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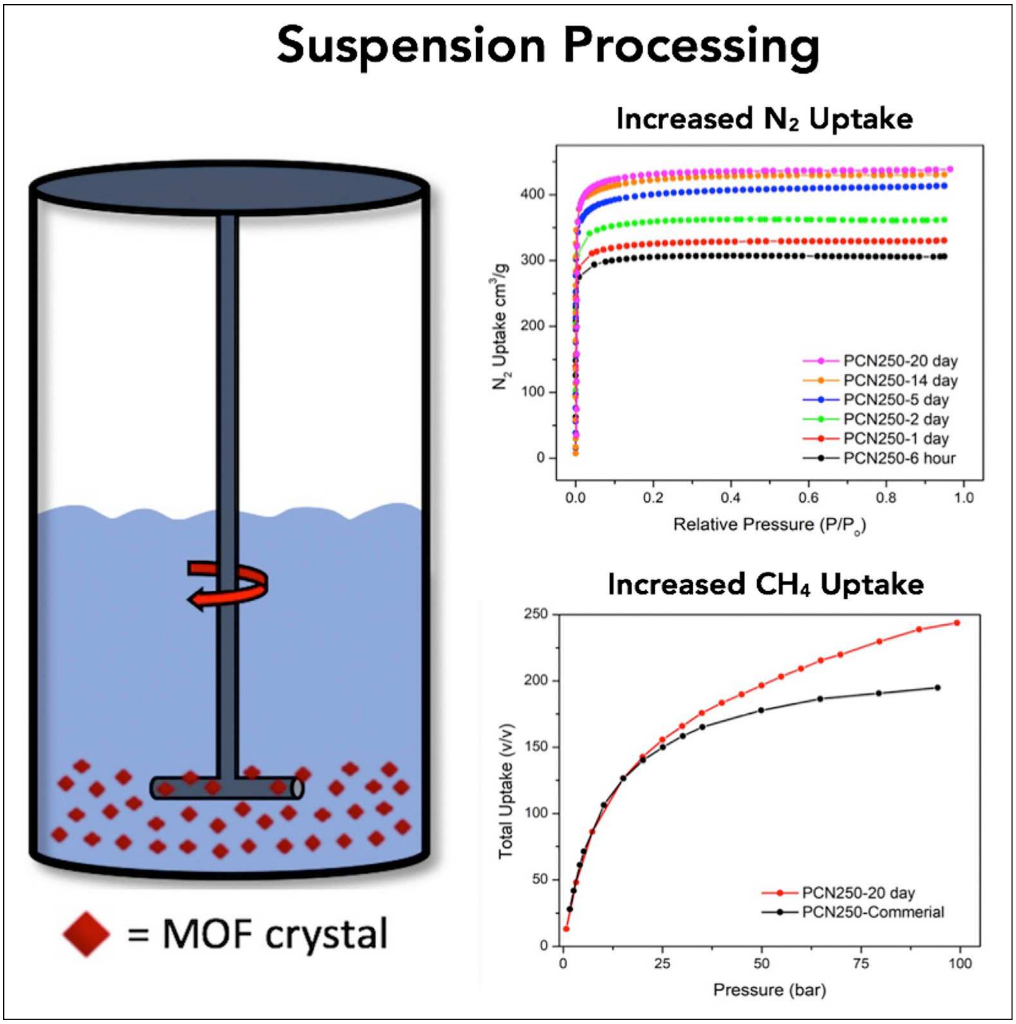
Suspension Processing of Microporous Metal-Organic Frameworks: A Scalable Route to High-Quality Adsorbents



Angelo Kirchon, Gregory S. Day, Yu Fang, Sayan Banerjee, Osman K. Ozdemir, Hong-Cai Zhou

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HIGHLIGHTS

Suspension processing is a viable alternative for traditional solvent exchange methods

PCN-250, UiO-66, and HKUST-1 all showed increased gas uptake and surface area

It provides efficient solvent exchange, pore cleaning, and surface defect removal

The total CH_4 uptake of PCN-250 increased by 11.9%, from 194 to 217 v/v

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Suspension Processing of Microporous Metal-Organic Frameworks: A Scalable Route to High-Quality Adsorbents

Angelo Kirchon,[1] Gregory S. Day,[1] Yu Fang,[1] Sayan Banerjee,[1] Osman K. Ozdemir,[2] and Hong-Cai Zhou[1,3,*]

SUMMARY

Metal-Organic Frameworks (MOFs) have been intensively studied for applications such as gas storage, gas separation, catalysis, drug delivery, and more. Typically, the development of MOFs involves a post-synthetic solvent exchange process, which usually requires a significant investment of time, energy, labor, and resources. Herein, we propose a novel post-synthetic processing methodology for commercial and laboratory-scale MOFs called "Suspension Processing." Suspension processing is a non-destructive, agitation-based technique that provides efficient solvent exchange, pore cleaning, and surface defect removal in MOFs. Suspension processing has shown the capability to significantly improve the surface area and gas uptake properties of microporous MOFs, including PCN-250, UiO-66, and HKUST-1. Suspension processing displays improved time, energy, and labor efficiency, as well as considerably enhanced product quality. These findings confirm suspension processing as a straightforward methodology with applicability as a universal technique for the production of high-quality microporous materials.

INTRODUCTION

Since their discovery in the late 1990s, Metal-Organic Frameworks (MOFs) have turned into one of the fastest growing classes of materials studied in the chemical literature. MOFs have shown promise in a wide range of applications, including gas storage, chemical separations, chemical sensing, catalysis, ion exchange, light harvesting, and even drug delivery (Kreno et al., 2012; Li et al., 2012; Ma and Zhou, 2010; Orellana-Tavra et al., 2015; Wang et al., 2016; Zhu et al., 2017). This wide range of potential applications can be attributed to the ultra-high surface area, tunable pore environments, and high crystallinity of MOFs (Cui et al., 2016; Li and Huo, 2015; Silva et al., 2015; Sun et al., 2016). Although the potential applications of MOFs have been described as endless, commercial and industrial breakthroughs utilizing MOFs have been few and far between. A major reason for the disconnect between basic MOF research and their commercial development is the large monetary and time cost for material processing and activation.

The activation and processing of MOFs has evolved over the years yielding three well-developed primary strategies: conventional activation, solvent exchange, and supercritical CO_2 activation (Mondloch et al., 2013). Conventional activation is the removal of solvent and/or other guest molecules by simultaneous heat and vacuum treatment. Unfortunately, conventional activation has resulted in minimal utility in accessing the full porosity of many MOFs owing to the harsh conditions, often resulting in the collapse or degradation of frameworks. Solvent exchange was developed to help combat the collapse of MOFs during activation. Solvent exchange methods replace a high-boiling-point solvent (e.g., dimethylformamide [DMF]), which is required for synthesis, with a lower-boiling-point solvent (e.g., chloroform), which is then removed under relatively mild conditions. Typically, lower-boiling-point solvents have weaker interactions with the MOF framework. The weaker interactions result in decreased surface tension and capillary forces exerted on the framework during the solvent removal. Solvent exchange is the most commonly used technique for MOF activation, but the time and resources required to perform a successful solvent exchange are typically too high for any production beyond the gram scale (Cui et al., 2016; Li and Huo, 2015; Silva et al., 2015) (Mondloch et al., 2013) (Cavka et al., 2008).

Another common technique for laboratory-scale research is supercritical CO_2 ($scCO_2$) activation. $scCO_2$ builds on the premise of solvent exchange, using liquid CO_2 as a solvent. For example, a solvent that is miscible with $scCO_2$ (e.g., ethanol) is exchanged within the MOFs pores for $scCO_2$ at high pressure (i.e., >73 atm) over the course of several hours. This method further reduces the surface tension during

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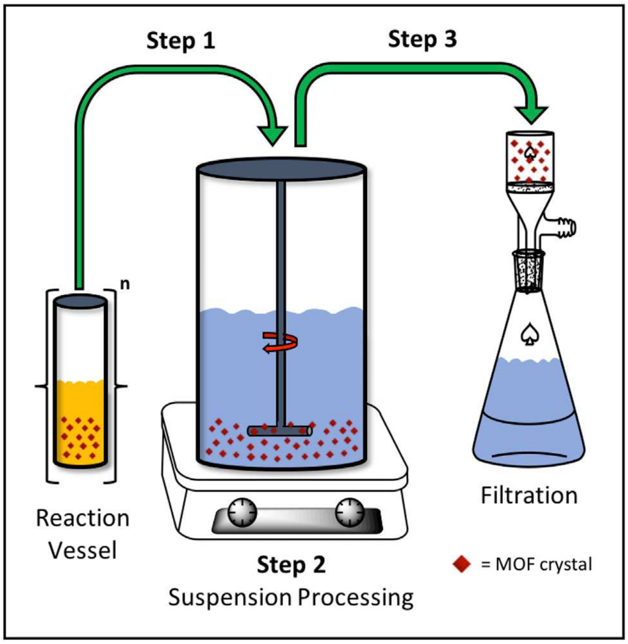

Figure 1. Suspension Processing Methodology

Step 1, addition of reaction vessel contents into suspension processing apparatus; step 2, suspension processing; step 3, filtration.

activation. Although $scCO_2$ has proven successful on the laboratory scale, the large capital cost associated with the development of commercial or industrial-scale equipment for $scCO_2$ has limited its adoption into large-scale systems.

