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# Filtration of Chlorine and Hydrogen Chloride Gas by Engineered UiO-66-NH<sub>2</sub> Metal-Organic Framework

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## Highlights

- The metal-organic framework UiO-66-NH<sub>2</sub> was pressed into 20 × 40 mesh granules
- Breakthrough testing was conducted against chlorine (Cl<sub>2</sub>) and hydrogen chloride (HCl) and compared to broad spectrum carbon (BSC)
- Both Cl<sub>2</sub> and HCl performance of granulated UiO-66-NH<sub>2</sub> met or exceeded that of BSC
- Data show the potential of metal-organic frameworks to be utilized in filtration devices

Keywords:

Chlorine, hydrogen chloride, metal-organic framework, UiO-66-NH<sub>2</sub>, breakthrough

## Abstract

Chlorine (Cl<sub>2</sub>) and hydrogen chloride (HCl) are heavily utilized industrial chemicals that present significant respiratory health risks. The metal-organic framework UiO-66-NH<sub>2</sub> has shown an unprecedented ability in powder form to remove chlorine gas. Here, we engineered UiO-66-NH<sub>2</sub> into 20 × 40 mesh granules and evaluated their ability to remove chlorine and hydrogen chloride gas challenges. The exposed materials were characterized with nitrogen isotherms, powder X-ray diffraction, and attenuated total reflectance – Fourier transform infrared spectroscopy. Breakthrough results revealed

that UiO-66-NH<sub>2</sub> sorption of chlorine and hydrogen chloride met or exceeded sorption of state-of-the-art metal-impregnated activated carbon materials on a mass and volume basis in engineered form.

## 1. Introduction

Metal-organic frameworks (MOFs) are versatile materials comprised of interconnected metal oxide-based nodes and organic linkers. Considerable scientific interest has focused on these materials in recent years due to their potential in gas storage [1, 2], catalysis [3], toxic chemical removal [4, 5] and sensing [6] applications. In sharp contrast to conventional adsorbents, the modular nature of MOFs can be utilized for systematic tuning of the chemical characteristics by attaching functional groups of different reaction chemistries, sizes, polarities, hydrophilicities and acidities to the organic linker, without altering the topology of the framework [7]. This functionalization allows for selective tuning of the physical and chemical properties on the material and affects sorption and selectivity properties, as well as its thermal and chemical stability [5, 8].

Among this class of materials, the UiO MOFs have shown exceptional stability over wide ranges of pH, humidity, temperature, and pressure conditions [8-12]. These materials are based on Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> octahedral nodes, forming lattices by 12-fold connection by terephthalic acid-based linkers, resulting in a cubic close-packed unit cell structure [13]. The high affinity of zirconium towards oxygen ligands in these materials accounts for its exceptionally high chemical and thermal stability [14]. While versatile itself, incorporation of reactive functional groups into the UiO MOF material is sometimes necessary towards tailoring for specific toxic chemical mitigation applications. Among its many analogues, UiO-66-NH<sub>2</sub>, in which terephthalic acid is replaced by aminoterephthalic acid, has shown widespread reactivity without sacrifice of the stability properties of the parent material [8, 12, 15].

Despite exhibiting promising toxic chemical removal capabilities as a powder, UiO-66-NH<sub>2</sub> must be appropriately engineered to be useful in filtration applications. Engineered particles must be formed from powders that optimize removal efficiency while minimizing the pressure drop. Often, engineering a material will result in a decrease in filtration efficacy of target chemicals as compared to the powder form, as a significant fraction of reactive sites in the material become inaccessible as a result of the compacting process. Thus, it becomes paramount to identify pressures at which this effect is minimized. Peterson et al [16] previously investigated the effects of pelletization pressure on UiO-66 MOFs at pressures ranging from 1,000 to 10,000 psi, with results indicating that the UiO-66 material does not show significant degradation in surface area or performance. The effects of pressurization on the physical properties and chemical removal performance of UiO-66-NH<sub>2</sub> against the toxic industrial chemicals (TICs) ammonia and cyanogen chloride has also been investigated [17], showing stability of structure and retention of removal capabilities at pressures up to 25,000 psi. This effort has been extended here to evaluate the UiO-66-NH<sub>2</sub> MOF against other heavily-produced and highly-prevalent TICs, namely chlorine (Cl<sub>2</sub>) and hydrogen chloride (HCl).

