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Functionalization of Cotton Fiber by Partial Etherification and Self-Assembly of Polyoxometalate Encapsulated in $Cu_3(BTC)_2$ Metal–Organic Framework

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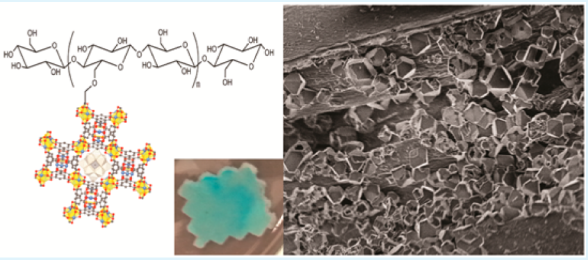
ABSTRACT: A combination of a Keggin-type polyoxometalate (POM), $[CuPW_{11}O_{39}]^{5-}$, with a $Cu_3(BTC)_2$ metal–organic framework (MOF-199/HKUST-1; where BTC is benzene-1,3,5-tricarboxylate), was successfully self-assembled on a cellulose substrate (cotton) with a room-temperature process. Cotton fibers were functionalized by partial etherification. $Cu_3(BTC)_2$ metal–organic framework and polyoxometalate encapsulated in $Cu_3(BTC)_2$ metal–organic framework were self-assembled on the carboxymethylate ion sites initiated with copper nitrate using ethanol and water as solvents. Octahedral crystals were observed on both MOF-cotton and POM-MOF-cotton; both contained copper while the POM-MOF-cotton also contained tungsten. Occupancy of POM in MOF cages was calculated to be about 13%. Moisture content remained at 3 to 4 wt % similar to that of untreated cotton. Reactivity to both hydrogen sulfide and methyl parathion was higher for POM-MOF-cotton due to the Keggin polyoxometalate and the extra-framework cations Cu^{2+} ions compensating the charges of the encapsulated Keggins. The POM-MOF material was found to effectively remove 0.089 mg of methyl parathion per mg of MOF from a hexane solution while MOF-cotton removed only 0.054 mg of methyl parathion per mg of MOF.



KEYWORDS: *metal–organic framework, polyoxometalate, Keggin heteropolyacid, cellulose, decontaminating, HKUST-1, MOF-199, organophosphate, fiber*

1. INTRODUCTION

Metal–organic frameworks (MOFs), crystalline nanoporous materials composed of metal clusters connected by multifunctional organic linkers, have attracted much interest due to their large surface area and controllable pore size.[1,2] They selectively adsorb chemicals and gases including organophosphates.[3−5] MOF-199, a copper(II)-benzene-1,3,5-tricarboxylate (CuBTC) MOF composed of dimeric cupric tetracarboxylate units with the chemical formula of $Cu_3BTC_2{\cdot}3H_2O$, acts as a Lewis acid due to the open metal sites on the Cu(II) coordination sphere.[6,7] This MOF framework has been found to contain three different types of pores: one (S1) is relatively small with a diameter of 4.9 Å while there are two larger pores; one (L2) represents the octahedral holes of the face-centered-cubic structure and has a diameter of 10.5 Å and the other (L3) has a diameter of 12.2 Å.[6,8] $Cu_3(BTC)_3$ has been grown on the surfaces of pulp fibers,[9] and a method to chemically attach MOF-199 on cellulose fibers was developed by da Silva Pinto et al.[10] providing the basis for fabrication of functionalized fibers.

In addition to the open Cu(II) metal sites in MOF-199, encapsulation of other active agents in the cages can increase function of the material. Polyoxometalates (POMs) have been incorporated in MOF structures resulting in enhancement of air-based oxidation.[11,12] Nanoporous materials have been synthesized by self-assembly of Cu_3BTC_2 that enclose Keggin-type heteropolyacids within the metal–organic framework.[12] Polyoxometalate (POM), $[PW_{12}O_{40}]^{3-}$, fits in the L2 pores of MOF-199 with Cu as exchangeable extra-framework cations being in the L3 pore.[14,15] The encapsulation of the Keggin polyoxometalate in the Cu_3BTC_2 metal–organic framework results in substantial synergistic stabilization of MOF and POM.[12,16] Bajpe et al.[13] presented evidence that these functional structures formed through molecular-level structure templating of a 3D porous framework. Self-assembled POM-MOFs are very promising materials for oxidative self-decontamination of chemical threats.[17,18]

Addition of Keggin-type heteropolyacid during synthesis of the nanoporous material has been shown to enable paddle wheel formation and, thus, the precipitation of Cu_3BTC_2 at room temperature along with systematic encapsulation of the Keggin ions in the pores.[14] In this manuscript, we present a room temperature self-assembling method to chemically attach POM-MOF structures on cellulosic fibers, i.e., cotton. Further, we demonstrate the ability of these materials to react with hydrogen sulfide and oxidize methyl parathion, an organophosphate. Functionalization of a textile with POM-MOF creates a multifunctional material for potential applications such as protective materials.[19,20]

