A biomimetic cellulose-based composite material that incorporates the antimicrobial metal-organic framework HKUST-1

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ABSTRACT: The synthesis and characterization of a biomimetic composite material composed of cellulose acetate embedded with a copper-based metal-organic framework, MOF-199 (HKUST-1), is reported and has been investigated for use as an adsorbent material in water remediation. Incorporation of MOF-199 into cellulose acetate enhances the stability of the metal-organic framework in water allowing for a flexible and tunable polymeric material. The adsorption of methylene blue to the cellulose-MOF199 composite was tracked spectroscopically over time and is best described by a mixed Langmuir–Freundlich isotherm adsorption model. The total remediation of methylene blue to the cellulose-MOF199 composite is comparable to that of pure cellulose, however, it is shown herein that incorporation of MOF-199 into cellulose acetate inhibits the growth of the Gram-negative bacterium Escherichia coli. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2018, 135, 46978.

KEYWORDS: adsorption; composite materials; coordination polymer; metal-organic frameworks; water remediation

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INTRODUCTION

There has been much interest reported in the literature on Metal-Organic Frameworks (MOFs) in recent years for a wide variety of applications, including gas sequestration, photochemical applications, catalysis, and waste remediation, due to the unique porous nature and tunability MOFs provide.1–21 Although often employed as a bulk material, the incorporation of MOFs into substrates is becoming a popular area of materials science, particularly in regards to sorption technologies. Several MOF-based sorbent materials have been reported in the literature since the early 1990’s, which have been used for a variety of applications that include different chemical sorbates.9–16 A MOF-5 composite material based on an anionic form of silk has been reported and utilized for the adsorption and recovery of congo red dye.14 More recently, Rodriguez et al. have shown that the Cu-containing MOF-199 immobilized onto a cellulose fiber can inhibit the growth of E. coli, and a similar report by Abdelhameed et al. of a MOF-199/cotton nanocomposite details the adsorption of an organic pesticide.15,16 Each of these MOF-based materials feature composite surfaces created through chemisorption of the MOF to the substrate surface that allowed for improved material functionality and tunability.9–16

While the design of advanced MOF-based materials has proven beneficial for a variety of different applications, there is little reported in the literature regarding MOF-based materials and their use in aqueous waste remediation. The unique characteristics of the MOF make their use in sorbent materials for water filtration and remediation an attractive pursuit. Worldwide access to clean, potable drinking water is a growing concern complicated by diminishing fresh water supplies, growing populations, and issues related to pollution and climate change.22–24 Most of the current water remediation solutions are either chemically driven or rely on adsorbent materials, but these technologies either lack efficiency, leave behind chemical byproducts, or are too costly. The need to develop more effective water remediation technologies has led to increased research interest in desalination techniques, photochemical processes, and advanced adsorbent materials. Desalination techniques provide a simple solution for a diverse range of locations, but the costs and energy required hamper its practicality.25,26 Photochemical processes are effective at remediating bacteria and organic pollutants, but require abundant sunlight and are incapable of remediating metal ion contaminants.27–29 The use of adsorbent materials for water
filtration, however, has proven to be an effective and low cost water remediation solution.

Most commercially available adsorbent materials, such as activated carbon, are effective at remediating organic pollutants but limited in capacity and the diversity of pollutants they are capable of remediating.27 Naturally adsorbent materials, such as cellulose, are ideal for aqueous waste remediation due to their high abundance and biomimetic nature which makes them relatively cost-effective; however, biomimetic materials have been shown to facilitate the growth of bacteria in water.30 Conversely, many metal-based substances, such as those containing Ag, Au, and Cu, have demonstrated antimicrobial efficiency toward a wide range of bacterium but are not effective adsorbents.31–35 An ideal adsorbent material for water remediation would be highly adsorptive, cost-effective, and antimicrobial. The incorporation of an antimicrobial MOF, such as the Cu-based MOF known as HKUST-1 (MOF-199), into a cellulosic matrix could combine the benefits of inorganic and biomimetic materials to create an effective, self-cleaning composite material for aqueous waste remediation.

The work presented herein focuses on the synthesis, characterization, and adsorption properties of a biomimetic cellulose-based composite material that incorporates MOF-199, which the authors will refer to as cellulose-MOF199 throughout this study. The incorporation of MOF-199 into a cellulosic matrix enhances its stability in water allowing for a tunable, antimicrobial composite material useful for a wide variety of applications, including water remediation. The adsorption properties of this material were studied in solution using the textile dye methylene blue (MB), which belongs to a known class of aqueous organic pollutants were studied in solution using the textile dye methylene blue (MB), which belongs to a known class of aqueous organic pollutants remediation. The adsorption properties of this material for aqueous waste remediation solution.

The use of MB in this study is not only relevant for filtration, however, biomimetic materials have been shown to facilitate the growth of bacteria in water.30 Conversely, many metal-based substances, such as those containing Ag, Au, and Cu, have demonstrated antimicrobial efficiency toward a wide range of bacterium but are not effective adsorbents.31–35 An ideal adsorbent material for water remediation would be highly adsorptive, cost-effective, and antimicrobial. The incorporation of an antimicrobial MOF, such as the Cu-based MOF known as HKUST-1 (MOF-199), into a cellulosic matrix could combine the benefits of inorganic and biomimetic materials to create an effective, self-cleaning composite material for aqueous waste remediation.