Suspension-based processing methods have been used for cell processing for many years. Suspension-based cell-growing procedures were first used in 1956 when a suspended magnetic stirrer was used to grow cells in round-bottom flasks. Further optimization of suspension cell growth methods has allowed for a quick and easy process for achieving large quantities of high-quality cell lines (Iyer et al., 1999; Ryan, 2008). Based on the success of suspension cell growth methods, as well as to combat the issues that exist with the three current MOF activation and processing methods, we have developed a method of MOF activation named suspension processing. Suspension processing provides a universal, scalable, cost-effective, and robust technique for the effective activation of MOFs.

RESULTS AND DISCUSSION

Suspension Processing Methodology

Suspension processing utilizes an enclosed cylindrical vessel with a suspended stir rod or agitator that extends from the top of the system downward without touching the bottom as shown in Figure 1. The as-synthesized MOF, still suspended within the reaction mixture (Figure 1 left, yellow colored area), is placed within the reaction vessel. Step 1 shows the addition of the full reaction vessel contents into the suspension processing apparatus. In step 2, the low-boiling-point solvent, such as methanol (MeOH, Figure 1 center, blue colored area), is added in an amount approximately 5x the volume of the solid product. The system is then heated to the boiling point of the low-boiling-point solvent (in the case of MeOH, the system was heated to 65°C). The system is then stirred at a low rate, typically 65 rpm, for the desired time. After the stirring has been stopped, in step 3 the contents of the suspension apparatus are filtered while heated, yielding a highly crystalline and porous MOF product with a filtrate consisting of a mixture of the process and reaction solvents as well as dissolved reaction by-products. The process requires minimal participation from the operator, with no solvent changes necessary during the timescale of the procedure. In addition, the apparatus utilized for laboratory-scale suspension processing is similar in design to commercial batch reactors that typically utilize suspended mechanical stirrers, allowing for this process to act as drop-in technology for existing chemical production.

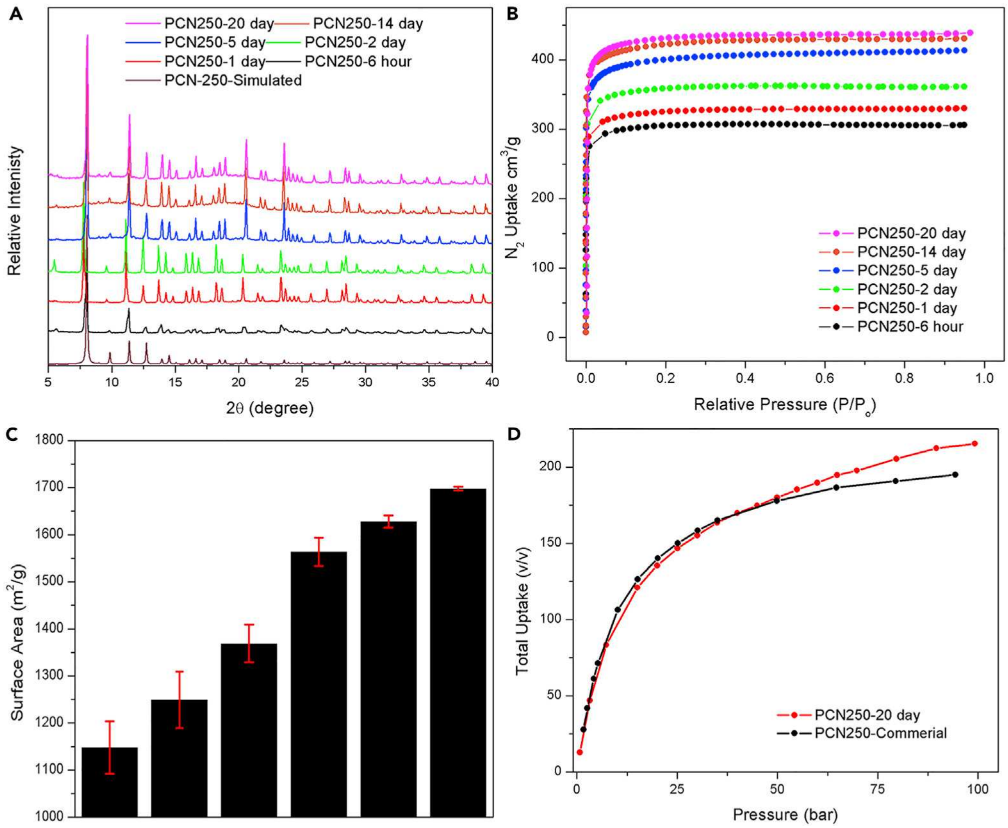

Figure 2. Suspension-Processed PCN-250 Characterization

(A) Powder X-ray diffraction pattern of suspension-processed PCN-250.

(B) N_2 adsorption isotherm at 77 K suspension-processed PCN-250.

(C) BET surface area vs. time of processing for suspension-processed PCN-250. Error bars were determined from three different measurments from three different samples.

(D) High-pressure methane uptake for PCN250-20 day compared with commercial PCN-250.

This method was first developed for PCN-250, also known as MIL-127, which is constructed from Fe_3-μ_3-oxo clusters and tetratopic azobenzene-based linkers (ABTC = 3, 3′, 5, 5′-azobenzenetetracarboxylate). The high gas uptake, available open metal sites, exceptional stability, and scalability of PCN-250 have made it a well-studied material for gas storage applications (Feng et al., 2014; Yuan et al., 2017). Although PCN-250 has exceptional gas storage properties, the solvent exchange process used to obtain the maximum gas uptakes is currently reported as an 8- to 10-day process with approximately 9–12 steps. These steps use three to four different solvents and require active participation from an individual to wash and exchange the solvent used in each step. The use of suspension processing in place of traditional methods not only yields a product with increased gas uptake properties, but does so with improved time, energy, and labor efficiency.

Nitrogen Gas Uptake

Analysis of the suspension processed materials was primarily conducted by powder X-ray diffraction (PXRD) and nitrogen gas uptake experiments. A sample of as-synthesized PCN-250 was subjected to suspension processing in MeOH, with samples removed after the following times: 6 hr, 1 day, 2 days, 5 days, 14 days, and 20 days. Figure 2A showcases the PXRD for the series of PCN-250 samples, showing that the crystallinity of PCN-250 improved over the course of the processing. In Figure 2B, the N_2 gas uptake of the samples displayed an increase in total gas uptake with increase in treatment time. Notably, the 5-day treated sample, PCN250-5 day, shows the same N_2 gas uptake as reported in the literature (Feng et al., 2014). However, compared with the three to four solvents used in the reported solvent exchange method, suspension processing did not require solvent replacement or addition, only utilizing the initial process solvent added to the reaction mixture. No active participation was needed once the process was initiated.

MOF	Traditional Solvent Exchange Process (m^2/g)	Commercial Product (m^2/g)	Suspension Processing (m^2/g)
PCN-250[a]	1,446	1,270	1,702
UiO66[a]	1,290	1,045	1,675
HKUST1[a]	1,617	1,615	1,808

Table 1. Comparison of BET Surface Area for Various MOFs

[a] Figures S1–S8 in Supplemental Information display all characterization of these samples.

Even without exchanging the solvent, improvements in gas uptake were still observed after 20 days of processing.

The surface area was found to dramatically increase during the first four treatments (6 hr–5 days). After the initial surface area response, the increase in surface area slows down until it reaches a peak of 1,702 m^2/g after the 20th day. This surface area represents a 15% improvement over the commonly published PCN-250 surface area (1,446 m^2/g). To our knowledge, this surface area is the record high among published PCN-250 samples.

Lastly, high-pressure methane (CH_4) uptake measurements were performed to determine the applicability of suspension processing to an MOF's end application. Compared with a commercial PCN-250, the total methane uptake at room temperature (313 K) and 95 bar increased by 11.9%, from 194 to 217 v/v as shown in Figure 2D.