Chlorine has a long history of military use as a chemical weapon and readily reacts in humid environments to form the harmful byproduct hydrogen chloride (HCl), providing a great respiratory threat. In previous filter applications, chlorine gas has largely been removed via activated carbons impregnated with copper and silver salts to form the corresponding metal chlorides upon reaction with the surface[18]. In contrast, it has been shown that with the powder-form MOF UiO-66-NH<sub>2</sub>, chlorine interacts at the amine group via an electrophilic aromatic substitution reaction[19]. Here, we evaluate engineered UiO-66-NH<sub>2</sub> against Cl<sub>2</sub> and HCl threats in simulated single-pass filter conditions and compare its performance to state-of-the-art materials.

## 2. Experimental

## 2.1 Materials development

### 2.1.1 UiO-66-NH<sub>2</sub> Synthesis

UiO-66-NH<sub>2</sub> was synthesized using established methods as noted previously [17]. A 12 g quantity of zirconium(IV) chloride and 3 mL of water were added to 800 mL of N,N-dimethylformamide (DMF) and stirred until fully dissolved. In parallel, 9.4 g of 2-Aminoterephthalic acid was added to 400 mL of DMF and stirred until fully dissolved. The two solutions were mixed in a BüchiGlasUster Ecoclave 075 batch reactor with a 1.6 L glass reactor vessel and then stirred at 500 RPM and held at 120 °C for 24 h. The resulting solid was then recovered via vacuum filtration. The material was then purified using a Soxhlet extraction process with methanol for 24 h. Remaining surface solvent was removed from the material by heating it in air at 85 °C. Solvent was then evacuated from the pores by depressurizing the samples to 50 mTorr and subsequently subjecting to a heating profile of 85 C for 4 h followed by 150 C for 18 h.

### 2.1.2 Engineering Granules

Engineered granules were made by pressing approximately 5 g batches of UiO-66-NH<sub>2</sub> into pellet form at 5K, 10K, 25K, and 50K psi with a 1.5 in. die in a Carver Press. The pellet was then crushed using a Sepor jaw crusher in order to break apart the material into smaller constituents, and the resulting distribution was then sieved to 20 × 40 mesh size particles, a common range employed in filters. The corresponding samples produced were referred to as UiO-66-NH<sub>2</sub>-5Kpsi, UiO-66-NH<sub>2</sub>-10Kpsi, UiO-66-NH<sub>2</sub>-25Kpsi, and UiO-66-NH<sub>2</sub>-50Kpsi. The efficiency of the process was approximately 25%, with many fine particles produced. This process was repeated multiple times to produce enough mass for breakthrough testing.

## 2.2 Performance Methods

### 2.2.1 Microbreakthrough

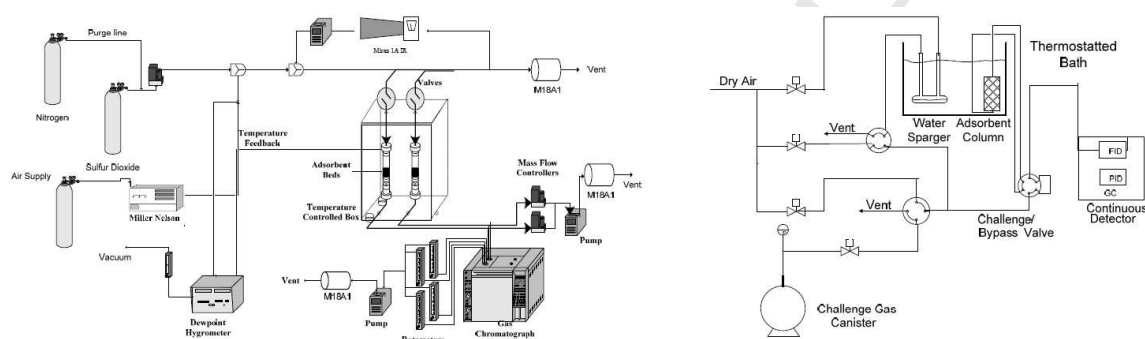
UiO-66-NH<sub>2</sub> materials were evaluated in a chemical microbreakthrough system as has been described previously [20, 21] and is also depicted in Figure 1. Briefly, a specific amount of Cl<sub>2</sub> gas was injected into a mixing ballast and subsequently pressurized to yield a concentration of 10,000 mg m<sup>-3</sup>. The ballast contents were then mixed with a diluent air stream under dry conditions at a rate necessary to achieve a challenge concentration of 2,000 mg m<sup>-3</sup>. The mixed stream then passed through a sorbent bed submerged in a temperature-controlled water bath at 20 °C. Approximately 50 mm<sup>3</sup> of each sample was packed into a 4 mm i.d. tube, corresponding to 4 mm of bed depth and a residence time of approximately 0.15 s. Samples were activated at 150 °C to remove impurities for 1 h before the test. The effluent stream then passed through a continuously operating Hewlett-Packard 5890 Series II gas chromatograph equipped with a photoionization detector with an 11.7 eV lamp. Loadings were calculated by integrating the breakthrough curves at saturation, as described previously [21]. The system exhibits approximately 10% deviation with respect to saturation loading.