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**EXPERIMENTAL**

**Materials**

Copper (II) nitrate trihydrate (reagent grade, FW: 241.60), methyl alcohol (absolute, reagent grade, FW: 32.04), and nitric acid (ACS Reagent, 15.8 M; assay; FW: 63.01) were obtained from Flinn Scientific (Batavia, IL, USA). Methylene Blue (high purity, biological stain, FW: 319.85) and 1,3,5-benzenetricarboxylic acid (trimesic acid) (98%, FW: 210.14) were obtained from Alfa Aesar (Haverhill, MA, USA). Cellulose acetate (FW: ~50,000) was obtained from Sigma Aldrich (St. Louis, MO, USA). Ethyl alcohol (anhydrous reagent, 95.4% v/v, FW: 46.07) and N,N-dimethylformamide (DMF) (ACS grade, FW: 73.09) were obtained from Fischer Chemical (Pittsburgh, PA, USA). N,N-dimethylacetamide (DMAc) (FW: 87.12) was purchased from SAFC Commercial (St. Louis, MO, USA). All chemicals were used as received without any modification or purification. Deionized water was used for all dilutions.

**Synthesis of HKUST-1**

HKUST-1 was synthesized using a procedure derived from Thi et al.43 A precursor solution of 72.8 mg (86.1 mM) copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) dissolved in 1.95 mL of DMF was added dropwise to a solution containing 100 µL of ethanol. The resulting precursor solution was heated at 50 °C for 6 h to give a light-blue precipitate. The HKUST-1 powder was collected by suction filtration and washed using methanol. The light blue powder precipitate was dried overnight at 90 °C in a vacuum oven and subjected to Fourier transform infrared spectroscopy (FTIR) spectrometry and thermogravimetric analysis (TGA).

**Experimental Methods**

The structure of HKUST-1 was confirmed using X-ray powder diffraction (XPRD) with a Rietveld full profile refinement performed using the EXPGUI-GSAS suite of programs. The effects of incorporating HKUST-1 into cellulose acetate were examined using Fourier transform infrared spectroscopy (FTIR) spectroscopy and thermogravimetric analysis (TGA). The nature of the surface was characterized using visible light microscopy and atomic force microscopy (AFM). The stability of the cellulose-MOF199 composite was studied by measuring the leaching of Cu²⁺ over time using an atomic absorption (AA) spectrometer. Isothermal and adsorption data were determined by monitoring the concentration of MB dye in solution as a function of time.

XRPD data were collected on a Rigaku Miniflex 600 benchtop diffractometer fitted with a Ni Kβ filter using Cu Kα radiation. FTIR spectra of the HKUST-1 powder, cellulose acetate polymer, and cellulose-MOF199 composite were collected using an Avatar Nicolet 360 spectrophotometer equipped with a Smart Endurance diamond ATR. The percent removal of MB dye was determined by tracking the decrease in absorbance at 663 nm wavelength on an OceanOptics RedTide UV–Vis spectrometer. AA experiments were carried out on a Persee AA990 using a Hollow Cathode Lamp made by Buck Scientific. The concentration of Cu²⁺ was determined by relating changes in the absorption at 324.75 nm to a calibration curve. TGA was carried out using a TA Instruments Q600 SDT simultaneous DSC-TGA on a powder sample of HKUST-1, a cellulose-MOF199 bead, and a control cellulose acetate bead. All samples were heated in air at a ramp rate of 25 °C/min to 450 °C, then held isothermally at 450 °C before ramping back down to 20 °C at 25 °C/min. Visible-light microscope images of cellulose acetate and cellulose-MOF199 composite films were taken with an AmScope MU633-FL camera attached to a National DC3-163 Digital Microscope. The images of the cellulose-MOF199 composite material were taken through a filter that blocked red light. AFM images were recorded using Nanosurf Easyscan 2 Flex AFM equipped with a Aspire CT170-25 tip from NanoScience Instruments. Images were recorded at 170 kHz tapping mode.
was then heated at 110 °C for 24 h to yield 35.0 mg (58 μmol) of dark blue HKUST-1 crystals.

Synthesis of Cellulose-MOF199 Composite Material
The cellulose-MOF199 composite beads were made by following a procedure similar to that reported by Rech et al. for the polymerization of cellulose acetate with a slight modification. After cellulose acetate is dissolved in DMAc to form a slurry, HKUST-1 powder is added prior to the polymerization process. The polymer-based dispersion was prepared by the addition of 3.54 g of cellulose acetate to 50 mL of DMAc, and stirred at room temperature for 18 h to allow for uniform dispersion. Approximately 0.500 g of pure HKUST-1 was added to this slurry to create a 1% by weight solution of HKUST-1 in cellulose acetate. Spherical bead-shaped polymers were formed by injecting the slurry through an 18-gauge needle using a New Era Pump Systems NE-300 syringe pump at a rate of 4.0 mL/min into 250 mL of water with ultra-sonication. The cellulose-MOF199 composite beads were formed by rapid solvent exchange upon addition of the composite dispersion to water. The resulting cellulose-MOF199 beads were stirred in water for approximately 30 min to ensure complete diffusion of DMAc from the composite polymer matrix. Cellulose-MOF199 polymer beads of ~4.0 mm in diameter were collected and allowed to dry at room temperature before characterization (Supporting Information Figure S1).