Universal Applicability

Owing to the success of suspension processing for PCN-250, we sought to investigate the universal applicability of this method by applying suspension processing to two other well-known, commercially available, and highly studied microporous MOFs, UiO-66 and HKUST-1. As seen with PCN-250, both MOFs were able to obtain higher gas uptake values using suspension processing compared with traditional solvent exchange procedures. In addition, an increase in gas uptake with an increase in processing time was also observed (Figures S3 and S4).

For UiO-66, a BET surface area of 1,675 m^2/g was achieved after only 2 days of processing. This outperformed the BET surface area of the traditional solvent exchange sample of 1,290 m^2/g. Furthermore, suspension processing of HKUST-1 was also observed to improve the BET surface area compared with traditional solvent exchange methods (1,808 vs 1,615 m^2/g, respectively). Samples of PCN-250, UiO-66, and HKUST-1 were purchased from commercial vendors and compared with the laboratory-scale samples before and after suspension processing. Typically, the commercially purchased MOF adsorbents have lower BET surface areas compared with the laboratory prepared samples as seen in Table 1. Suspension processing of PCN-250, UiO-66, and HKUST-1 led to an increase in BET surface area and gas uptake properties over their commercially available counterparts.

Mechanism Study

Mechanistic analysis of suspension processing was studied *via* scanning electron microscopy and thermal gravimetric analysis (TGA). Figure 3A shows that the as-synthesized PCN-250 particles were heavily aggregated. However, in Figure 3B, after suspension processing, the particles were well dispersed. This phenomenon indicates that unreacted organic ligands or surface residues have been successfully removed after the treatment. On the other hand, seed-like small particles are observed on the surface of as-synthesized HKUST-1 samples. However, they were completely removed after 48 hr of treatment, resulting in a smooth crystal surface for HKUST-1 (Figures 3D and 3E). This suggests the complete removal of solvent residues and defects from the MOF pores and surface. A similar phenomenon was also observed for UiO-66 samples (Figures 3G and 3H).

The discussed observations are the result of the removal of low-crystallinity phases within or on the surface of the MOF by suspension processing. These results suggest that suspension processing aids in the removal of unreacted material, minor surface defects, and low-crystallinity coordination polymers *via*

MOF	Traditional Solvent Exchange Process ($)	Suspension Processing ($)	Reduction in Operating Cost (%)
PCN-250	4,901.50	795.75	84
UiO66	5,868.00	264.50	95
HKUST1	6,163.50	1,689.50	73

Table 2. Total Operational Costs in US Dollars ($)

efficient dissolution and mass transport due to increased agitation and material-solvent contact. This improvement in bulk material purity and removal of non-porous by-products allowed for an increase in gas uptake performance compared with the as-synthesized samples.

As seen in Figures 3C, 3F, and 3I, the thermal stability of PCN-250, HKUST-1, and UiO-66 all increased following longer suspension processing times. The overall stability of the 20-day processed PCN-250 increased by 3°C compared with the 6-hr processed sample. The TGA curve of PCN250-6hr displays a mass loss of 6.3% below 100°C, likely the removal of MeOH from the framework. Between 100°C and 185°C, PCN250-6hr displays a mass loss event comprising 16.5%, which should correspond to the removal of DMF from the framework. In comparison, PCN250-20 day displays a significantly different TGA curve, showing a major mass loss of 20.5% below 100°C but with no significant mass loss between 100°C and 185°C (5.2%), which suggests that most of the DMF has been removed from the framework during suspension processing. More importantly, the mass loss event in the median temperature range (185°C–397/400°C) displays major differences, likely due to the effective removal of unreacted starting material, by-products, and surface defects. The mass loss decreased significantly from 19.6% for PCN250-6 hr to 9.7% for PCN250-20 day. Similar behavior was observed for HKUST-1 and UiO-66. We attribute the stability enhancement to improvements in pore cleaning and the removal of surface defects. Furthermore, it should be noted that further tests are currently ongoing to investigate the possibility of an internal defect self-healing mechanism.

It should be noted that suspension processing can be compared with other processes such as Soxhlet extraction (Hong et al., 2009). Soxhlet extraction is more similar to traditional solvent exchange as they are both solvent exchange processes, but Soxhlet extraction uses constant and automatic replacement of solvent, whereas traditional solvent exchange involved a manual solvent replacement. Soxhlet extraction, to the best of our knowledge, has been reported to be a good procedure for efficient pore cleaning and solvent exchange but has not been reported to help remove surface defects from MOFs. Moreover, the integration of suspension processing into current large-scale reactors system would be much more practical in our minds.

Cost Analysis

To analyze the practicality of suspension processing, we performed an operational cost analysis comparing suspension processing with traditional solvent exchange methods. For this analysis, we defined operational costs as the cost of solvent used plus the cost of labor for the duration of the process. In all cases, suspension processing had a significantly lower operating cost compared with traditional solvent exchange methods. The traditional solvent exchange for PCN-250 was performed over a 7-day period and involves a total of 14 separate washing procedures, involving 3 different solvents (full process is listed in the Supplemental Information). In total as displayed in Table 2, the solvent used in this procedure costs approximately $4,800.00 per kg of MOF. Including labor, the total cost per kg of PCN-250 using traditional solvent exchange is approximately $4,901.50. For comparison, a 5-day suspension processing has a total operating cost of approximately $795.75, which represents an 84% reduction in cost. Similar improvements in operating cost were also seen with UiO-66 and HKUST-1 (Figure 4). This section, along with how the analysis was performed, given in detail in the Supplemental Information, provides additional support to the claims that suspension processing not only leads to higher-quality MOF products but also does so with a major reduction of the cost and time. It should be noted that this is a preliminary cost analysis of the technique. Further analysis could be performed, which would be beneficial to the development of the technology in the future, such as taking into account alternative solvents such as hexane (Ma et al., 2017) or CH_2Cl_2 (Bae et al., 2017) or even to account for possible recycling of solvent.

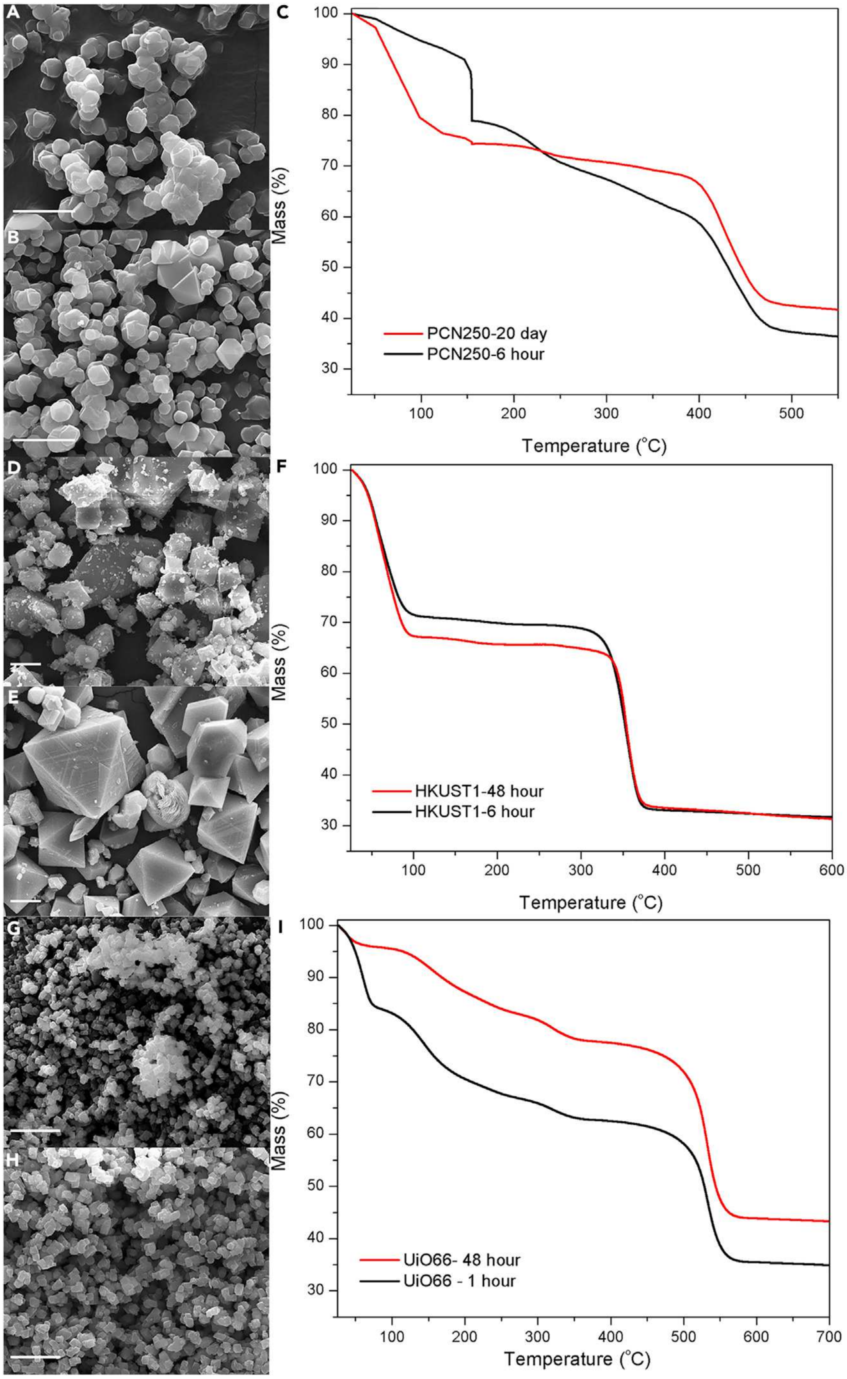

Figure 3. Scanning Electron Micrographs and Thermal Gravimetric Analysis Curves

(A) Scanning electron micrographs of PCN250-6 hr.