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2. EXPERIMENTAL SECTION

2.1. Materials. POM, $K_5[CuPW_{11}O_{39}]$, was provided by Craig Hill from Emory University (Atlanta, GA). Desized and unbleached cotton print cloth (Style #: 400U; Lot #: 1722) was purchased from Testfabrics, Inc. (West Pittston, PA). Copper(II) nitrate trihydrate, trimesic acid, sodium chloroacetate, and hydrogen sulfide were purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Sodium hydroxide was from Mallinckrodt (Hazelwood, MO). HPLC grade hexane, HPLC grade acetonitrile, and *N*,*N*-dimethylformamide (DMF) were purchased from EMD Millipore (Gibbstown, NJ). Ethanol was purchased from Pharmco Products (Brookfield, CT). All water used was filtered using a Milli-Q Advantage A10 system and a LC-pak polisher from Millipore (Billerica, MA). Basolite C-300 (BASF, Florham Park, NJ), a commercially available MOF-199, was used as a standard for XRD and IR analyses. Methyl parathion and its degradation products, methyl paraoxon (PS-613), *O*,*O*,*O*-trimethyl phosphoric thiourate (F2570), and 4-nitrophenol (O-896), were purchased from Chem Service Incorporated (West Chester, PA).

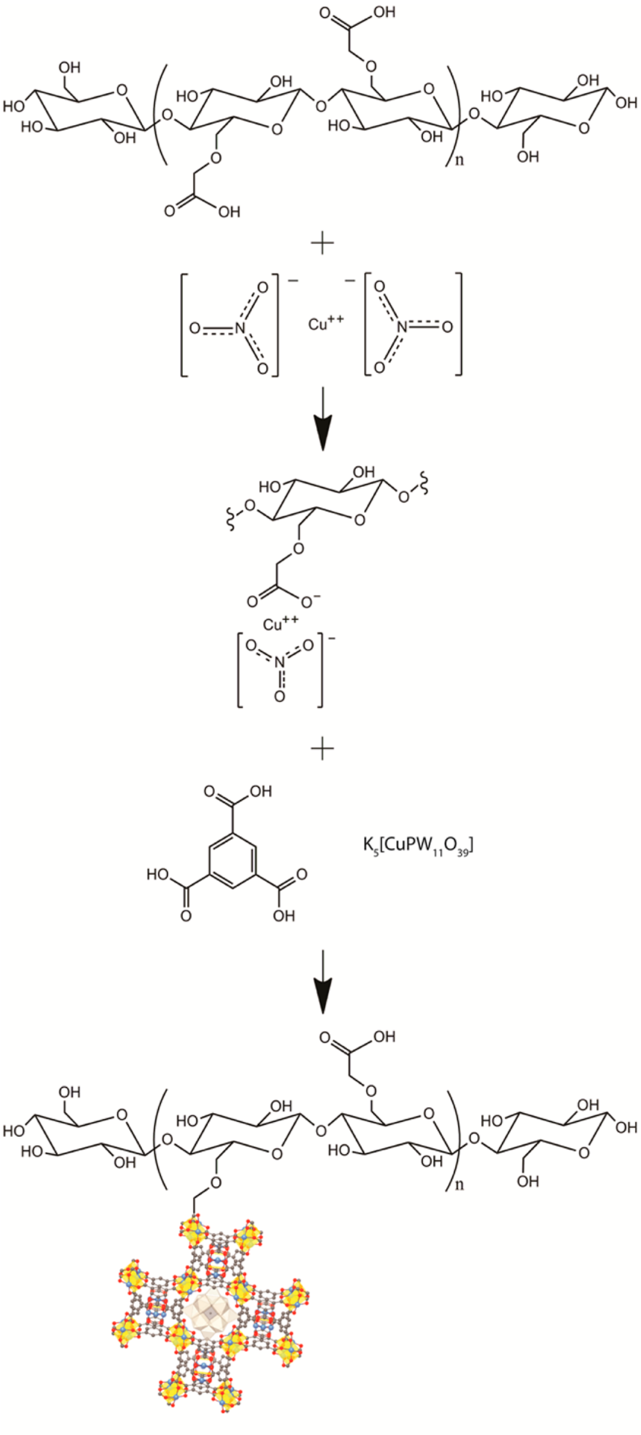
2.2. Assembly of MOF and POM-MOF Structures on Cellulosic Fibers. To assemble the MOF structure on the cotton fiber, an anionic site was created for bonding with the Cu ions. This was achieved by creating carboxymethylated cellulose using the following procedure that is based on a classic reaction between chloroacetate salt and cellulose using sodium hydroxide as a catalyst.[21] Four untreated cotton specimens (5.08 × 5.08 cm) were submerged in 150 mL of water containing 30 g of sodium hydroxide for 10 min. The specimens were patted dry and then heated to 45 °C for 12 min before soaking in 150 mL of water containing 30 g of sodium chloroacetate for 5 min to create carboxylate groups. The specimens were again patted dry and heated to 85 °C for 30 min. Water was used to vigorously wash the specimen to remove any unreacted materials before acidification with 150 mL of a 2 g/L acetic acid aqueous solution. Specimens were washed again with water before air-drying.