Stability of HKUST-1 and Cellulose-MOF199 Materials
The stabilities of HKUST-1 and the cellulose-MOF199 beads in solution were determined under static conditions by measuring the amount of Cu²⁺ that leached from each material into deionized water at 15-min intervals for 4 h. Approximately 1.0 g of cellulose-MOF199 beads and 0.010 g of pure HKUST-1 were placed in each 100 mL of water. Samples containing 4.00 mL aliquots of water from each experiment were prepared for AA analysis by diluting with 1.00 mL of 1% by volume HNO₃ to a sample pH of approximately 1.00. The relative amounts of free Cu²⁺ in solution were determined by measuring the absorbance at 324.75 nm as a function of time. The fraction of Cu²⁺ leaching from HKUST-1 is reported at time intervals over a 4-h period taking into account dilution factors. This fraction of Cu²⁺ mass loss is determined by calculating the mass of Cu²⁺ in solution relative to the original mass of MOF-199 used in the experiment at each time interval.

Batch Adsorption of Methylene Blue
The adsorptive capacity of cellulose-MOF199 composite beads to MB dye was determined spectroscopically using batch studies. These results were compared to the adsorption capacity of pure cellulose acetate using the same procedure for comparative analysis. Approximately 2.00 g of hydrated cellulose-MOF199 beads were added to 50.00 mL solutions of MB at varying concentrations. Solutions of 5.00, 10.0, 15.0, 20.0, 25.0, and 30.0 μM MB were made from 250.00 mL of a 0.500 mM stock solution and concentrations were verified via calibration curve using Beer’s Law. The beads were allowed to stir at 250 rpm in covered beakers over time intervals up to 8.0 h. The amount of MB in solution was tracked over time by monitoring the absorbance at 663 nm to determine the amount of dye adsorbed to cellulose and cellulose-MOF199. The adsorption of MB dye as a function of time was calculated using eq. (1).

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

where \( C_0 \) and \( C_t \) are the initial concentration of dye and the concentration of dye at time \( t \), respectively, \( V \) is the volume of solution, and \( m \) is the mass of the substrate. The adsorption equilibrium \( (q_e) \) was computed by determining the concentration of dye in solution at adsorption equilibrium, \( C_e \), and substituting for \( C_t \) in eq. (1). The concentration at adsorption equilibrium was determined by averaging the concentrations of MB in solution over the steady state region where changes in absorbance were less than 60 nM. The total percent removal of MB dye from solution was determined using eq. (2).

\[ \text{Removal} = \frac{C_0 - C_t}{C_0} \times 100\% \]  

Antimicrobial Studies
Kirby-Bauer experiments based on a procedure reported by Rinehart et al. were conducted to determine the bacterial inhibition of cellulose-MOF199 toward E. coli on contact. A culture of E. coli in TSB was grown to an optical density (OD660) of 0.500 then aseptically swabbed onto Mueller-Hinton Agar (MHA) plates. Pure cellulose beads and cellulose-MOF199 beads (~4.0 mm) or small disks (6.35 mm in diameter) of films were placed onto the MHA plates and incubated at 37 °C for 18 h. Plates were then analyzed to determine a zone of inhibition (ZOI) for insights into the antimicrobial activity of each material. The rate of bacterial growth and inhibition was quantified by measuring the optical density of a TSB solution as a function of time. A solution of 3.0 mL TSB was inoculated with E. coli in the presence of either pure cellulose or cellulose-MOF199 film or beads. The cultures were incubated at 37 °C and the turbidity of the TSB solutions were monitored spectrophotometrically at 660 nm over the course of 24 h to assess the antimicrobial activity of each material in solution.

RESULTS AND DISCUSSION
Characterization of HKUST-1
The XRPD pattern (red; Figure 1) matched the ICDD PDF-2 database entry number 00-062-1183 of [Cu₃(TMA)₃(H₂O)₃]n (HKUST-1) with no discernible impurities (green; Figure 1). Rietveld refinement based on XRPD data (purple; Figure 1) was carried out using the space group Fm3 with the lattice parameters and atomic coordinates reported in the supplementary information by Chui et al. used as a structural model. Lattice parameters, atomic coordinates, histogram scale factor, pseudo-Voight peak profiles, and background linear interpolation parameters were all refined simultaneously, with isotropic thermal parameters fixed at 0.01 Å².

The refined lattice parameter \( a = 26.429(3) \) Å is in good agreement with the established value of \( a = 26.3103 \) Å. The refined atomic coordinates, bond lengths, and angles (Tables I and II) are reasonable.

The FTIR spectra of the HKUST-1 powder product, cellulose acetate, and the cellulose-MOF199 composite are shown in Figure 2. The HKUST-1 powder spectrum (red spectrum; Figure 2) shows a strong asymmetric stretching band from the trimesate (BTC)
carboxylate groups at 1645 cm\(^{-1}\) (Supporting Information Figure S2).\(^{7,8,12}\) The symmetric stretch of the unbound BTC ligand is slightly shifted to lower frequency (1371 cm\(^{-1}\)) upon coordination to the Cu(II) metal center in the HKUST-1, whereas the asymmetric stretch is shifted dramatically from the 1716 cm\(^{-1}\) observed in the unbound linker. This shift in the asymmetric stretch is highly indicative of coordination of the trimesate carboxylate group to the copper metal center.\(^{7,12}\) Additionally, a Cu-O stretch at 728 cm\(^{-1}\) in the HKUST-1 powder is indicative of coordination of the trimesate carboxylate group to the copper metal center.\(^{7,12}\) The sharp peak at 761 cm\(^{-1}\) present in both the unbound and bound BTC linker arises from the C=H stretching on the aromatic ring\(^{45}\) and the peak at 1448 cm\(^{-1}\) is due to the C=C aromatic stretching.\(^{45}\)

