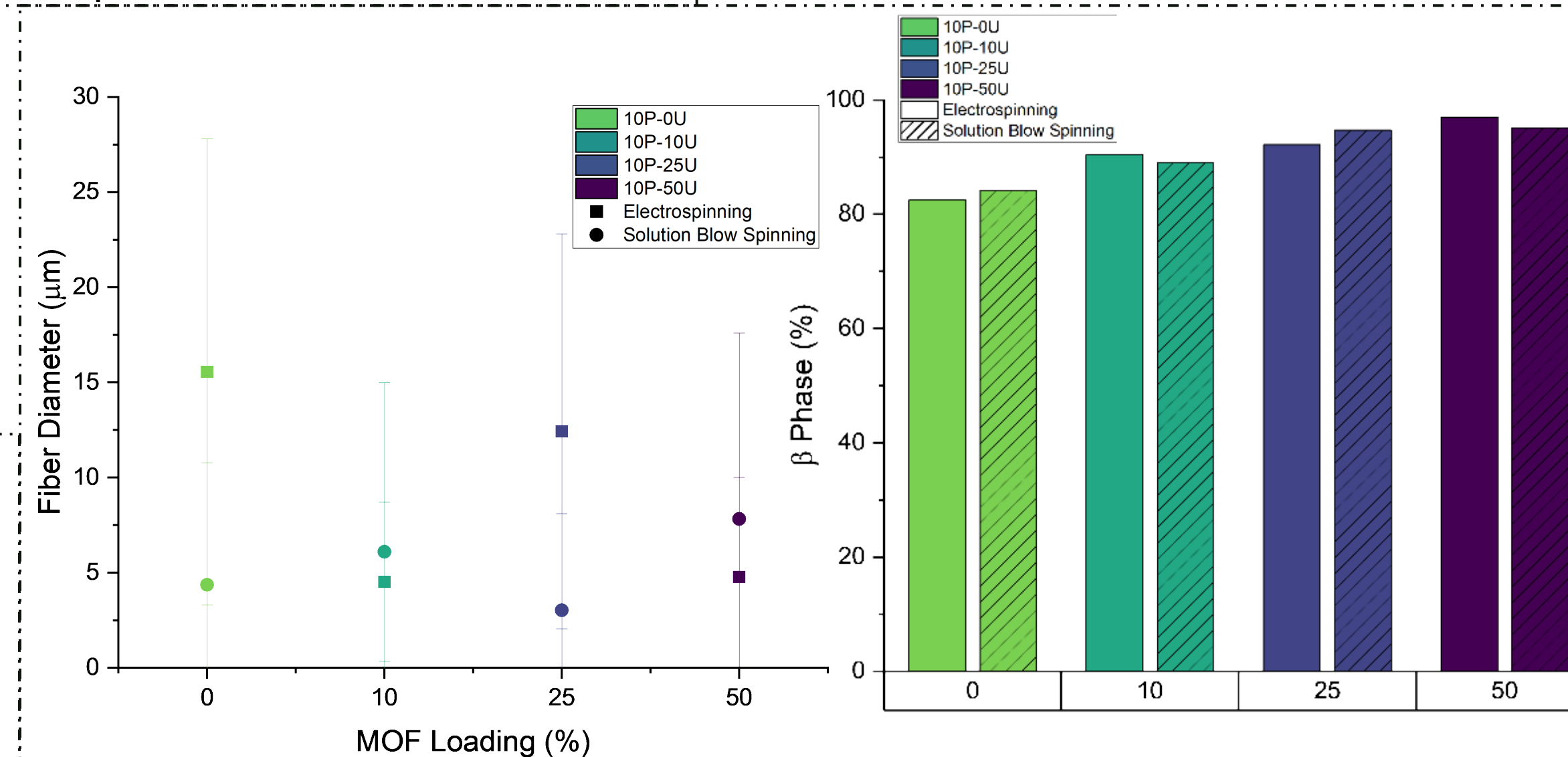


Figure 3. Fiber diameter (left) is relatively similar within error of all samples. FT-IR analysis of the β -phase within fiber samples (right). No significant differences in fiber diameter or β -phase content between fabrication methodologies.