### 2.2.2 Breakthrough Tube

Breakthrough testing was conducted on a push-pull-vented system, as shown in Figure 1. In separate tests, chlorine and hydrogen chloride were individually fed from a compressed gas cylinder via a mass flow controller to a manifold, where it was mixed with pretreated air at 15% RH and 25 °C to achieve a challenge concentration of 2000 mg m<sup>-3</sup>. From this excess flow stream, a vacuum was pulled through a 4.1 cm i.d. cylindrical glass tube. The tube was filled via storm-filling to a bed depth of 1 cm, which corresponded to approximately 8 g of UiO-66-NH<sub>2</sub> granules and approximately 17 g of BSC carbon (no pretreatment other than initial activation of the powder). The airflow velocity through the packed bed was 6.6 cm s<sup>-1</sup>, corresponding to a flow rate of 5.2 L min<sup>-1</sup> and a residence time of approximately 0.15 s. The effluent concentration was continuously monitored using electrochemical cell detectors. During the Cl<sub>2</sub> experiments, both Cl<sub>2</sub> and HCl were monitored simultaneously, as HCl is a potential product of Cl<sub>2</sub>

reaction with the sorbent. Breakthrough times were calculated to toxic concentration levels of 1 and 5 ppm for  $\text{Cl}_2$  and  $\text{HCl}$ , respectively, corresponding to Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs). Loading values, expressed in terms of grams of chemical removed per gram of sorbent utilized, were calculated according to equation (1).

$$\text{Loading (g g}^{-1}\text{)} = \frac{[C_{t_{\text{feed}}}(\text{mg min}^{-1}) - C_{t_{\text{break}}}(\text{mg min}^{-1})] \times \text{flow rate (m}^3 \text{ min}^{-1}) \times \frac{1 \text{ g}}{1000 \text{ mg}}}{\text{mass sorbent (g)}} \quad (1)$$



**Fig. 1.** Breakthrough Tube (left) and Microbreakthrough (right) System Schematics

## 2.3 Materials Characterization

### 2.3.1 X-ray Diffraction

X-ray diffraction (XRD) pattern measurements were performed with a Rigaku MiniFlex 600 X-ray diffractometer equipped with a D/teX X-ray detector with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV voltage and 15 mA current. MiniFlex Guidance software was used for data acquisition, and PDXL 2 diffraction analysis software was used to process the measured data and subtract the background. Samples were loaded onto Rigaku 906165 Flush Si 510 zero-background sample holders coated with an ultrathin layer of laboratory-grade Vaseline (Sigma-Aldrich) and scanned from a  $2\theta$  range of 3 to 90 degrees at a rate of  $5 \text{ degrees min}^{-1}$ .