Cellulose acetate (green spectrum; Figure 2) shows stretching frequencies characteristic of cellulose acetate at 1053 cm\(^{-1}\) (C=O glycosidic bond), 1240 cm\(^{-1}\) (C=O in-plane deformation), and 1736 cm\(^{-1}\) (C=O stretch of the acetyl groups). The small peak observed at 1381 cm\(^{-1}\) is due to C=H deformation on the pyranose ring and the presence of a small peak at 1635 cm\(^{-1}\) is indicative of water hydrogen-bonding to the polymer surface.\(^{46,47}\) Many of the peaks in the cellulose-MOF199 composite polymer (blue spectrum; Figure 2) are similar to those of cellulose acetate but shifted slightly. The stretching frequencies of the cellulose glycosidic bond (1053 cm\(^{-1}\)) and the C=O stretch of the acetyl group (1748 cm\(^{-1}\)), however, are unaltered in the cellulose-MOF199 composite material. The intense signals at 1216 and 1228 cm\(^{-1}\) are similar to the free C=O stretch in the cellulose acetate but shifted slightly lower in energy and split as a doublet. This is likely the result of increased hydrogen-bonding due to cellulose acetate-HKUST-1 interactions inhibiting the C=O deformation in the composite material. The symmetric COO\(^{-}\) stretch (1365 cm\(^{-1}\)), C=C stretches (1435 cm\(^{-1}\)), and asymmetric COO\(^{-}\) stretch (1652 cm\(^{-1}\)) in the cellulose-MOF199 composite material resonate at frequencies similar to the HKUST-1 powder, but the peaks are slightly broadened. The stretching frequency of the acetyl C=O group (1740 cm\(^{-1}\)) shows a dramatic increase in intensity in the cellulose-MOF199 composite material, which could be further evidence of strong intermolecular interactions between HKUST-1 and cellulose acetate.\(^{45}\)

**Stability of HKUST-1 and HKUST-1 Composite Material**

HKUST-1 as a bulk material has previously been reported as having poor stability in water and typically falls apart after ~4 h.\(^{48}\) This was confirmed by AA results, which showed a large loss of copper from the MOF to solution after only 30 min (Figure 3). The relative amount of Cu\(^{2+}\) in solution is about three times greater than that of the MOF embedded polymer material, cellulose-MOF199, indicating that the polymer matrix enhances stability. The lack of stability that HKUST-1 shows in water could be attributed to the hydrophilic nature of the open Cu\(^{2+}\) sites and the dynamic nature of the coordination bonds. Subsequent displacement of the trimesate ligands through ligand substitution with water could readily break apart the MOF. When incorporated inside a cellulosic matrix, the leaching of Cu\(^{2+}\) ions

**Table I.** Refined Atomic Coordinates and Lattice Parameters of HKUST-1 (Thermal Parameters Fixed at 0.01 Å\(^2\))

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
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</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>0.2809(6)</td>
<td>0.2809(6)</td>
<td>0</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.339(1)</td>
<td>0.339(1)</td>
<td>0</td>
</tr>
<tr>
<td>O(11)</td>
<td>0.3112(8)</td>
<td>0.2334(9)</td>
<td>-0.0612(8)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.333(2)</td>
<td>0.167(2)</td>
<td>-0.121(2)</td>
</tr>
<tr>
<td>C(10)</td>
<td>0.310(2)</td>
<td>0.190(2)</td>
<td>-0.088(3)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.376(2)</td>
<td>0.207(2)</td>
<td>-0.124(2)</td>
</tr>
<tr>
<td>O(1 W)</td>
<td>0.312(2)</td>
<td>0.266(2)</td>
<td>0</td>
</tr>
</tbody>
</table>

Crystallographic data: a = 26.429(3) Å; \(\chi^2 = 6.529\); \(R_{wp} = 10.51\%\); \(R_p = 8.05\%\). Isotropic thermal parameters were fixed at 0.01 Å\(^2\).

**Table II.** Refined Bond Lengths and Angles for HKUST-1

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tbody>
<tr>
<td>Cu(1)-O(11)</td>
<td>2.20(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1)</td>
<td>2.19(6)</td>
</tr>
<tr>
<td>Cu(1)-Cu(1)</td>
<td>2.31(4)</td>
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<tr>
<td>O(11)-C(10)</td>
<td>1.36(4)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.55(4)</td>
</tr>
<tr>
<td>C(1)-C(10)</td>
<td>1.20(6)</td>
</tr>
<tr>
<td>C(10)-O(11)</td>
<td>1.36(4)</td>
</tr>
</tbody>
</table>
is greatly inhibited over the same 4-h period, which is likely due to the polymer matrix slowing ligand substitution at the MOF sites. The electronegative oxygen-based groups in cellulose acetate may form noncovalent interactions with the open Cu$^{2+}$ sites, thereby decreasing the affinity for water. The large variation in the release of Cu$^{2+}$ from the HKUST-1 powder could be due to the heterogeneity of the mixture after MOF decomposition. The mixture appears colloidal after decomposition, which may be the result of free ligand aggregation (potentially micellular) preventing full dissolution of Cu$^{2+}$ and giving inconsistent results. This inconsistency is not observed in cellulose-MOF199 because the HKUST-1 remains mostly intact inside the polymer matrix.