Synthesis of the POM-MOF on the surface of the cellulose substrate (POM-MOF-cotton) was based on two modified methods from the literature.[7,10] First, three separate solutions were made: 800 mg of trimesic acid was dissolved in 12 mL of ethanol, 1.00 g of $CuNO_3 \cdot 3H_2O$ was dissolved into 14 mL of ethanol, and 800 mg of $K_5CuPW_{11}O_{39}$ was dissolved in 14 mL of H_2O. All three solutions were sonicated for 30 min. 250 mg of carboxymethylated cotton was added to the $CuNO_3 \cdot 3H_2O$/ethanol solution and stirred for 24 h. Then, over 10 min, the following solutions were added dropwise to the $CuNO_3 \cdot 3H_2O$/ethanol solution in this order: 7 mL of POM/water, 6 mL of trimesic acid/ethanol, 7 mL of POM/water, and finally 6 mL of trimesic acid/ethanol. This was stirred at room temperature for 45 h. Fabric was removed from the reaction vessel and stirred in 20 mL of water for 3 h, followed by 20 mL of DMF for 3 h, and finally ethanol for 3 h. On the basis of the procedures of da Silva Pinto et al.,[10] all modified cotton specimens were washed with distilled water, DMF, and methanol to remove any MOF-199 or other reactants that were not chemically attached to the cellulose fibers. The fabric was then vacuumed dried overnight at room temperature. MOF-cotton samples were prepared with the same procedure except the POM was not added to the water. The proposed mechanism for POM-MOF-cotton formation is shown in Scheme 1.

A solvent system was chosen to solubilize both POM and trimesic acid. In the previously reported room temperature synthesis of MOF-199 on cellulose,[7,10] DMF, ethanol, and water were used in equal parts to encourage self-assembly of the MOF structure. Trimesic acid is not very soluble in water, and POM is not very soluble in DMF; therefore, DMF was replaced with ethanol in the solvent system for nearly a 2:1 ratio of ethanol and water for these experiments.

2.3. Morphological and Chemical Characterization. Field emission scanning electron microscopy (FESEM) was completed using a LEO 1550 FESEM from Carl Zeiss, Inc. (Thornwood, NY) at an accelerating voltage of 3 keV. Specimens were sputter coated with carbon for 30 s prior to FESEM imaging. A FESEM image analysis of the particle size was performed using ImageJ (National Institutes of Health, Bethesda, MD) by averaging a total of 90 particle size measurements from 3 different images (30 measurements per image) for each sample. X-ray energy dispersive analysis was performed with a Bruker AXS X-ray Microanalysis Quantax system (Berlin, Germany) with a primary energy of 7 keV to evaluate the presence of copper and tungsten in the microstructures assembled on the fiber surfaces. The Mα adsorption edge for tungsten is 1.774 keV, and the copper Lα peak

Scheme 1. Procedure and Proposed Mechanism for POM-MOF Formation on Carboxymethylated Cellulose[a]



[a]The POM-MOF structure is from the literature. Reprinted from ref 12. Copyright 2011 American Chemical Society.

for copper is 0.930 keV. The takeoff angle was 35° relative to the substrate.

A Nicolet Magna IR 560 spectrometer FTIR (Thermo Fisher Scientific Inc., Waltham, MA) with a MIRacle Attenuated Total Reflectance (ATR) attachment (PIKE Technologies, Madison, WI) was used to obtain all IR spectra. FTIR scans had a resolution of 2 cm^{-1}, and 64 scans were performed for each sample. A Scintag Theta−Theta X-ray Diffractometer (XRD) was used to analyze the crystal structure by scanning from 3 to 60 degrees at 2.5 degrees per min. A current of 40 mA and applied voltage of 40 kV were used with a Cu (λ + 1.5405 Å) standard target. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed by IMR Test Laboratories (Ithaca, NY) to determine weight percent of elemental copper and tungsten present on MOF-cotton and POM-MOF-cotton. Contact angles were determined through wetting force using a KSV Sigma 701 tensiometer from Biolin Scientific, Inc. (Linthicum Heights, MD) by averaging 240 measurements for each sample. Hydration of the synthesized structures was measured by thermogravimetric analysis (TGA) using a TGA Q500 from TA Instruments (New Castle, DE) ramping from 20 to 1000 °C at 10 °C/min. Data at 100 °C was used to determine moisture content based upon the Chui et al.[6] report that dehydration of $Cu_3(BTC)_2$ could be achieved by heating to 100 °C in air.