When exposed to ambient conditions, UiO-66-NH₂ changes color from its initial yellow to brown. As shown in Figure 4, the brown coloration of the electrospun mats with 10% and 25% MOF loading indicates greater exposure of the MOF to the environment, whereas the more yellow appearance of the solution blow spun mats suggests better encapsulation. At 50% MOF loading, the electrospun mats exhibit improved MOF encapsulation, although the solution blow spun mats maintain a higher overall MOF loading, evident in Figure 5.

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MOF Loading and Availability

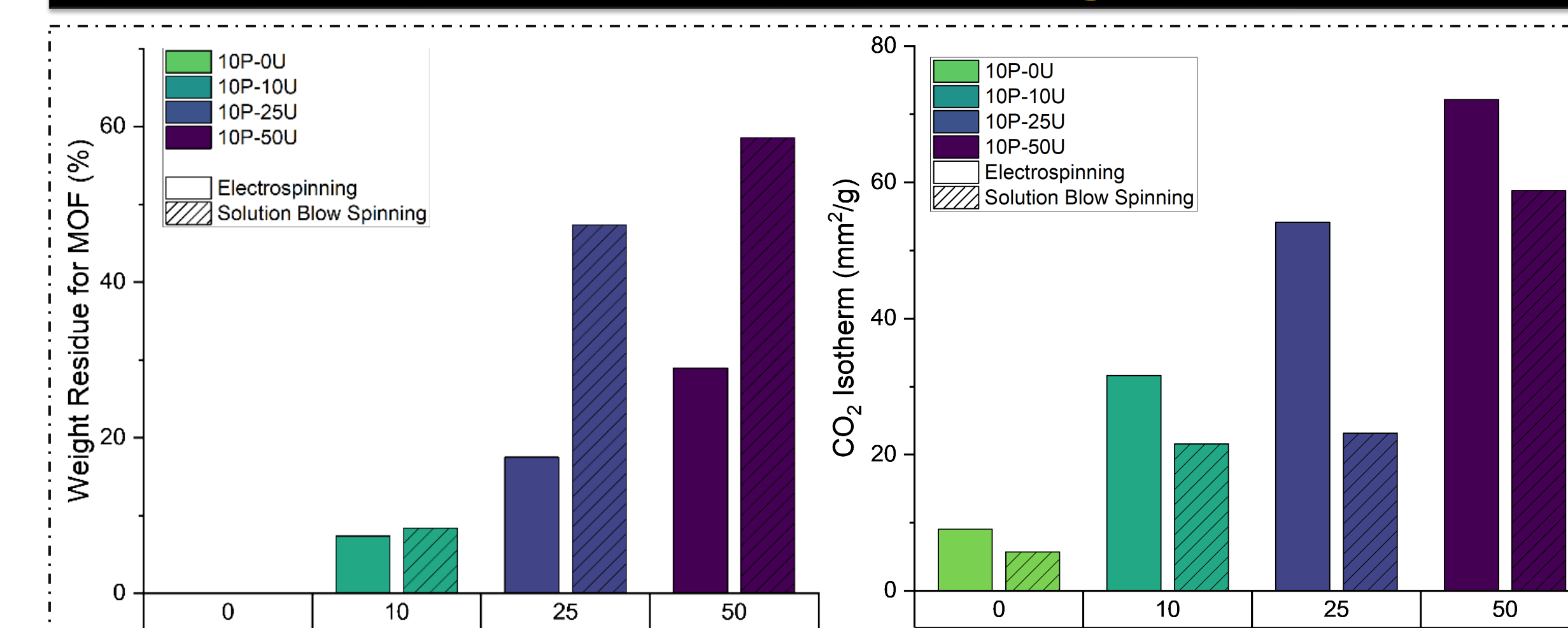


Figure 5. MOF loading by weight percent calculated via thermogravimetric analysis (TGA) (left). CO₂ Isotherm analysis indicating porosity of the sample (right). Electrospinning consistently has higher porosity over solution blow spinning, while solution blow spinning allows for higher MOF loading.

Although both processing methods used the same solution to produce fibers, their MOF content and availability differ significantly. As shown in Figure 5, MOF loading in solution blow spun fibers is nearly double that of electrospun fibers. However, the porosity of the electrospun mats is consistently higher, which suggests increased availability of MOF sites. This higher porosity indicates an enhanced capacity for capturing toxic chemicals.