Surface Characterization
Optical images of a cellulose film show a highly fibrous network with macropores as large as ~200 μm [Figure 4(a)]. These macropores result from rapid flux of DMAc from the slurry solution during solvent exchange with water to initiate polymerization. The presence of smaller nanopores of ~0.5–1 μm within the cellulose surface is evident in the 25 × 25 μm AFM image [Figure 4(b)]. In the cellulose-MOF199 composite polymer films, large portions of the macropores are congested with aggregates of HKUST-1. These MOF aggregates, shown in bright green on Figure 4(c), range in size from ~10 to 30 μm. The sizes of the MOF aggregates are small enough to settle inside the macropores of the surface, but also large enough to obstruct the nanopores created by the cellulose acetate network. Additionally, a cross-sectional image of both the cellulose and cellulose-MOF199 beads shows a mostly hollow core [Figure 4(d)]. This hollow core is likely created by a rapid polymerization process in which the outer shell of the spherical dispersion droplet polymerizes first upon contact with water, causing the remaining DMAc solvent to rapidly efflux from the inner core. The presence of a hollow core in both beads is further evidenced by the TGA results, which show a high mass percent loss in the material due to water evaporation.

Thermogravimetric Analysis
The cellulose acetate and cellulose-MOF199 composite beads are composed of 70 and 73% adsorbed water, respectively [Figure 5(a)]. As shown by the first-derivative plot, dehydration in both materials begins at 50 °C and is complete by 250 °C. While the cellulose-MOF199 composite material dehydrates in one step, the cellulose beads dehydrate in two stages [Figure 5(b)]. This two-stage dehydration in the cellulose beads is likely the result of initial evaporation from larger macropores on the surface of the material, followed by evaporation of water embedded within the nanopores of the material. The nanopores in the cellulose-MOF199 composite beads are obstructed by HKUST-1, which leads to a more rapid dehydration consistent with the initial dehydration temperature of the cellulose beads. Decomposition of the cellulose beads occurs at 372 °C, in agreement with the results reported by Lecena et al.49 The cellulose-MOF199 beads decompose at slightly lower temperatures (352 °C), which is further evidence of a disrupted cellulose network in the composite material. Upon decomposition, 3% of the mass remains as polymer residue in both substances; however, there is an additional 2% of mass that remains in the cellulose-MOF199 beads, which we attribute to MOF-related byproducts.

Adsorption Kinetics, Isotherm, and Mechanism
The adsorption of MB dye to cellulose acetate beads and cellulose-MOF199 composite beads was investigated in solution
at concentrations ranging from 5 to 30 μM MB. Experiments were conducted in open air at room temperature (22 °C) with the initial solution pH values varying between 5.3 and 5.5. At this pH, the dye has a strong cationic character, and the zeta potential of the cellulose acetate sites in both materials are negatively charged due to the electronegative hydroxyl, carboxylate and/or acetate groups present. The initial adsorption of MB to the pure cellulose acetate beads is uniform and consists of a rapid attraction to the surface followed by diffusion. In contrast, the adsorption of MB to the cellulose-MOF199 composite beads is disrupted by the heterogeneous polymer matrix, which decreases both the rate of adsorption and diffusion. This is followed by a second region where the rate of adsorption slows until it reaches zero, causing a "plateau" region. The adsorption and desorption of MB are in a steady-state during this plateau region, allowing for determination of the equilibrium adsorption capacity ($q_e$) of the material (Supporting Information Figure S4). In the steady-state region, fewer sites are available for binding and charge repulsion between MB molecules is more dominant which leads to fluctuation in adsorption at longer saturation times.

The mechanism of MB adsorption to each material was determined by modeling adsorption data according to the nonlinear Langmuir [eq. (3)] and Freundlich [eq. (4)] models (Figure 6).

$$q_e = \frac{q_{\text{max}}K LC_e}{1 + K LC_e} \quad (3)$$

$$q_e = K_F C_e^n \quad (4)$$

where $q_{\text{max}}$ is the maximum monolayer adsorption capacity of adsorbate (MB) and $q_e$ is the equilibrium adsorption capacity. $K_L$ is the Langmuir constant that relates free energy and the MB affinity to the surface sites, $K_F$ is related to the adsorption capacity in the Freundlich isotherm model, and $C_e$ is the concentration of dye in solution at equilibrium. The unitless quantity $n$ for the Freundlich model is related to the nature of the adsorbate surface in which a higher value indicates a more favorable Freundlich-like adsorption. The Langmuir isotherm model assumes monolayer adsorption with no adsorbate (MB-MB) interactions, and a logarithmic decrease in surface energy with

![Figure 4. Optical image of a cellulose acetate surface (a) and cellulose-MOF199 composite surface (c) showing macropores and HKUST-1 aggregates. AFM image of the nanopores of a cellulose acetate surface (b) and the cross-sectional area of a cellulose-MOF199 bead (d). [Color figure can be viewed at wileyonlinelibrary.com]](image1)

![Figure 5. Thermogravimetric analysis of a cellulose acetate bead (red) and a cellulose-MOF199 bead (blue) showing changes in percent mass as a function of temperature (a), and the first derivative of the change in mass as a function of temperature (b). [Color figure can be viewed at wileyonlinelibrary.com]](image2)
coverage. The Freundlich isotherm is an empirical model that assumes a more nonideal and heterogeneous surface with the potential of multilayer formation and intermolecular adsorbate interactions.