### 2.3.2 Nitrogen isotherm

Nitrogen isotherm data were collected at 77 K using a Micromeritics ASAP 1200 system. Samples were off-gassed at 120 °C under nitrogen for approximately 16 h. Surface area measurements were calculated using the Brunauer–Emmett–Teller (BET) method, and the pore volume was calculated at a relative pressure of 0.975. Pore size distributions were calculated using density functional theory (DFT) and a carbon slit pore kernel. A silica–alumina standard run on the system exhibits less than 1% standard deviation on surface area measurements.

### 2.3.3 Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy

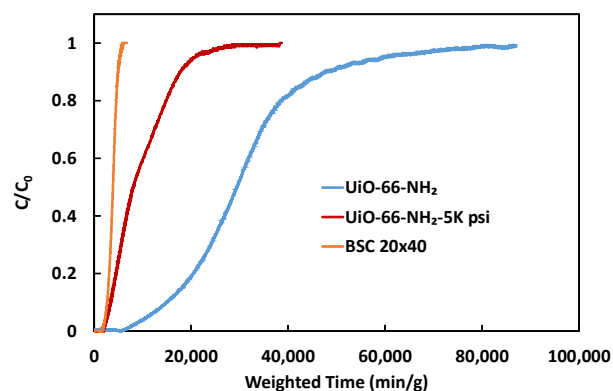
A Bruker Tensor 27 Fourier Transform Infrared (FTIR) Spectrometer equipped with a diamond Bruker Platinum Attenuated Total Reflectance (ATR) accessory and OPUS software was used for infrared spectroscopy measurements. Samples were scanned at a resolution of 2 cm<sup>-1</sup>, utilizing 16 scans for the sample and background over a range of 4000 to 400 cm<sup>-1</sup> with a quartz beam splitter, an aperture of 6 mm, and a scanner velocity of 10 kHz.

## 3. Results and Discussion

### 3.1 Microbreakthrough

As a baseline evaluation of the effect of pelletization, powder and granular UiO-66-NH<sub>2</sub>, as well as a sample of 20x40 mesh size BSC carbon (3M), were tested in a microbreakthrough system against Cl<sub>2</sub> challenge, with the results shown in Table 1. A notable decrease in Cl<sub>2</sub> loading was observed from the powder form material to the lowest-pressure granulated form, UiO-66-NH<sub>2</sub>-5Kpsi, but only a marginal drop in loading was subsequently observed from additional pressurization up to 25K psi. An additional noticeable drop in performance then occurred upon pressurization to 50K psi. The microbreakthrough

system measurements are considered to have a margin of error of  $\pm 10\%$ [21], which likely explains the slight increase in loading calculated between UiO-66-NH<sub>2</sub>-5Kpsi and UiO-66-NH<sub>2</sub>-10Kpsi; these two materials have effectively identical performance within error bars. These data were used to down select the 5K psi sample for tube breakthrough performance evaluation based on loading performance and energy minimization of material synthesis, which is lower for the 5K psi analogue than the 10K psi analogue. Figure 2 shows the breakthrough curves, and Table 1 data shows that the resulting capacity of the engineered form for Cl<sub>2</sub> is greatly reduced upon pelletization but still achieves a capacity of 5.2 mol kg<sup>-1</sup>, which far exceeds BSC's capacity of 2.2 mol kg<sup>-1</sup>. These performance differences between powder and granule may be due to a high percentage of adsorption sites becoming blocked from the compacting process. This blockage of sites may also impede diffusion processes of challenge through the material, which would leave the majority of the active sites for adsorption residing closer to the granule surface than for the uncompacted material.



**Fig. 2.** Cl<sub>2</sub> Microbreakthrough for UiO-66-NH<sub>2</sub> Materials and BSC

**Table 1.** Cl<sub>2</sub> Microbreakthrough Data for Various Pelletization Pressures of UiO-66-NH<sub>2</sub>

| Material                        | Cl <sub>2</sub> loading<br>(mol kg <sup>-1</sup> ) | Cl <sub>2</sub> loading<br>(g g <sup>-1</sup> ) |
|---------------------------------|----------------------------------------------------|-------------------------------------------------|
| UiO-66-NH <sub>2</sub> (powder) | 17.0                                               | 1.20                                            |
| UiO-66-NH <sub>2</sub> -5K psi  | 5.2                                                | 0.37                                            |
| UiO-66-NH <sub>2</sub> -10Kpsi  | 5.7                                                | 0.41                                            |
| UiO-66-NH <sub>2</sub> -25Kpsi  | 4.0                                                | 0.28                                            |
| UiO-66-NH <sub>2</sub> -50Kpsi  | 1.9                                                | 0.14                                            |
| BSC                             | 2.2                                                | 0.16                                            |