(B) Scanning electron micrographs of PCN250-20 day.

(C) TGA curve for PCN250-6 hr (black) and PCN250-20 day (red).

(D) Scanning electron micrographs of HKUST1-6 hr.

(E) Scanning electron micrographs of HKUST1-48 hr.

(F) TGA curve for HKUST1-6 hr (black) and HKUST1-48 hr (red).

(G) Scanning electron micrographs of UiO66-1 hr.

(H) Scanning electron micrographs of UiO66-48 hr.

(I) TGA curve for UiO66-1 hr (black) and UiO66-48 hr (red).

Scale bars 10μm.

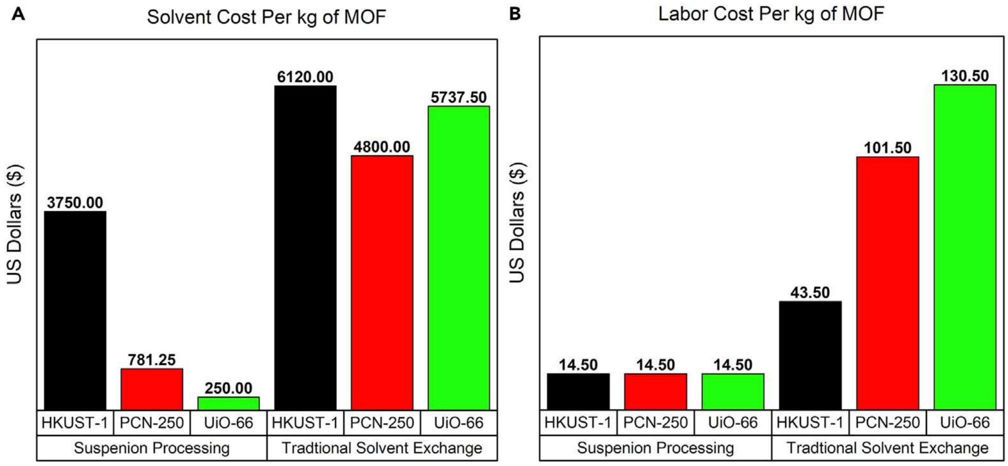

Figure 4. Operational Cost Analysis for Suspension Processing vs. Traditional Solvent Exchange

(A) Solvent cost per kg of MOF.

(B) Labor cost per kg of MOF.

Conclusion

In conclusion, we introduced suspension processing as a method for the successful post-synthetic treatment of MOFs that is a viable alternative for traditional solvent exchange methods for both laboratory and commercial MOF syntheses. Through this treatment, three commercially available MOFs, with different compositions, stabilities, and porosities, have shown promising improvements in gas adsorption capabilities. We ascribe the gas uptake and surface area improvements to efficient pore cleaning and defect removal of the MOFs after treatment. Furthermore, the treatment itself is energy saving, economically efficient, and user friendly. Overall, suspension processing is a potentially universal, economical, and efficient post-treatment method for industrial-scale porous materials.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Transparent Methods and eight figures and can be found with this article online at https://doi.org/10.1016/j.isci.2018.06.009.

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AUTHOR CONTRIBUTIONS

Conceptualization, A.K. and G.S.D.; Methodology, A.K.; Investigation, A.K., G.S.D., and S.B.; Writing – Original Draft, A.K.; Writing – Review & Editing, A.K., G.S.D., and Y.F.; Supervision, Y.F.; Project Administration Y.F. and O.K.O.; Funding Acquisition Y.F., O.K.O., and H.-C.Z.

DECLARATION OF INTERESTS

An invention disclosure has been submitted to the Texas A&M Technology Comedication (TTC) office.

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REFERENCES

Bae, J., Choi, J.S., Hwang, S., Yun, W.S., Song, D., Lee, J., and Jeong, N.C. (2017). Multiple coordination exchanges for room-temperature activation of open-metal sites in metal–organic frameworks. ACS Appl. Mater. Interfaces *9*, 24743–24752.

Cavka, J.H., Jakobsen, S., Olsbye, U., Guillou, N., Lamberti, C., Bordiga, S., and Lillerud, K.P. (2008). A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. J. Am. Chem. Soc. *130*, 13850–13851.

Cui, Y., Li, B., He, H., Zhou, W., Chen, B., and Qian, G. (2016). Metal–organic frameworks as platforms for functional materials. Acc. Chem. Res. *49*, 483–493.

Feng, D., Wang, K., Wei, Z., Chen, Y.-P., Simon, C.M., Arvapally, R.K., Martin, R.L., Bosch, M., Liu, T.-F., Fordham, S., et al. (2014). Kinetically tuned dimensional augmentation as a versatile synthetic route towards robust metal–organic frameworks. Nat. Commun. *5*, 5723.

Hong, D.-Y., Hwang, Y.K., Serre, C., Férey, G., and Chang, J.-S. (2009). Porous chromium terephthalate MIL-101 with coordinatively unsaturated sites: surface functionalization, encapsulation, sorption and catalysis. Adv. Funct. Mater. *19*, 1537–1552.

Iyer, V.R., Eisen, M.B., Ross, D.T., Schuler, G., Moore, T., Lee, J.C., Trent, J.M., Staudt, L.M., Hudson, J., Boguski, M.S., et al. (1999). The transcriptional program in the response of human fibroblasts to serum. Science *283*, 83–87.

Kreno, L.E., Leong, K., Farha, O.K., Allendorf, M., Van Duyne, R.P., and Hupp, J.T. (2012). Metal–organic framework materials as chemical sensors. Chem. Rev. *112*, 1105–1125.

Li, J.-R., Sculley, J., and Zhou, H.-C. (2012). Metal–organic frameworks for separations. Chem. Rev. *112*, 869–932.

Li, S., and Huo, F. (2015). Metal-organic framework composites: from fundamentals to applications. Nanoscale *7*, 7482–7501.

Ma, J., Kalenak, A.P., Wong-Foy, A.G., and Matzger, A.J. (2017). Rapid guest exchange and ultra-low surface tension solvents optimize metal-organic framework activation. Angew. Chem. Int. Ed. *56*, 14618–14621.

Ma, S., and Zhou, H.-C. (2010). Gas storage in porous metal–organic frameworks for clean energy applications. Chem. Commun. *46*, 44–53.

Mondloch, J.E., Karagiaridi, O., Farha, O.K., and Hupp, J.T. (2013). Activation of metal–organic framework materials. CrystEngComm *15*, 9258–9264.

Orellana-Tavra, C., Baxter, E.F., Tian, T., Bennett, T.D., Slater, N.K.H., Cheetham, A.K., and Fairen-Jimenez, D. (2015). Amorphous metal–organic frameworks for drug delivery. Chem. Commun. *51*, 13878–13881.

Ryan, J.A. (2008). Growing More Cells: A Simple Guide to Small Volume Cell Culture Scale-Up, Corning Incorporated. Life Sciences.

Silva, P., Vilela, S.M.F., Tomé, J.P.C., and Almeida Paz, F.A. (2015). Multifunctional metal-organic frameworks: from academia to industrial applications. Chem. Soc. Rev. *44*, 6774–6803.

Sun, M.-H., Huang, S.-Z., Chen, L.-H., Li, Y., Yang, X.-Y., Yuan, Z.-Y., and Su, B.-L. (2016). Applications of hierarchically structured porous materials from energy storage and conversion, catalysis, photocatalysis, adsorption, separation, and sensing to biomedicine. Chem. Soc. Rev. *45*, 3479–3563.

Wang, L., Han, Y., Feng, X., Zhou, J., Qi, P., and Wang, B. (2016). Metal–organic frameworks for energy storage: batteries and supercapacitors. Coord. Chem. Rev. *307*, 361–381.