Adsorption of MB to the cellulose acetate bead fits best with the Langmuir isotherm model over all concentrations, indicating the formation of a monolayer on the surface. The cellulose-MOF199 composite material, however, gives a poor fit for both isotherm models. The Freundlich and Langmuir plots for adsorption to cellulose-MOF199 give $R^2$ values of 0.8546 and 0.8409, respectively, as opposed to the cellulose acetate beads that show a good fit for Langmuir adsorption with $R^2 = 0.9715$ (Table III). The poor fit in the nonlinear isotherm plots for cellulose-MOF199 are likely the result of a change in the adsorption mechanism, which is evidenced by the “break” observed in the plots at initial MB dye concentrations above 15 μM. In order to provide further insight into the adsorption mechanism of the composite material, results for MB adsorption to cellulose-MOF199 were plotted according to the linearized Freundlich and Langmuir Type 2 models [eqs. (5) and (6), respectively] over initial MB concentration ranges of 5–15 and 20–30 μM.

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_F C_e} \quad (5)
\]

\[
\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (6)
\]

Plots of the linearized isotherm models over these two concentration ranges show a distinct change in the adsorption mechanism at initial solution concentrations above 15 μM (Figure 7). At concentrations of 15 μM MB and lower, adsorption data fits well for the linearized Langmuir model suggesting that adsorption at low adsorbate concentrations is similar to the cellulose acetate. When the initial MB concentration is above 15 μM, the adsorption data is best described by the linearized Freundlich model suggesting multilayer formation at higher adsorbate concentrations. This multilayer adsorption is characteristic of a material with a heterogeneous surface and assumes adsorbate–adsorbate interactions that could affect surface adsorption. The adsorption of MB to cellulose acetate shows the best fit for the linearized Langmuir model at all MB concentrations consistent with the nonlinearized model.

### Table III. Langmuir and Freundlich Isotherm Parameters for Cellulose Acetate and Cellulose-MOF199 Composite

<table>
<thead>
<tr>
<th></th>
<th>Cellulose acetate</th>
<th>Cellulose-MOF199</th>
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<tbody>
<tr>
<td>Non-linearized isotherms</td>
<td></td>
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<tr>
<td>Freundlich</td>
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<td>$n$</td>
<td>1.23</td>
<td>0.90</td>
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<td>$K_F$ (L/μg)</td>
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<td>0.010</td>
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<tr>
<td>$R^2$</td>
<td>0.9661</td>
<td>0.8546</td>
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<td>Langmuir</td>
<td></td>
<td></td>
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<tr>
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<td>396.4</td>
<td>1193.0</td>
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<tr>
<td>$K_L$ (L/μg)</td>
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<td>2.36 x 10^{-5}</td>
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<tr>
<td>$R^2$</td>
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<td>0.8409</td>
</tr>
<tr>
<td>Linearized isotherms</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose acetate</td>
<td>Cellulose-MOF199</td>
</tr>
<tr>
<td></td>
<td>(5-15 μM)</td>
<td>(&gt;15 μM)</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
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<td>0.48</td>
</tr>
<tr>
<td>$K_F$ (L/μg)</td>
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<td>6.20 x 10^{-6}</td>
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<tr>
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<td>-23.4</td>
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<tr>
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<td>-3.18 x 10^{6}</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9878</td>
<td>0.9994</td>
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![Figure 6](#) Non-linear Langmuir (a) and Freundlich (b) adsorption isotherm models for cellulose acetate beads (red) and cellulose-MOF199 composite beads (blue). The solid lines indicate the calculated values. [Color figure can be viewed at wileyonlinelibrary.com]
The initial concentration of MB dye solution, thus, provides important insights into the adsorption mechanism and surface interactions of the cellulose-MOF199 composite material. The change in the mechanism, evidenced by the discontinuity in the linearized isotherm models, suggests adsorption to the composite surface occurs in two distinct stages. Initially, adsorbate interacts with the surface in a Langmuir-type fashion, however, as more dye molecules adsorb to the surface, the heterogeneity influences the adsorption mechanism and multilayers begin to form. These multilayers likely occur after binding sites on the surface are saturated by dye molecules, and result from a disruption of monolayer formation due to embedded HKUST-1 at the surface affecting the number of surface sites available for adsorption. After dye molecules have formed the disrupted monolayer on the surface, adsorbate-adsorbate interactions become more prevalent and multilayers begin to form. The parameters of the Langmuir and Freundlich isotherm models, thus, cannot accurately be determined because of this change in adsorption mechanism. The parameters of the adsorption mechanism for MB to the cellulose acetate beads, however, are accurately given by the nonlinearized Langmuir model (Table III).

Comparison of the isotherm constants, $K_L$ and $K_F$, given by the nonlinear models indicate that the cationic MB shows a higher affinity for the cellulose acetate surface than the composite surface. It should be noted, however, that the values for cellulose-MOF199 in the nonlinear models are less reliable due to the poor fit over all MB concentrations. This is further evidenced by the discrepancy in the $q_{\text{max}}$ values between cellulose acetate and cellulose-MOF199. Comparison of $K_L$ values in the linearized models also supports this reasoning, which gives a negative value for $K_L$ in the cellulose-MOF199 composite. This $K_L$ value is determined by extrapolation of the slope for the line fit to the concentration range of 5–15 μM. The $K_L$ value determined from the linear plot is likely an inaccurate representation of the actual $K_L$ value and possibly due to the small concentration range over which the Langmuir model is considered valid. The best method for comparison of the two substrates is therefore given by the overall MB dye remediation from solution at equilibrium, $q_e$ (Figure 8).