Surface area and pore volume measurements were conducted on each of the UiO-66-NH<sub>2</sub> analogues, as summarized in Table 2. The BET surface area, t-plot micropore volume, and total pore volume of the pelletized UiO-66-NH<sub>2</sub> materials closely mirror their corresponding Cl<sub>2</sub> loadings, as a sharp drop in surface area and pore volume is observed from the powder form to the 5,000 psi granulated form, but only moderate reductions in those properties occur at higher pressures. UiO-66-NH<sub>2</sub> has a pore size distribution largely concentrated in the 10-20 angstrom region and maintains this distribution throughout the range of pelletization pressures utilized, as evaluated previously [17].

**Table 2.** Physical Properties of Compressed UiO-66-NH<sub>2</sub> Samples

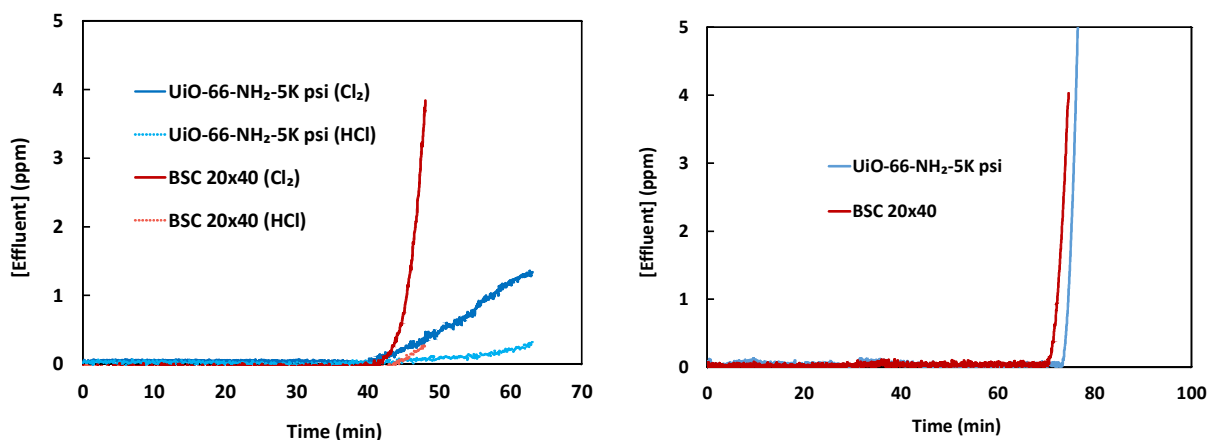
| UiO-66-NH <sub>2</sub> pressure (psi) | BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | t-plot micropore volume (cm <sup>3</sup> g <sup>-1</sup> ) | Total pore volume (cm <sup>3</sup> g <sup>-1</sup> ) |
|---------------------------------------|----------------------------------------------------|------------------------------------------------------------|------------------------------------------------------|
| 0 (powder)                            | 1074                                               | 0.38                                                       | 0.40                                                 |
| 5,000                                 | 827                                                | 0.23                                                       | 0.26                                                 |
| 10,000                                | 775                                                | 0.27                                                       | 0.31                                                 |
| 25,000                                | 627                                                | 0.21                                                       | 0.26                                                 |
| 50,000                                | 589                                                | 0.20                                                       | 0.24                                                 |

### 3.2 Tube Breakthrough Tests

The 5K psi batch of 20×40 mesh granules of UiO-66-NH<sub>2</sub> was downselected for further evaluation due to its high Cl<sub>2</sub> removal capacity and energy minimization of synthesis relative to the 10K psi analogue. It was evaluated in a breakthrough tube system under parameters described in the methods section to simulate large-scale conditions in a filter environment. Utilization of a granular sample is necessary under the elevated flow rates in this setup to avoid unacceptably high pressure drop. Samples were compared to Broad Spectrum Carbon (BSC, 3M), an impregnated activated carbon used in several chemical, biological, radiological, and nuclear (CBRN) respiratory filters.