2.4. Fabric Performance. Three replicates for each sample (POM-MOF-cotton, MOF-cotton, carboxymethylated cotton, commercially available MOF-199, and unattached POM) were exposed to a stream of hydrogen sulfide in sealed vials for 10 s. Color change was observed and recorded immediately after exposure.

Four replicates of three fabric types (cotton, MOF-cotton, POM-MOF-cotton) were cut into 1.5 cm-diameter circles. All fabric specimens were heated to 120 °C for 1 h to remove water. Each fabric specimen was submerged in 100 mL of a 20 mg/L methyl parathion/hexane solution and put on a New Brunswick Scientific Innova 2300 platform shaker (Edison, NJ) at 200 rpm. Two mL aliquots were removed from each reaction vessel after 0.5, 1, 2, 6, 12, and 24 h, filtered with a Titan2 nylon 0.20 μm pore sized syringe filter (SUN-Sri, Rockwood, TN), and transferred to HPLC vials for analysis. The amount of methyl parathion (mg) was calculated from HPLC data.

A reverse phase high-performance liquid chromatograph (HPLC) attached to a diode array UV−vis detector (DAD) from Agilent (Santa Clara, CA) HP series 1200 was utilized to measure methyl parathion concentration. The injection volume was 20 μL. An Agilent XDB-C18 reversed phase column with 5 μm particle size, 4.6 × 150 mm dimension was used at a temperature of 25 °C. A 50:50 volume ratio of acetonitrile and water with 1 vol % formic acid was used as the mobile phase. Run-time for each sample was 22 min. The UV−vis detector was set to scan at 230, 280, and 320 nm. Methyl parathion has a maximum absorption near 280 nm, while 4-nitrophenol, an expected degradation product of methyl parathion, has a maximum absorption near 320 nm. Methyl parathion standards and calibration curves were used to adjust for drift of the HPLC-DAD instrument and to calculate the amount of methyl parathion.

To account for sampling and evaporation of hexane during testing, a set of four 100 mL controls of 20 mg/L methyl parathion/hexane solutions was used. These controls were sampled at identical times to the test specimens to adjust for hexane evaporation in calculating the concentration of methyl parathion.

3. RESULTS AND DISCUSSION

POM-MOF-cotton and MOF-cotton fabric samples exhibited an aqua blue color with POM-MOF having a darker/deeper color (Figure 1). Octahedral crystals were observed on MOF-cotton and POM-MOF-cotton with the microstructures in POM-MOF-cotton being more truncated (Figure 2). There was a significant difference in the size of the crystals; the average size for POM-MOF-cotton was 1.51 μm (±0.68 μm) while for MOF-cotton the average size was 0.52 μm (±0.30 μm). For both of these materials, the crystal sizes were much smaller than 20−25 μm, reported for materials from a typical solvothermal synthesis.[22]

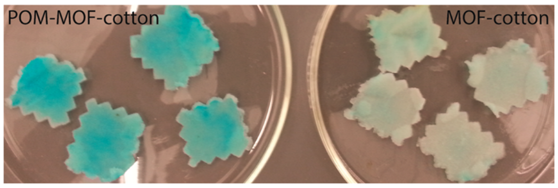


Figure 1. Optical image of POM-MOF-cotton (left) and MOF-cotton fabrics (right).

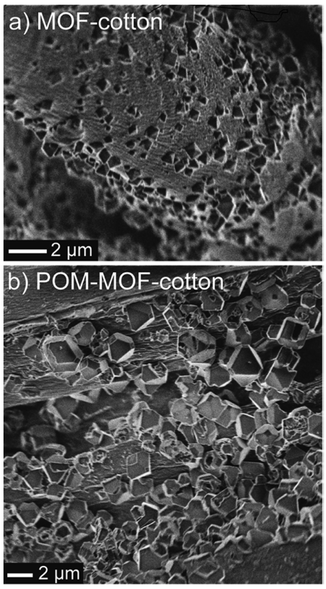


Figure 2. FE-SEM of (a) MOF-cotton and (b) POM-MOF-cotton.