The dye adsorption at equilibrium for both pure cellulose and cellulose-MOF199 increases with increasing initial MB concentration. The cellulose-MOF199 beads, however, give lower $q_e$ values at all MB concentrations when compared to pure cellulose acetate, but still exhibit good adsorption capacity overall. The higher adsorption observed for the pure cellulose beads is likely due to greater porosity of the matrix, which becomes disrupted by the addition of HKUST-1 in the composite material. Although MOF-199 has electronegative oxygen groups on terminal BTC linkers that could serve as additional MB binding sites, the disruption of the matrix by the addition of MOF appears to have a more detrimental effect on MB adsorption.

The porous structure of both cellulose and cellulose-MOF199 beads is further evidenced by the intraparticle diffusion model [eq. (7)],

$$q_t = k_p t^{1/2} + C$$  \hspace{1cm} (7)

where $k_p$ is the diffusion rate constant (μg/g t$^{1/2}$) and $C$ is the thickness of the boundary layer. The discontinuity in the diffusion plot suggests two stages of adsorption common to cellulose acetate, which we also observe for the cellulose-MOF199 composite material. The first region consists of rapid adsorption to the cellulose surface sites whereas the second region shows a slower rate indicative of diffusion into the pores of the material (Figure 9).
Both the rate of diffusion and thickness of the boundary layer are higher in the pure cellulose beads due to its more porous nature and uniform surface. The adsorption of MB to the cellulose-MOF199 beads gives a boundary layer thickness that is significantly lower than pure cellulose acetate indicating a rough, heterogeneous surface by comparison (Supporting Information Table S1). The increased surface roughness due to heterogeneity leads to slower saturation of the composite surface and slower rates of intraparticle diffusion. Additionally, the rapidly established initial equilibrium at lower MB concentrations experiences disruption in the steady state region at longer time intervals in cellulose-MOF199 [Figure 9(b)]. This disruption in the steady state region is likely due to nonuniform surface interactions and further evidence of the heterogeneity at the surface. At higher MB dye concentrations, the cellulose-MOF199 surface sites are completely saturated and bulk effects of MB in solution ensure a steady state at equilibrium.

The overall dye adsorption process is best-described using pseudo-first-order and pseudo-second-order rate laws. MB adsorption to pure cellulose and cellulose-MOF199 [eq. (8)] and pseudo-second order [eq. (9)] kinetic models.\(^{56}\)

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{\ln(10)} t
\]  \hspace{1cm} (8)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  \hspace{1cm} (9)

where \(q_t (\mu g/g)\) is the adsorption at time \(t\) (min) and \(k_1\) (min\(^{-1}\)) and \(k_2\) (\(\mu g/g\) min) are the pseudo-first and pseudo-second-rate constants, respectively. For both the cellulose acetate and the cellulose-MOF199 beads, adsorption was best fit to the pseudo-second order model for all concentrations, indicative of chemical interactions (Table IV).\(^{57}\) For trials with higher MB dye concentrations, however, small amounts of MB are easily desorbed upon ultrasonication of saturated beads indicating the outer layers of MB dye on the surface are physically adsorbed through intermolecular attractions.

Although the cellulose beads show greater overall dye remediation (Supporting Information Figure S5), the cellulose-MOF199 composite beads show comparable remediation capabilities but with increased versatility through the addition of a tunable MOF. The HKUST-1 embedded within the polymer provides a platform through which further functionalization could easily be introduced. Additionally, the cellulose matrix stabilizes MOF-199 in aqueous solution, which has previously shown poor stability in water.\(^{58}\) The maximum amount of MB dye removed in the

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Substrate} & \text{Initial concentration (\(\mu M\))} & \text{Pseudo-first order } R^2 & \text{Pseudo-second order } R^2 & \text{Pseudo-second order rate } (\mu g/g \text{ min}) \\
\hline
\text{Cellulose acetate} & 5 & 0.8869 & 0.9997 & 2.4 \times 10^{-3} \\
 & 10 & 0.8989 & 0.9999 & 1.0 \times 10^{-3} \\
 & 15 & 0.8701 & 0.9998 & 6.5 \times 10^{-4} \\
 & 20 & 0.9303 & 0.9998 & 5.0 \times 10^{-4} \\
 & 25 & 0.9461 & 0.9990 & 3.0 \times 10^{-4} \\
 & 30 & 0.9361 & 0.9989 & 2.6 \times 10^{-4} \\
\hline
\text{Cellulose-MOF199 composite} & 5 & 0.9536 & 0.9991 & 8.7 \times 10^{-3} \\
 & 10 & 0.8221 & 0.9991 & 1.6 \times 10^{-3} \\
 & 15 & 0.9922 & 0.9988 & 6.5 \times 10^{-4} \\
 & 20 & 0.8724 & 0.9958 & 2.4 \times 10^{-4} \\
 & 25 & 0.9578 & 0.9988 & 3.6 \times 10^{-4} \\
 & 30 & 0.9902 & 0.9982 & 2.5 \times 10^{-4} \\
\hline
\end{array}
\]
presence of cellulose beads was observed at 20 \( \mu \text{M} \), whereas the maximum MB dye adsorption in the presence of cellulose-MOF199 beads was observed at 15 \( \mu \text{M} \). At higher MB concentrations (>15–20 \( \mu \text{M} \)), efficiency toward adsorbate removal decreases in both materials due to strong bulk effects that limit the adsorption of MB to the surface. The superior adsorption observed in the pure cellulose beads further emphasizes the role of both intraparticle diffusion and surface uniformity in adsorption capacity.