Figure 3 shows the breakthrough profiles of BSC and UiO-66-NH<sub>2</sub>-5Kpsi upon Cl<sub>2</sub> and HCl exposure, and Table 3 shows the calculated breakthrough times and loadings. The data demonstrate that UiO-66-NH<sub>2</sub> is able to match or surpass the performance of BSC against both chemicals. The HCl breakthrough profiles are similar for both materials, as HCl elutes at nearly identical times and have similarly steep profiles. With Cl<sub>2</sub> challenge, the breakthrough profile is much more gradual with UiO-66-NH<sub>2</sub> than the activated carbon, suggesting potentially slower reaction kinetics or a diffusion-limited reaction in the UiO-66-NH<sub>2</sub> material.

One likely cause for the difference in the Cl<sub>2</sub> breakthrough profiles is the difference in the adsorption mechanism. It has been suggested that Cl<sub>2</sub> is removed by UiO-66-NH<sub>2</sub> via an electrophilic aromatic substitution mechanism, where chlorine atoms are substituted on the aminoterephthalic acid linker, and the resulting HCl byproduct can cleave the bond between the linker and Zr<sub>6</sub>O<sub>6</sub> node or form an adduct with the amine groups on the linker [19]. In contrast, on impregnated activated carbons, reaction with Cl<sub>2</sub> may be faster and also less complex due to the “feeder pore” structure of these materials. While hydrolysis still occurs first, as shown by the generation of HCl byproduct, the pore structure allows for more efficient transport of Cl<sub>2</sub> to adsorption sites and mitigates diffusional limitations present in the UiO-66-NH<sub>2</sub>. When challenged directly with HCl, similar performance was observed among both materials, with a sharp breakthrough wavefront observed in both cases. This corresponds to direct reaction mechanisms – HCl with the SBU on UiO-66-NH<sub>2</sub> and with metal impregnants on the BSC.



**Fig. 3.**  $\text{Cl}_2$  (left) and  $\text{HCl}$  (right) Breakthrough Curves for UiO-66- $\text{NH}_2$ -5K psi and BSC

**Table 3.**  $\text{Cl}_2$  and  $\text{HCl}$  Breakthrough Data for UiO-66- $\text{NH}_2$ -5K psi and BSC

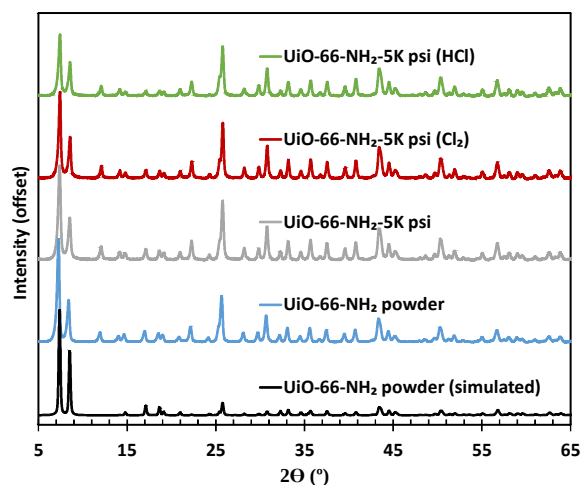
| Chemical      | Parameter*                                              | BSC     | UiO-66- $\text{NH}_2$ |
|---------------|---------------------------------------------------------|---------|-----------------------|
| $\text{Cl}_2$ | Break time (min)                                        | 45.4    | 54.8                  |
|               | Ct ( $\text{mg} \cdot \text{min} \cdot \text{m}^{-3}$ ) | 90,800  | 109,600               |
|               | Loading ( $\text{g} \cdot \text{g}^{-1}$ )              | 0.054   | 0.062                 |
| $\text{HCl}$  | Break time (min)                                        | 77.1    | 76.5                  |
|               | Ct ( $\text{mg} \cdot \text{min} \cdot \text{m}^{-3}$ ) | 154,200 | 153,000               |
|               | Loading ( $\text{g} \cdot \text{g}^{-1}$ )              | 0.091   | 0.086                 |