Yuan, S., Sun, X., Pang, J., Lollar, C., Qin, J.-S., Perry, Z., Joseph, E., Wang, X., Fang, Y., Bosch, M., et al. (2017). PCN-250 under pressure: sequential phase transformation and the implications for MOF densification. Joule *1*, 806–815.

Zhu, L., Liu, X.-Q., Jiang, H.-L., and Sun, L.-B. (2017). Metal–organic frameworks for heterogeneous basic catalysis. Chem. Rev. *117*, 8129–8176.

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Supplemental Information

Suspension Processing of Microporous Metal-Organic Frameworks: A Scalable Route to High-Quality Adsorbents

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Supplemental Information

Materials

All the reagents and solvents were commercially available and used as received or synthesized according to the literature reported procedures. PCN-250 and UiO-66 commercial samples were purchased from Stream Chemicals while the HKUST-1 (Basolite C300) commercial sample was purchased from Sigma Aldrich. $Fe(NO_3)_3$-$9H_2O$ (CAS:7782-61-8), $Cu(NO_3)_2$ $2.5H_2O$,ACS, 98.0-102.0%(CAS: 19004-19-4), 1,3,5-Benzenetricarboxylic acid, 98% (CAS: 554-95-0), Zirconium dichloride oxide octahydrate, 98% (CAS: 13520-92-8), BDC (Terephthalic acid ≥99.0%)(CAS: 100-21-0), 5-Nitroisophthalic acid, 99.0% (CAS: 618-88-2) and D-(+)-Glucose, anhydrous ≥99.5% (CAS: 50-99-7) were purchased from VWR.

Suspension processing apparatus (3 L Celstir) was purchased from DWK Life Sciences.

Instrumentation

Powder X-ray diffraction (PXRD) was carried out with a Bruker D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$ Å) at 40 kV and 40 mA.

Scanning Electron Microscopy (SEM) measurements were carried out on JEOL JSM-7500F. JEOL JSM-7500F is an ultra-high-resolution field emission scanning electron microscope (FE-SEM) equipped with a high brightness conical FE gun and a low aberration conical objective lens.

Thermal Gravimetric Analysis (TGA) was performed using a Mettler-Toledo TGA/DSC STAR*e*-1 system which was equipped with a GC100 gas controller.

N2 sorption measurements were conducted using a Micromeritics ASAP 2020 and 2420 system.

High-Pressure CH_4 adsorption isotherms were carried out on HPVA II high pressure volumetric analyzer from micromeritics.

Transparent Methods

3,3',5,5' Azobenzene-tetra-carboxylic acid (H_4ABTC) Synthesis: A mixture of 5-nitroisophthalic acid (19 g, 90 mmol) and NaOH (50 g, 1250 mmol) in 250 mL of distilled water was placed into a 1 L 3-neck round bottom flask and stirred vigorously at 50 C. To this slurry, 100 g of D-glucose dissolved in 150 mL of distilled water was slowly added. The resulting brown mixture was cooled down to room temperature, and air was bubbled for 4 hours always under stirring. The reaction mixture was cooled in an ice-bath and the sodium salt of ABTC recovered by filtration and washed with small amount of cold water. The resulting yellow solid was then dissolved in 200mL of distilled water and this solution was acidified down to pH = 1 by the addition of HCl 37 %. The resulting orange solid was recovered by filtration, washed with distilled water and dried at 100 C under vacuum. Yield 70%

PCN250 Synthesis: $Fe(NO_3)_3$-$9H_2O$ (5.4 g), ABTC (1.8 g), Acetic Acid (3 L) and DMF (6 L) were added into a jacketed 10 L Pyrex high pressure reaction vessel. The vessel was then heated to 150 ºC for 12 h. The resulting reaction slurry was then removed and used without further purification. Multiple batches were synthesized in parallel to achieve kg quantities.

HKUST1 Synthesis: HKUST-1 was synthesized following the literature procedure (Lin et al., 2012) with minor changes to allow for larger scales. $Cu(NO_3)_2$ $2.5H_2O$ (24.0 g) was dissolved in 1 L of solvent consisting of equal parts of ethanol and deionized water. This was followed by the addition of BTC (8.0 g) into the solution. The resultant solution mixture was transferred into a 2 L Pyrex high pressure reaction vessel and placed in an oven at 110 ºC for 18 h. The resulting reaction slurry was then removed and used without further purification. Multiple batches were synthesized in parallel to achieve kg quantities.

UiO66 Synthesis: 1 L of DMF was added to a 2 L RBF equipped with a stir bar and preheated to 140 ºC. Then $ZrOCl_2$ (24.0 g), BDC (24.0 g) and 400 ml of Formic Acid were added to the RBF. The flask was vigorous stirred at 140 ºC for 2 hours. The resulting reaction slurry was then removed and used without further purification. Multiple batches were synthesized in parallel to achieve kg quantities.

Suspension Processing: Following the synthesis of each MOF, the 0.5L of the reaction slurries were added directly into a suspension processing apparatus with a volume of 3 L. Then 2.5 L MeOH was added to the suspension processing apparatus bringing the total volume to approximately 3 L. Next the suspension processing apparatus was put on top of a hot/stir plate and was heated to 65 ºC while the suspended stir bar was stirred at 65 rpm for the desired amount of time (1h, 6h, 12h, etc…). Once the desired time was reached the contents of the reaction vessel were filtered without allowing the solution to cool, and the desired MOF product was obtained.

Drying and Activation: Following the isolation of the desired MOF, the material was dried in air at 70ºC for 1 day. The MOF was then activated under vacuum at the following temperatures for 10 hours (PCN250-185ºC, UiO66-120ºC, HKUST1-150ºC).

TGA Method

PCN-250: Heating at 10ºC/min from 25 ºC-150 ºC, then a 10 min isothermal step, followed by a 2.5ºC/min heating ramp up to 550 ºC, all under a 50 mL/min flow of nitrogen

UiO-66: Heating at 5ºC/min from 25 ºC-700 ºC under a 50 mL/min flow of nitrogen

HKUST-1: Heating at 5ºC/min from 25 ºC-600 ºC under a 50 mL/min flow of nitrogen

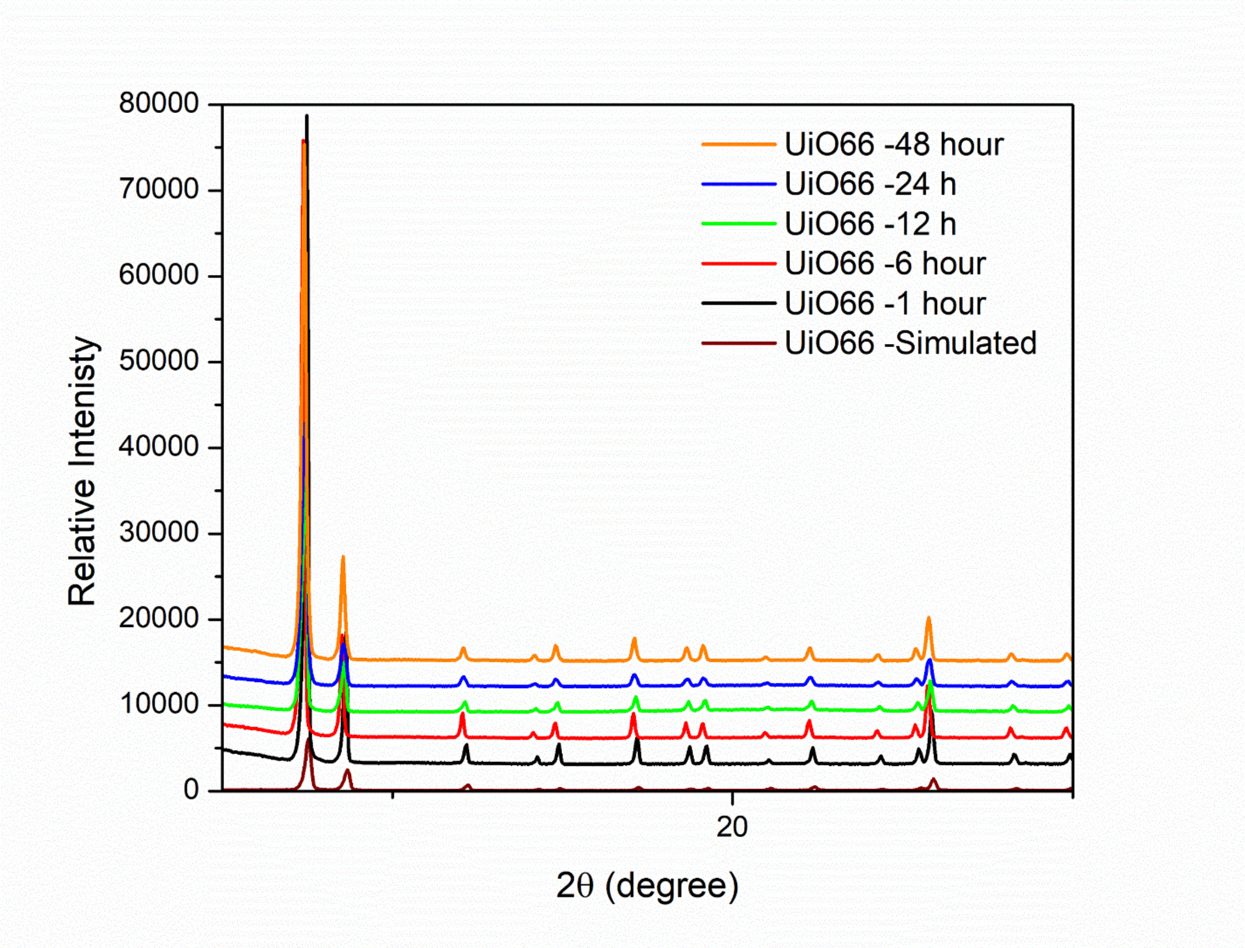

Figure S1 – UiO-66 Powder X-Ray Diffraction (PXRD)- "Related to Table 1"