X-ray diffraction patterns of MOF-cotton and POM-MOF-cotton correspond to crystalline MOF-199 and crystalline cellulose (Figure 3). MOF-199 exhibited 2θ peaks at 5.7, 6.6, 9.5, 11.5, 13.4, 19.0, 26.0, and 29.3. Of these MOF-199 peaks, 5.7, 6.6, 9.5, 11.5, and 29.3 do not overlap with the diffraction pattern for untreated cotton and are thus useful for

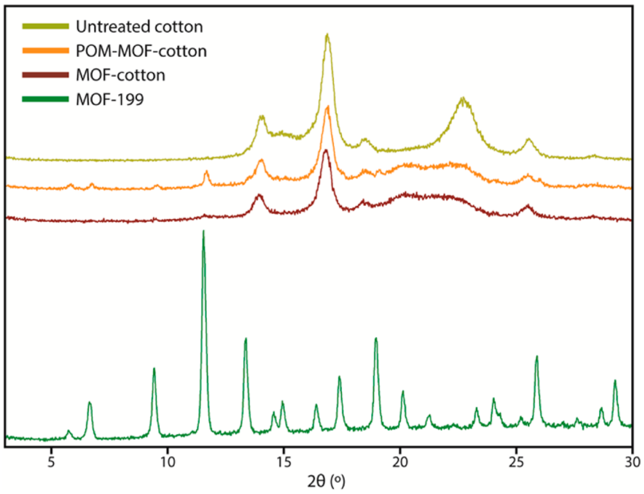


Figure 3. X-ray diffraction patterns of MOF-199, MOF-cotton, POM-MOF-cotton, and cotton. The POM as supplied was noncrystalline.

identification of MOF formation on the cellulose substrate. In the POM-MOF-cotton diffraction pattern, major peaks for MOF-199 were easily observed. For MOF-cotton, 2θ peaks at 6.6, 9.4, 11.5, and 13.4 were observed in addition to those corresponding to cellulose.

In addition, Fourier transform infrared spectra were consistent with the presence of MOF-199 structures in the POM-MOF-cotton and MOF-cotton (Figure 4). Consistent with the literature for MOF-199,[12] significant IR peaks at 728, 760, 1369, 1446, and 1646 cm^{-1} were observed. Peaks related to POM were not discernible from those related to MOF and/or cellulose.

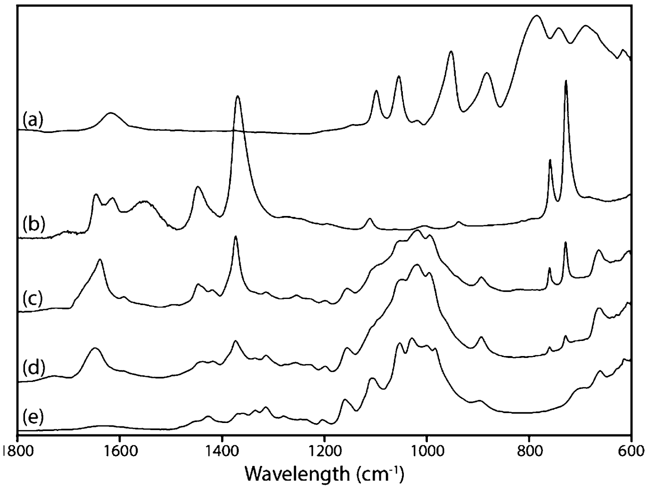


Figure 4. Infrared spectra of (a) POM, (b) MOF-199, (c) POM-MOF-cotton, (d) MOF-cotton, and (e) untreated cotton.

Significant washings after self-assembly of the microstructures on the fabrics suggest that MOF and POM-MOF structures are bonded to the cellulose polymers as previously reported.[10] The morphologies of these assembled crystals on POM-MOF-cotton and MOF-cotton shown are similar to those previously reported for the MOF-199 structure on cotton fibers,[10] and the octahedral shape agrees with the cubic crystal system with a *Fm*3*m* space group previously reported in the literature for MOF-199.[6,12,22]

The presence of copper and tungsten in the microstructures assembled on the fiber surfaces for MOF-cotton and POM-MOF-cotton was evaluated using X-ray energy dispersive analysis. In POM-MOF-cotton, a small peak (2.1 counts) was observed at 1.774 keV corresponding with the Mα adsorption edge for tungsten but not for the MOF-cotton (0 counts). Both samples exhibited a copper Lα peak at 0.930 keV. Weight percent of elemental copper and tungsten present on MOF-cotton and POM-MOF-cotton are presented in Table 1. A small amount of copper was present in the untreated cotton control, but little or no tungsten was observed. The weight percent of Cu was significantly higher for MOF-cotton and POM-MOF-cotton than the untreated cotton. More copper and tungsten were observed in POM-MOF-cotton than MOF-cotton. These results are consistent with known chemical structures of the MOF $[Cu_3(C_9H_3O_6)_2]$ and POM $[CuPW_{11}O_{39}]^{5-}$.