\*Breakthrough times, Ct values, and loadings to OSHA PELs of 1.0 ppm for  $\text{Cl}_2$  and 5.0 ppm for  $\text{HCl}$

### 3.3 Characterization

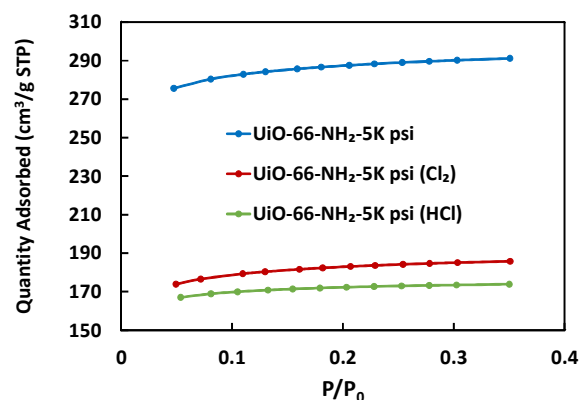
X-ray diffraction patterns of the 5,000 psi  $\text{Cl}_2$ -exposed UiO-66- $\text{NH}_2$  material shows a negligible change in the crystal structure relative to the base material, as shown in Figure 4. This is in sharp contrast to the powder form [19], which demonstrated a complete degradation upon  $\text{Cl}_2$  exposure. The diffraction patterns suggest that the long-range order of the material remains largely intact in granulated form. A possible explanation may be due to a high percentage of sites becoming inaccessible for adsorption after compaction in the pelletized form, or it may be due to the granulated-form materials not being exposed for enough time to fully saturate all available sites. Upon  $\text{HCl}$  exposure, a minor loss in

crystallinity is observed in the UiO-66-NH<sub>2</sub> material, indicated by slight attenuation in the low-angle XRD peaks.



**Fig. 4.** XRD Patterns of UiO-66-NH<sub>2</sub>-5K psi Samples

The granulated version of UiO-66-NH<sub>2</sub> exhibited a much lower BET surface area than the powder, as shown in Table 4. N<sub>2</sub> isotherms of the granulated versions are depicted in Figure 5. A P/P<sub>0</sub> range of 0.05 to 0.35 was used in this measurement as the Rouquerol transform of the data indicated that this was a sufficient region for accurate calculation of the BET surface area. Notable reductions in surface area were observed in the Cl<sub>2</sub>-exposed forms of both powder and 5K psi granule UiO-66-NH<sub>2</sub>. This again suggests that the compaction process of the material ultimately limits the toxic chemical accessibility of the material.

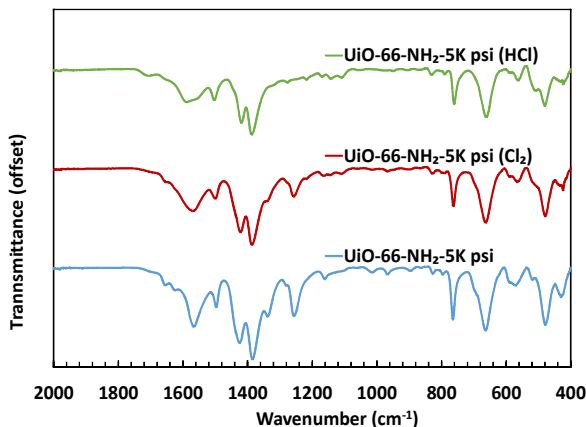


**Fig. 5.** N<sub>2</sub> Isotherms of UiO-66-NH<sub>2</sub> Granulated Samples**Table 4.** BET Surface Area Data of UiO-66-NH<sub>2</sub> Materials

| Material                                                   | BET surface area (m <sup>2</sup> g <sup>-1</sup> ) |                |
|------------------------------------------------------------|----------------------------------------------------|----------------|
|                                                            | Powder                                             | 5K psi Granule |
| UiO-66-NH <sub>2</sub>                                     | 1074                                               | 827            |
| UiO-66-NH <sub>2</sub> -<br>after Cl <sub>2</sub> exposure | 925                                                | 529            |
| UiO-66-NH <sub>2</sub> -<br>after HCl exposure             | N/A                                                | 493            |