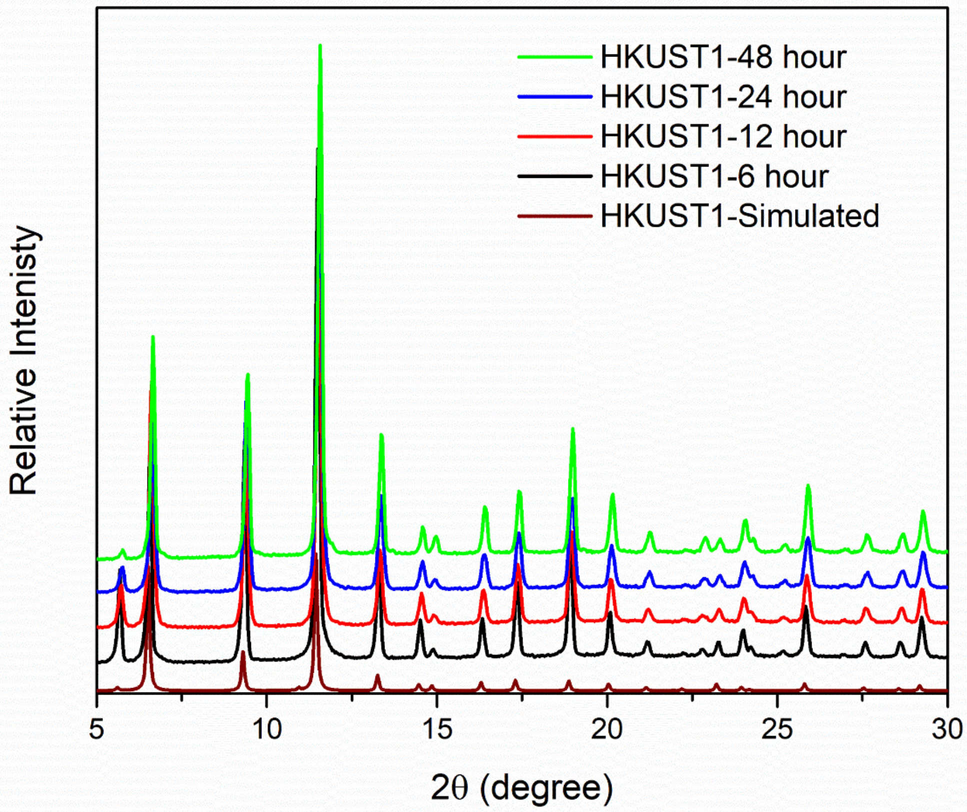

Figure S2 – HKUST-1 Powder X-Ray Diffraction (PXRD) "Related to Table 1"

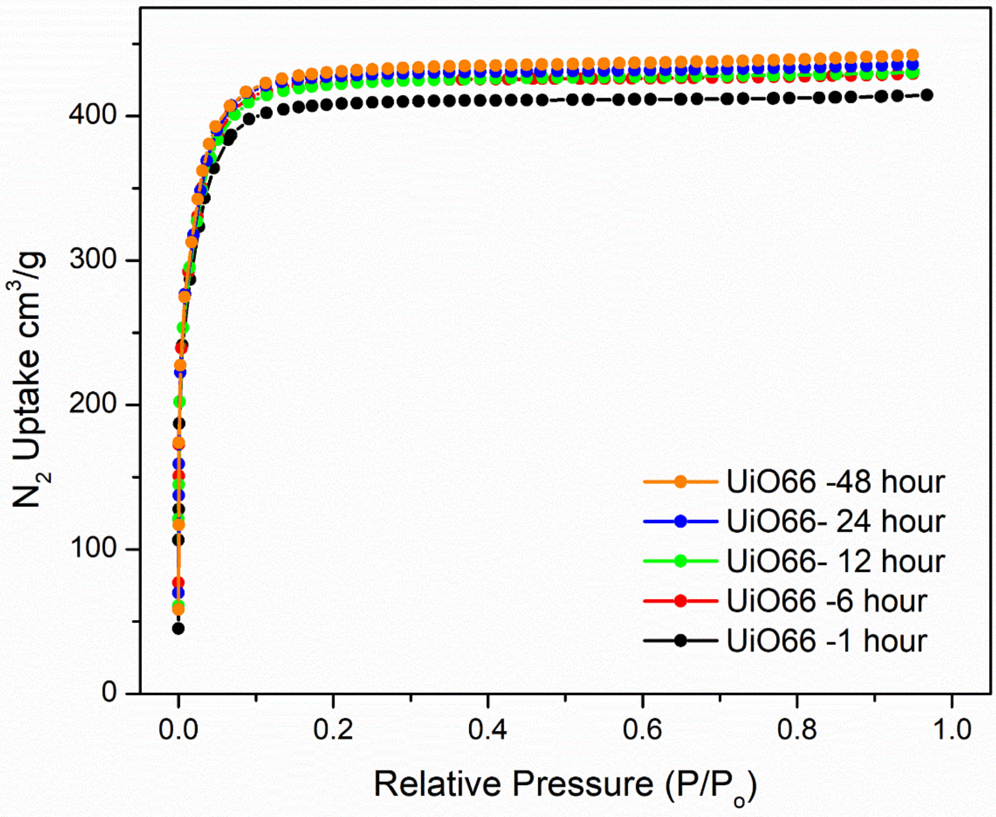

Figure S3 –UiO-66 N$_2$ Isotherms at 77K-"Related to Table 1"

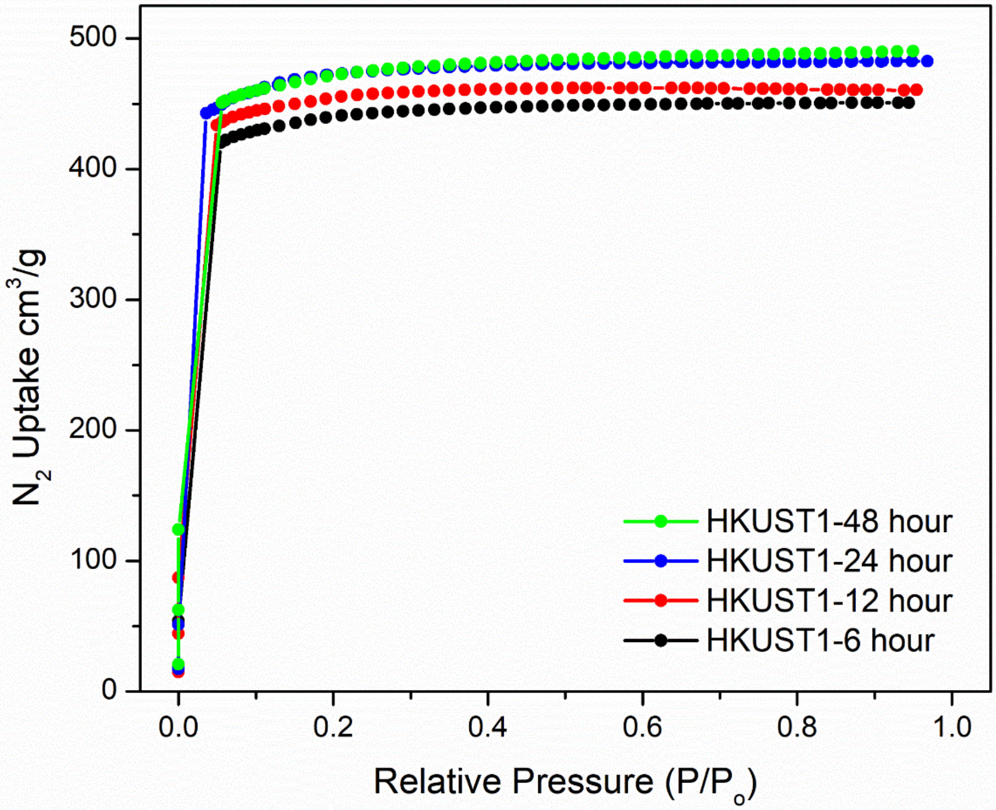

Figure S4 –HKUST-1 N$_2$ Isotherms at 77K- “Related to Table 1”