Table 1. Copper and Tungsten Weight % in Cotton, MOF-Cotton, and POM-MOF-Cotton[a]

element	cotton (%)	MOF-cotton (%)	POM-MOF-cotton (%)
Cu	0.04	0.88	1.30
W	<0.01	0.01	0.42

[a] Detection limits were 0.01 wt %.

Self-assembly of the microstructures for MOF-cotton and POM-MOF-cotton are in agreement with those reported in the literature.[6,13] A higher MOF content for POM-MOF-cotton compared to MOF-cotton (Table 2) may indicate the POM promoted self-assembly of the POM-MOF microstructure. Bajpe et al.[13−15] reported that the addition of Keggin-type heteropolyacids in aqueous solution at room temperature resulted in instantaneous and stoichiometric formation of a $Cu_3(BTC)_2$-type metal−organic framework with the Keggin ions partially occupying L2 pores. POM-MOF-cotton had 65 μmol/g fabric of $Cu_3(BTC)_2$ with about 13% POM occupancy in the MOF cages while MOF-cotton had 44 μmol/g fabric of $Cu_3(BTC)_2$ (Table 2).

Table 2. Weight of POM and $Cu_3(BTC)_2$ in POM-MOF-Cotton and MOF-Cotton Calculated from ICP-AES Data[a]

modifier of cotton	$Cu_3(BTC)_2$ (mg/g of fabric)	$Cu_3(BTC)_2$ (μmol/g fabric)	POM (mg/g of fabric)	POM (μmol/g fabric)
POM-MOF	40	65	6	2.1
MOF	27	44	0	0

[a] Formula weight: $Cu_3(BTC)_2$, 604.87 g mol^{-1}; POM, 2740.69 g mol^{-1}.

3.1. Wettability.

All three fabrics had moisture content between 3.2% and 3.7% by fabric weight. Hydrophilicity was further investigated by measuring contact angle (Table 3). POM-MOF-cotton and MOF-cotton had contact angles equal to or smaller than untreated cotton indicating that all specimens are hydrophilic. For some applications, it may be important for the functionalization of the cellulosic fibers not to change the hydrophilic character of the fabric.

Table 3. Water Contact Angle for Untreated Cotton, MOF-Cotton, and POM-MOF-Cotton[a]

sample	contact angle (deg)
POM-MOF-cotton	11 (12)
MOF-cotton	22 (11)
untreated cotton	38 (6)

[a] Standard deviations are in parentheses.

In many fiber applications, stability in an aqueous environment is critical. MOFs containing carboxylate-metal bonds such $Cu_3(BTC)_2$ (MOF-199) have been shown to lack stability when in direct contact with liquid water or high humidity.[23,24] MOF-199 decomposes within minutes in aqueous solution at pH 4.8. Moisture is capable of degrading the MOF structure to a level that impacts effectiveness in some potential applications. DeCoste et al.[24] found that both humidity and temperature affected the rate and degree of degradation. They suggest two mechanisms: first, surface degradation and cracking and, second, the collapse of pores at longer exposure times of 7 days at 90% relative humidity and 25 °C. There was only minor evidence of structural changes for samples aged 7 and 14 days at 90% relative humidity and 40 °C. FTIR results show changes in the chemical species present that indicate transformation of the Cu-BTC carboxylate groups to their protonated acid analogs. The structural changes in MOF-199 with exposure to water at 80 °C for 24 h are irreversible.[23] Tan et al.[25] presented approaches that could be utilized to increase water stability of MOFs. Cu-BTC has been treated with plasma-enhanced chemical vapor deposition of perfluorohexane resulting in hydrophobic cavities that encapsulate water clusters and thus do not change the structure upon immersion in water.[26]

The literature reports that $[CuPW_{11}O_{39}]^{5-}$ is hydrolytically stable in solutions with pH in the range of 2.0−5.9 and that it decomposes rapidly in basic aqueous solution.[27] Song et al.[12] found that the POM-MOF material had higher hydrolytic stability than either MOF or POM alone. They demonstrated POM-MOF stability at pH 11 for at least 12 h.

3.2. Reaction with Hydrogen Sulfide. A reaction with Cu^{2+} in both the POM and MOF to form copper sulfide, which has a dark color, was observed (Figure 5). Enhanced removal of hydrogen sulfide by POM structures has been reported by Song et al.[12] Less reactivity was observed for MOF-cotton than POM-MOF-cotton (Figure 6). Higher reactivity of POM-MOF-cotton over that of MOF-cotton is most likely due to the presence of different available Cu sites. With encapsulation of the Keggin structure in the MOF framework, there are three forms of copper: Cu^{2+} coordinated with BTC making up the MOF framework (in the paddle wheels), Cu in the $[CuPW_{11}O_{39}]^{5-}$ unit, and extra-framework cations Cu^{2+} ions compensating the charges of the encapsulated Keggins.[15,28] The increase in Cu^{2+} due to the extra-framework cations with encapsulation of POM, as well as higher MOF content, resulted in higher reactivity (Table 2, Figure 6).