In the investigation of the fibers' chemical capture performance, the electrospun fibers demonstrated a higher overall capture efficiency compared to solution blow spun fibers. The electrospun mats exhibited a stronger capacity for capturing CEES, while both fiber production methods showed comparable effectiveness for capturing chlorine. Outliers observed during testing will be reconfirmed.

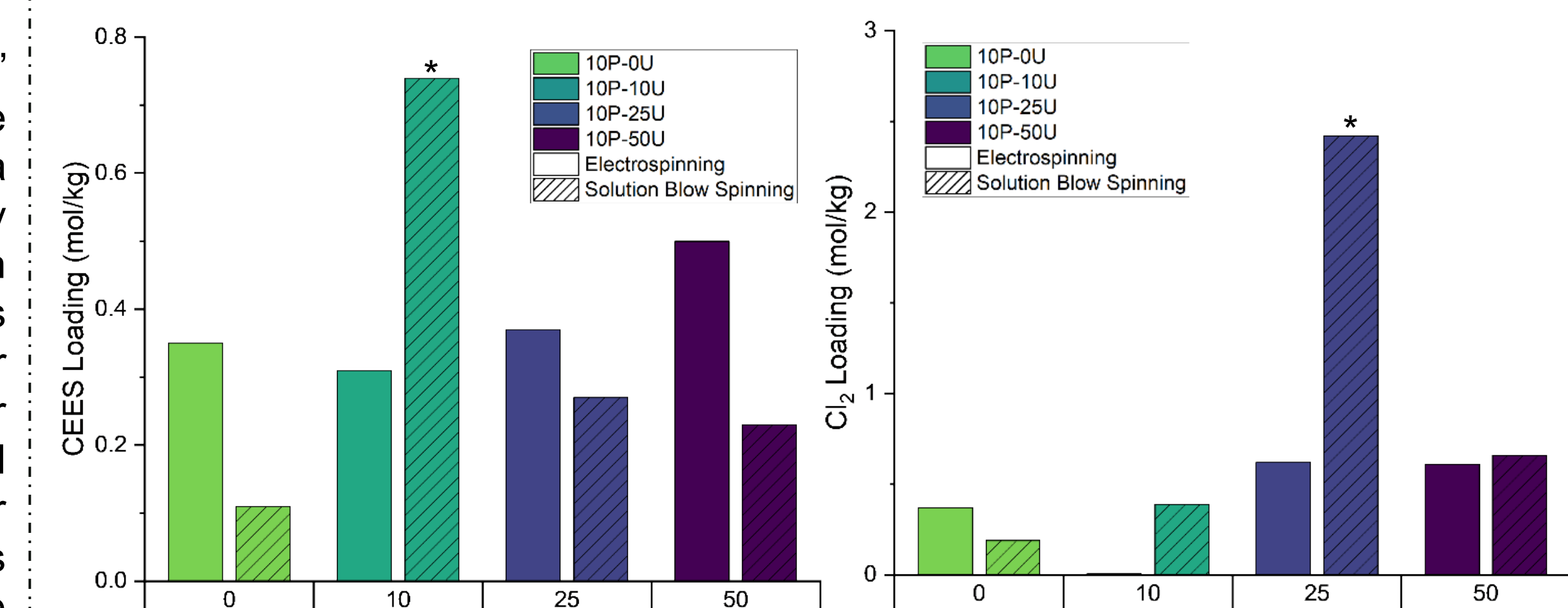


Figure 6. Microbreakthrough loading for 2-chloroethyl ethyl sulfide (CEES) (left) and chlorine (Cl₂) (right) for electrospun and solution blow spun samples. Outliers of trend indicated by *.

Conclusions

Electrospinning and solution blow spinning are effective techniques for producing nano- and microscale fibers capable of incorporating reactive particles, though the distinct processing methods lead to different outcomes. While fibers produced by solution blow spinning exhibit a higher loading capacity for MOFs, electrospun fibers demonstrate greater MOF availability for chemical capture. This difference arises from the flow rates in each process: solution blow spinning operates at millimeter per minute, whereas electrospinning functions at milliliter per hour. The slower flow rate allows for the MOF particles more time to settle out of solution, increasing the likelihood of surface deposition on the horizontally spun fibers. Further research is needed to explore the impact of post-processing on fiber properties, with the aim of optimizing MOF availability and enhancing fiber properties.