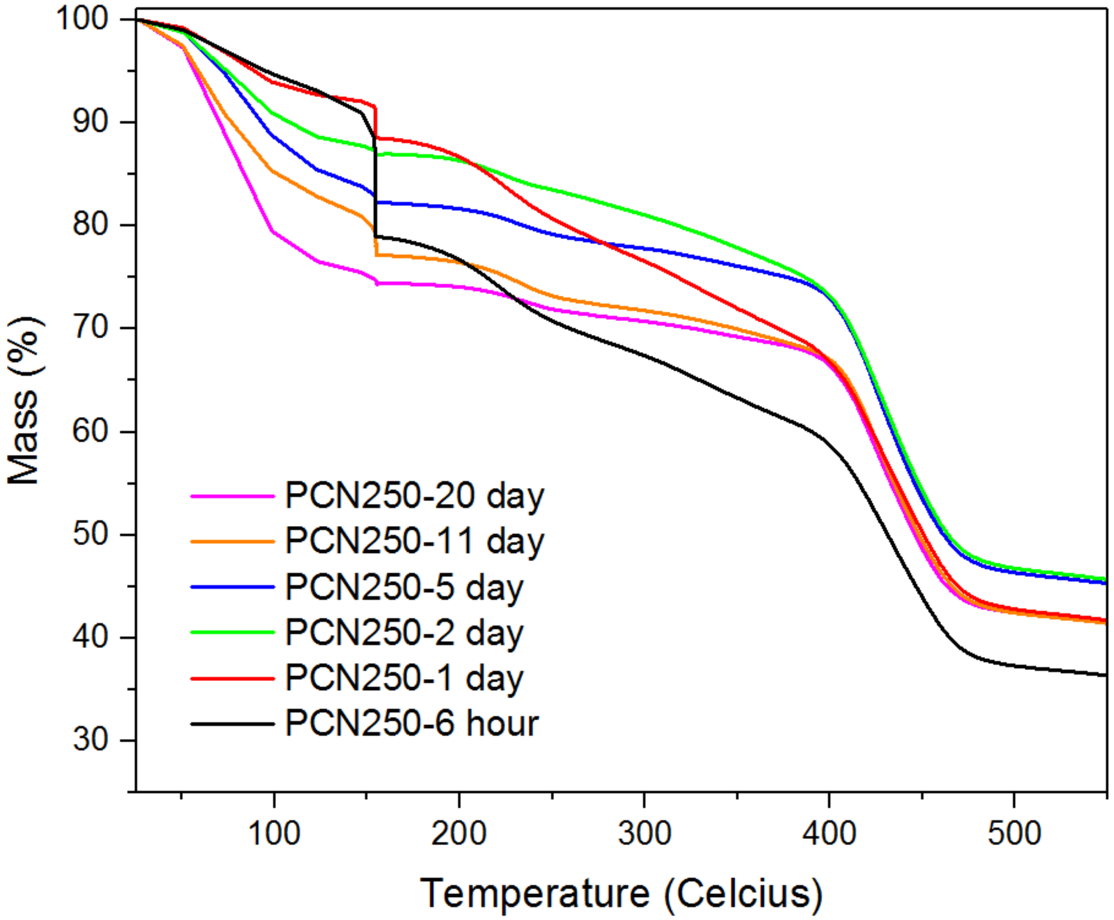

Figure S5 – Thermal Gravimetric Analysis (TGA) of all PCN-250 Samples- “Related to Table 1”

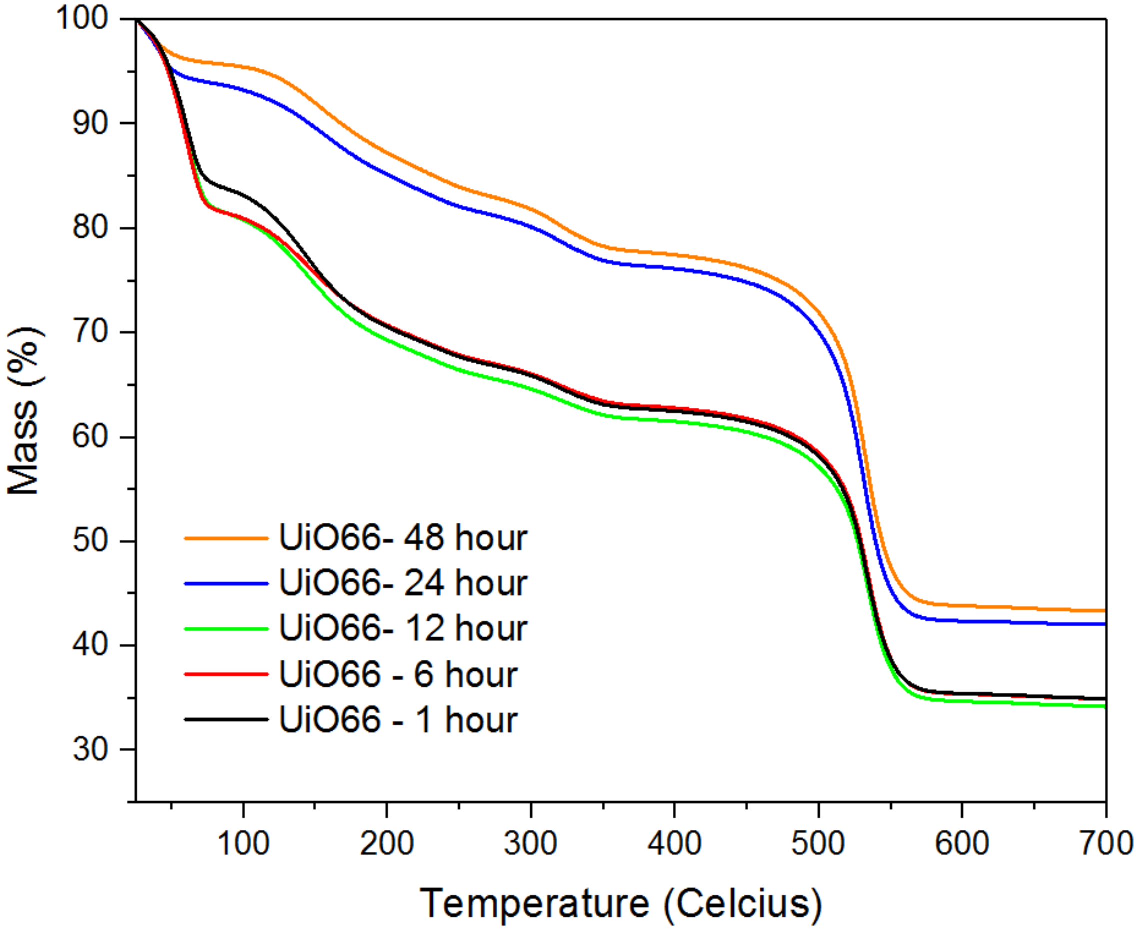

Figure S6 – Thermal Gravimetric Analysis (TGA) of all Ui-O66 Samples- “Related to Table 1”