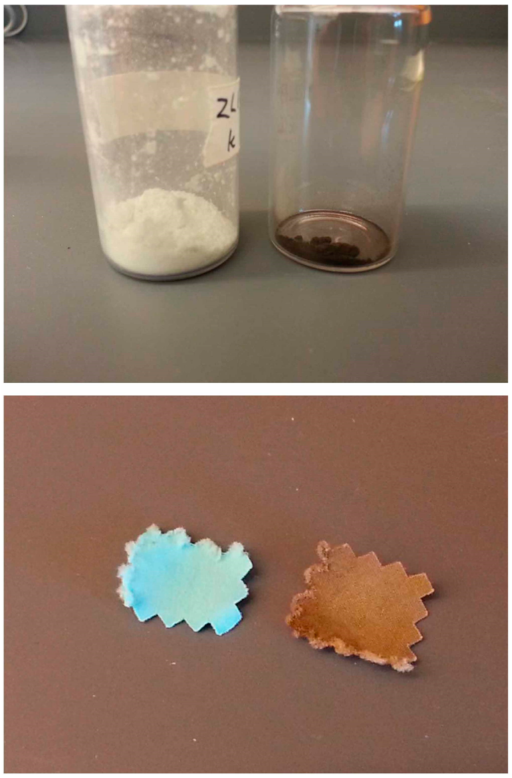


Figure 5. Materials before (left) and after (right) exposure to hydrogen sulfide. (top) POM powder specimen; (bottom) POM-MOF-cotton.

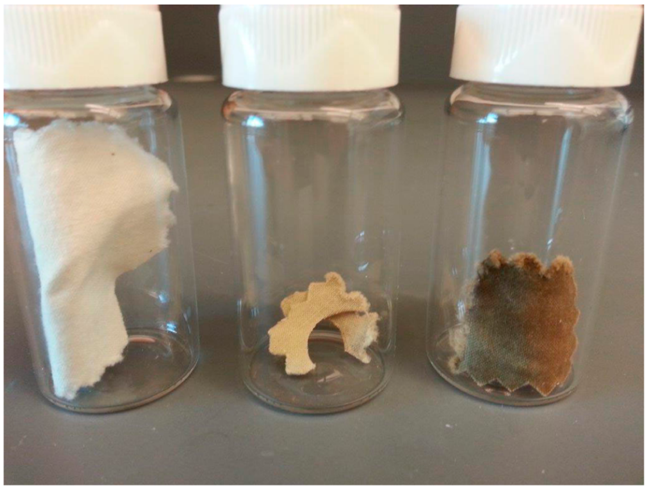


Figure 6. Materials after being exposed to hydrogen sulfide: untreated cotton (left), MOF-cotton (center), and POM-MOF-cotton (right).

3.3. Removal of Methyl Parathion. All fabrics removed methyl parathion from a hexane solution (Figure 7), and no expected degradation products (methyl paraoxon, *O*,*O*,*O*-trimethyl phosphoric thiourate, and 4-nitrophenol) were observed in the HPLC chromatograms of the treatment solutions. After adjusting the data to normalize MOF content, we found that POM-MOF-cotton removed more methyl parathion than MOF-cotton (Figure 8). After 6 h, no further significant amounts of methyl parathion were removed by any of the three substrates.

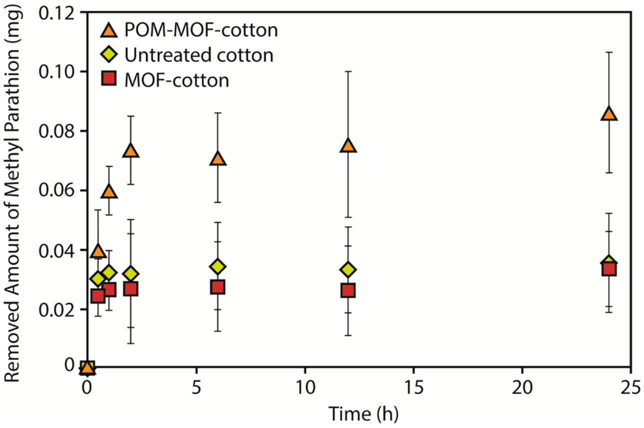


Figure 7. Amount of methyl parathion (mg) removed for the three different substrate types (POM-MOF-cotton, MOF-cotton, and untreated cotton). Error bars indicate the standard deviation in both directions.