FTIR spectra of the Cl<sub>2</sub>-exposed granulated sample showed negligible deviation from the baseline material, as demonstrated in Figure 6. This is again in sharp contrast to the powder form, where a notable decrease occurred for the peak at 1600 cm<sup>-1</sup> with corresponding appearance of a new peak at 1680 cm<sup>-1</sup>. The peak at 1680 cm<sup>-1</sup> forms from protonation of the carboxylate group upon linker-SBU bond breakage and is indicative of formation of a ZrOCl<sub>2</sub> species, suggesting that the node is a secondary adsorption site for Cl<sub>2</sub> after HCl decomposes the MOF [19]. There is slight deterioration in the peaks around 1570 cm<sup>-1</sup> and 480 cm<sup>-1</sup> with the HCl-exposed material, corresponding to O-C-O stretching modes and  $\mu$ 3-OH stretching modes in the Zr<sub>6</sub>O<sub>6</sub> node, respectively. Furthermore, complete loss of the peak at 1260 cm<sup>-1</sup> occurs, which corresponds to C-N stretching modes in the aromatic amine group in the linker [22]. HCl likely reacts directly with the amine group of the aminoterephthalic acid linker of UiO-66-NH<sub>2</sub> to form an ammonium chloride-type species, whereas this is not immediately formed with

Cl<sub>2</sub> exposure because the amine group acts as a catalytic site for ortho-para substitution of Cl atoms on

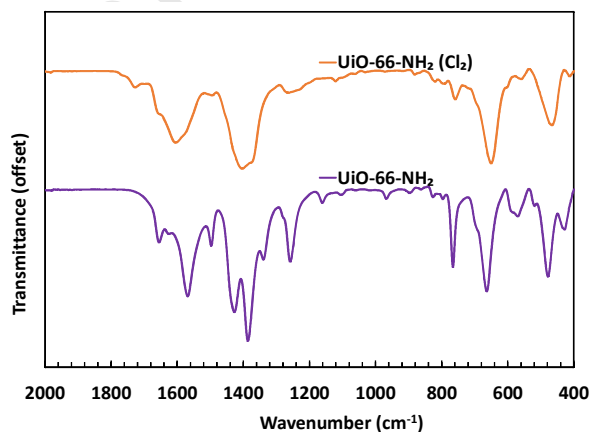


the aminoterephthalic acid linker.

**Fig. 6.** FTIR Spectra of 5K psi UiO-66-NH<sub>2</sub> Samples (left) and powder-form UiO-66-NH<sub>2</sub> Samples (right)

#### 4. Conclusions

UiO-66-NH<sub>2</sub> demonstrated exceptional Cl<sub>2</sub> and HCl removal capabilities in an engineered form that exceeded state-of-the-art activated carbon material in performance capabilities. Data from the N<sub>2</sub> isotherm showed that the surface area of



the material is notably reduced upon granulation when compared to the powder form, and the Cl<sub>2</sub> removal capability is reduced by a corresponding percentage, but the material compacted at 5,000 psi still achieves a high Cl<sub>2</sub> loading of 5.2 mol kg<sup>-1</sup>. This suggests that compaction may block active sites involved in the Cl<sub>2</sub> adsorption process and possibly inhibit the diffusion of the chemical challenge through the micropores of the material. The breakthrough wavefront of Cl<sub>2</sub> through engineered UiO-66-NH<sub>2</sub> was much slower than through the state-of-the-art BSC activated carbon material due to either those diffusion limitations or the more complex mechanism of Cl<sub>2</sub> adsorption in UiO-66-NH<sub>2</sub>. Against the HCl challenge, the adsorption wavefront had similar steep profiles for both materials, suggesting a simple mechanism of adsorption and reaction on easily accessible sites. Mild reductions in surface area,

micropore volume, and  $\text{Cl}_2$  loading occur with increased pressure of the granules, but significant deterioration of performance is not observed until 50,000 psi compaction. Overall, data show that UiO-66- $\text{NH}_2$  is a promising material for filtration applications.

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