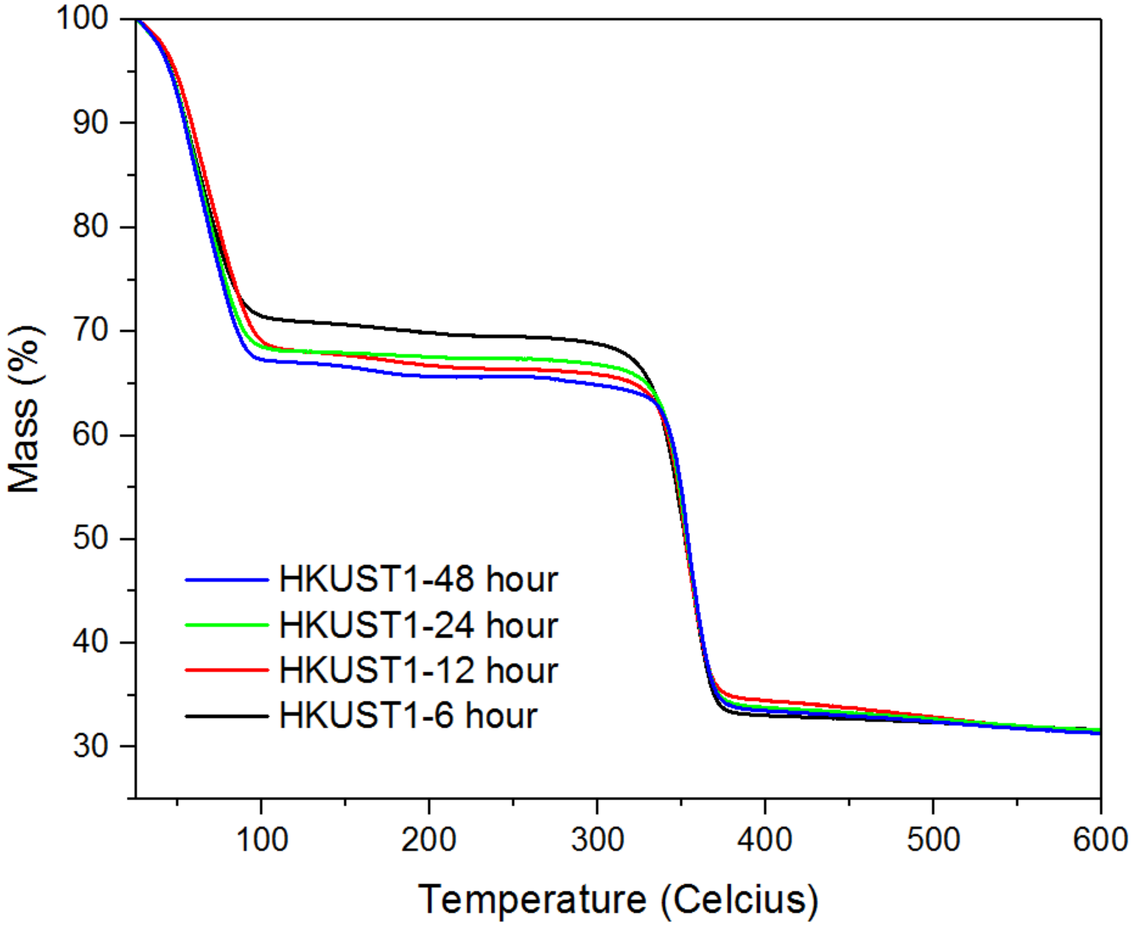

Figure S7 – Thermal Gravimetric Analysis (TGA) of all HKUST-1 Samples - "Related to Table 1"

Operating Cost Analysis for Traditional Solvent Exchange vs. Suspension Processing

Cost is calculated based on VWR prices for solvents
Price of water is considered negligible
Labor cost based on single user processes

DMF average price: $10.25 per liter
MeOH average price: $2.50 per liter
CH_2Cl_2 average price: $7.50 per liter
EtOH (190 Proof) average price: $40.80 per liter
US federal minimum wage: $7.25/hour

PCN-250

7 Days Traditional Solvent Exchange – Surface Area 1446 m^2/g

As synthesized PCN-250 was washed with DMF 4 times and immersed in DMF over a 2-day period. Then it was washed with methanol 4 times and immersed in methanol over a 2-day period at 65 °C. Finally, it was washed CH_2Cl_2 6 times and immersed in CH_2Cl_2 over a 3-day period at 65 °C.

Each solvent wash or immersion used 50 mL per gram of MOF

Total solvent usage: 200 mL of MeOH and DMF, and 300 mL of CH_2Cl_2 per gram of MOF

For one kg of MOF

- 200 L of DMF = $2050.00
- 200 L of MeOH = $500.00
- 300 L of CH_2Cl_2 = $2250.00
- $4800.00 Total Cost of Solvent

Process time per wash: 1 hour.
Total number of washes: 14
14 hours of Labor - $101.50 per one kg Batch

5 Days Suspension Processing– Surface Area 1564 m^2/g

Approximately 8 grams of MOF present in .5 L of reaction slurry

2.5 L MeOH used per 8 grams of MOF
312.5 mL of MeOH per 1 g MOF
312.5 L per 1 kg of MOF
$781.25 of MeOH per kg of MOF

2 steps: Loading and filtering: 1 hour per step
Total labor: 2 hours - $14.50 per kg Batch

UiO-66

2 Days Traditional Solvent Exchange – Surface Area 1290 m^2/g

As synthesized UiO-66 was washed with DMF 9 times and immersed in DMF over a 3-day period. Then it was washed with methanol 9 times and immersed in methanol over a 3-day period at 65 °C.

Each solvent wash or immersion used 50 mL per gram of MOF

450 mL of MeOH and 450 mL of DMF utilized for one gram of MOF.

For one kg of MOF
- 450 L of DMF = $4612.50
- 450 L of MeOH = $1125.00
- $5737.50 Total Cost of Solvent

Process time per wash: 1 hour
Total number of washes: 18
18 hours of Labor - $130.50 per kg Batch

2 Days Suspension Processing– Surface Area 1675 m2/g

Approximately 5 grams of MOF present in .5 L of reaction slurry

2.5 L MeOH used per 5 grams of MOF
100 mL of MeOH per 1 g MOF
100 L per 1 kg of MOF
$250.00 of MeOH per kg of MOF

2 steps: Loading and filtering: 1 hour per step
Total labor: 2 hours - $14.50 per kg Batch

HKUST-1

2 Days Traditional Solvent Exchange – Surface Area 1617 m^2/g

As synthesized HKUST-1 was washed and immersed in distilled water 3 times and washed with 95% ethanol 3 times over a 2-day period.

Each wash or immersion used 50 mL per gram of MOF

450 mL of 95% ethanol and 450 mL of distilled water were used for one gram of MOF.

For 1 kg of MOF
- 450 L of Water = Negligible
- 450 L of 95% EtOH = $6120.00
- $6120.00 Total Cost of Solvent

Process time per wash: 1 hour
Total number of washes: 6
6 hours of Labor - $43.50 per kg Batch

2 Days Suspension Processing– Surface Area 1808 m2/g

Approximately 3.73 grams of MOF present in .5 L of reaction slurry

2.5 L MeOH used per 3.73 grams of MOF

670 mL of MeOH per 1 g MOF
670 L per 1 kg of MOF
$1675.00 total Solvent Cost per kg MOF

2 steps: Loading and filtering: 1 hour per step
Total labor: 2 hours - $14.50 per kg Batch

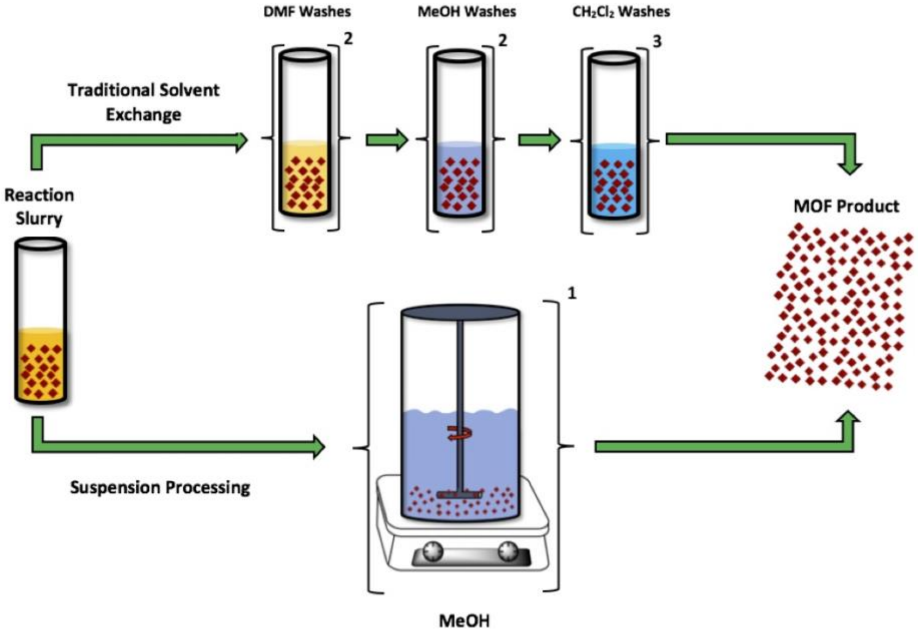

Figure S8 – Process comparison of traditional solvent exchange and suspension processing. – 'Related to Figure 5"

References:

Lin, K.-S., Adhikari, A.K., Ku, C.-N., Chiang, C.-L., Kuo, H., 2012. Synthesis and characterization of porous HKUST-1 metal organic frameworks for hydrogen storage. Int. J. Hydrog. Energy, ICCE-2011 37, 13865–13871.