MOF-cotton and untreated cotton removed similar amounts of methyl parathion with most removal occurring within the first 2 h (Figure 7). Since removal was similar for these two fabrics, it is thought that it is due mainly to adsorption. In previous research, Cu-BTC metal−organic framework (MOF-199) particles were immobilized by enmeshing them in nonwoven polyacrylonitrile (PAN) nanofibers creating a fibrous membrane that effectively adsorbed methyl parathion.[29] On the basis of solubility theory and experimental results, partitioning into the MOF was proposed as the main mechanism of removal. Thus, the early removal of methyl parathion from the hexane solution in all three materials,

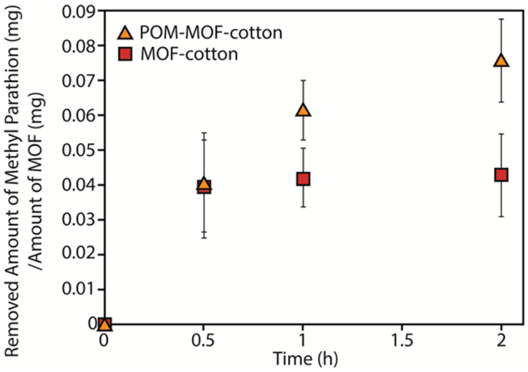


Figure 8. Removed amount of methyl parathion (mg) divided by amount of MOF (mg) over time for the two different substrate types (POM-MOF-cotton, MOF-cotton). Error bars indicate the standard deviation in both directions.

cotton, MOF-cotton, and POM-MOF-cotton, is thought to be mainly by adsorption including selective partitioning into the MOFs.

With reaction times greater than 2 h, POM-MOF-cotton removed more methyl parathion than untreated cotton or MOF-cotton indicating degradation due to incorporation of Keggin polyoxometalate. In addition to physisorption by cellulose and MOF, degradation of methyl parathion is expected at Cu^{2+} sites that act as Lewis acids. Research using ^{31}P solid state NMR confirmed that methyl parathion was adsorbed by MOF-199, particularly within the larger hydrophilic pores (L3). They also confirmed that constitutional isomerization and subsequent hydrolysis likely occurred in the larger hydrophilic pores that have uncoordinated copper sites.[30] Within POM-MOF-cotton, there are Cu^{2+} ions coordinated with BTC making up the MOF framework (in the paddle wheels) and extra-framework cations Cu^{2+} ions compensating the charges of the encapsulated Keggins. These increases in Cu^{2+} due to the extra-framework cations with encapsulation of POM resulted in higher reactivity for POM-MOF-cotton.

A third mechanism that contributes to the higher reactivity of the POM-MOF-cotton after normalizing for the amount of MOF on the fabric is oxidation of methyl parathion by the polyoxometalate. Aerobic oxidation by $[CuPW_{11}O_{39}]^{5-}$ within this POM-MOF structure has been reported by Song et al.[12] Our results support stoichiometric oxidation/hydrolysis rather than catalytic oxidation. The reaction was limited by the concentration of reactants which is probably the amount of water and oxygen in the hexane environment since HPLC measurement indicates that there is still MP present after 25 h. Hydrolysis initiated by the reduction of the POM is the most probable mechanism of enhanced removal of MP due to the presence of water adsorbed by both cotton and MOF. There is no evidence of reactivation of the POM in our experiment. Catalytic oxidation of dialkyl sulfides has been reported in the literature, but it is also noted that it may be necessary to heat in a vacuum at 80 °C to oxidize and thus reactivate the POM.[17]

4. CONCLUSIONS

A Keggin-type polyoxometalate (POM), $[CuPW_{11}O_{39}]^{5-}$, was self-assembled within a $Cu_3(BTC)_2$ metal−organic framework on cellulosic fibers using a room-temperature process. Hydrophilicity of the cotton was maintained with moisture content of 3 to 4 wt %. Reactivity to both hydrogen sulfide and methyl parathion was higher for POM-MOF-cotton than MOF-cotton. POM-MOF-cotton removed 0.089 mg of methyl parathion per mg of MOF while MOF-cotton removed 0.054 mg of methyl per mg of MOF. Higher reactivity of POM-MOF-cotton to both hydrogen sulfide and methyl parathion is due to the Keggin polyoxometalate and the extra-framework cations Cu^{2+} ions compensating the charges of the encapsulated Keggins. Given that no degradation products were observed in the hexane solution by HPLC, it was concluded that either degradation products were adsorbed into the surrounding MOF pores or methyl parathion was completely mineralized. This self-decontaminating property in conjunction with adsorption properties could make these POM-MOF functionalized materials appropriate for applications needing removal of organic contaminates. In utilizing these functionalized materials, human toxicity must be considered. POM and MOF as reactive materials have high toxicity from inhalation, ingestion, and dermal exposure. The study of the toxicity of the immobilized microstructures of these reactive materials on the fiber surfaces needs additional investigation. Further research on serviceability including exposure to an aqueous environment and toxicity to humans and environments would be required before selecting an application.

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Notes

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