**Antimicrobial Effectiveness**

The antimicrobial efficiency of the cellulose-MOF199 composite material was evaluated by measuring the ZOI for both beads and films on a Kirby-Bauer disc diffusion plate (Figure 10). After 18 h of incubation, the on-contact inhibition of *E. coli* was confirmed by a lightening of the agar under both cellulose-MOF199 composites beads and discs. The results over several experiments were inconsistent with no ZOI observed in some instances, while other plates displayed ZOIs of 6.10 ± 0.71 mm for a 4 mm bead and 6.78 ± 0.26 mm for a 6.35 mm disk. The inconsistencies suggest that the cellulose-MOF199 composite materials do not have sufficient contact with the bacteria on the inoculated plates thereby preventing the bacteria from docking to the surface to initiate copper-induced toxicity. There was no ZOI or on-contact inhibition observed for cellulose acetate beads and discs indicating that the pure cellulose polymer is ineffective at bacterial inhibition.

The optical density of a TSB solution inoculated with *E. coli* was measured at time intervals over 18 h to better quantify the bacterial inhibition of the cellulose-MOF199 composite (Figure 11). An increase in optical density is associated with increased light scattering caused by the growth of bacterial colonies in the TSB solution. The initial absorbance values for both pure cellulose and cellulose-MOF199 materials are statistically similar to the TSB control, which established a consistent baseline response. After 4 h of incubation at 37 °C, the optical density of the TSB solution containing the cellulose-MOF199 composite film was significantly lower than the control TSB and the TSB solution containing pure cellulose acetate, indicating significant antimicrobial behavior in the composite material. After 24 h of incubation, the optical density of the TSB solution containing cellulose-MOF199 increased slightly whereas the optical density of the control TSB solution increased by a factor of 50. The optical density of the TSB solution containing cellulose acetate was statistically lower than the control TSB solution, but still significantly higher than cellulose-MOF199. The pure cellulose material did show large variations in optical density at this 24-h mark, which could be the result of broth containing bacteria adsorbing to the cellulose material. This variation was not observed in the cellulose-MOF199 composite, suggesting no adsorption of broth containing bacteria due to the antimicrobial nature of the material.

The cellulose-MOF199 composite beads showed superior inhibition of bacterial growth as compared to cellulose acetate and TSB controls. The greater consistency observed in the optical density measurements compared to the Kirby–Bauer experiments is likely
due to increased surface contact between cellulose-MOF199 and bacteria when suspended in solution. This increased surface contact allows for copper-induced toxicity by diffusion of Cu$^{2+}$ into the cell wall.$^{28}$ It should also be noted that a small absorption peak was observed at 594 nm in TSB solutions containing cellulose-MOF199, which could be attributed to some leaching of Cu$^{2+}$ from the material. Conversely, this peak was not observed in the TSB solutions containing pure cellulose beads. The presence of a small absorption peak due to Cu$^{2+}$ leaching from HKUST-1 in the cellulose-MOF199 beads is supported by the AA results and likely aids in the inhibition of E. coli growth. The antimicrobial activity of HKUST-1 has been well established,$^{15}$ and is related to the copper sites inducing intracellular damage through the Gram-negative cell wall. The contact of copper with the cell is also associated with disruption to DNA replication, interference with enzymatic reactions, and the expulsion of cellular contents.$^{58,59}$

**CONCLUSIONS**

This research detailed the synthesis, characterization, and adsorption properties of a novel, biomimetic cellulose-MOF199 composite material that shows antimicrobial behavior toward the Gram-negative bacterium E. coli. The adsorption properties of the composite material were determined in the presence of the textile dye MB in an effort to develop advanced adsorbent materials for water filtration and remediation. The HKUST-1 MOF was synthesized as a powder and added to a dispersion of cellulose acetate in DMAc and polymerized by solvent exchange in water to yield a highly fibrous and biomimetic material with an electronegative surface favorable for dye adsorption. The adsorption of the cellulose-MOF199 beads is best described by a mixed Langmuir/Freundlich adsorption isotherm model and pseudo-second order kinetics. Adsorption is both physical and chemical in nature, with diffusion being a dominant factor in the rate of adsorption. Although the cellulose-MOF199 composite has a lower overall adsorption for MB compared to cellulose, the adsorption capacity is comparable to that of pure cellulose. Weaknesses in the cellulose-MOF199 matrix cause leaching of Cu$^{2+}$ over an extended period of time, however, the unique adsorption mechanism of the composite could lead to an effective point-of-access/disposable water filtration system. Moreover, the presence of HKUST-1 in the material results in a composite polymer with antimicrobial efficiency toward E. coli.

**ACKNOWLEDGMENTS**

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**CONFLICT OF INTEREST**

There are no conflicts to declare.

**REFERENCES**