

**METAL-ORGANIC FRAMEWORKS
FUNCTIONALIZED MULTIFUNCTIONAL
TEXTILES**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

NOVEMBER 2023

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by

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Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

NOVEMBER 2023

Dedicated to

my parents (S. Mahinder Singh and Smt. Naresh Rani)

and

to all the teachers

Especially to my supervisors

Prof. Manjeet Jassal and Prof. Ashwini K. Agrawal

CERTIFICATE

This is to certify that the thesis titled “**Metal-Organic Frameworks Functionalized Multifunctional Textiles,**” being submitted by **Mr. Hardeep Singh** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. He has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis, which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

ਸੂਹੀ ਮਹਲਾ ੫ ॥

ਸੰਤਾ ਕੇ ਕਾਰਜ ਆਪਿ ਖਲੋਇਆ ਹਰਿ ਕੰਮੁ ਕਰਾਵਣਿ ਆਇਆ ਰਾਮ ॥

**“The Lord Himself has stood up to resolve the affairs of the Saints; He has
come to complete their tasks.”**

I would like to take this opportunity to extend my deepest gratitude to all those who have played a significant role in the completion of this Ph.D. thesis. Their unwavering support, guidance, and encouragement have been instrumental in shaping both this research and my academic growth.

First and foremost, I want to start by expressing my sincere thankfulness to God, who guided me internally throughout my research journey. God's spiritual power greatly assisted me in overcoming my fears and served as a lighthouse on this difficult path.

Further, I extend my heartfelt gratitude to my esteemed supervisors, Prof. Manjeet Jassal and Prof. Ashwini K. Agrawal from the Department of Textile and Fibre Engineering at IIT Delhi, for their exceptional mentorship throughout this journey. Their expertise, constructive feedback, and constant motivation have played a pivotal role in pushing the boundaries of my research and ensuring its quality. Working under their mentorship has been a truly enriching and transformative experience. Throughout this journey, Prof. Manjeet and Prof. Ashwini demonstrated an unparalleled commitment to excellence and a genuine passion for the subject matter. I would like to express my sincere appreciation for the time and effort both supervisors

invested in guiding me through the various stages of this thesis. Their dedication to my academic and professional growth has left a lasting impact. I am confident that the skills I have acquired under their tutelage will serve me well in my future endeavors. I am also thankful to the esteemed members of my SRC (Student Research Committee), Prof. B S Butola, Prof. Bhanu Nandan, and Prof. Sampa Saha, for generously dedicating their time and expertise to evaluating and refining my research work. Their insightful comments and suggestions have significantly contributed to the overall improvement of this thesis.

I am thankful to Prof. R. Alagirusamy, the Head of the Department of Textile and Fibre Engineering, and the former Heads of the Department, Prof. R.S. Rengasamy and Prof. B. K. Behara, for their constant support during this thesis work. Further, I would also like to acknowledge the technical staff of the Textile and Fibre Engineering department, especially Mr. Amarjit, Mr. Raj Kumar, and Mr. Rajinder Khatter, for their technical support in my research work. Their support has been invaluable in the pursuit of my research endeavors.

I want to extend my appreciation to the Ministry of Textiles (MHRD) and the Department of Science and Technology (DST), Government of India, for their financial assistance and various research grants. I want to express my gratitude to the members of CRF (Central Research Facility) and NRF (National Research Facility), especially Mrs. Kumud, Mr. Animesh Bhowal and Ms. Aastha Sharma, for their invaluable support in characterizing my samples during my Ph.D. Their assistance has been very crucial in the successful completion of my research work.

I am filled with gratitude for the incredible friends I have encountered on this journey, especially Ms. Kriti, Dr. Jasdeep Singh, Dr. Lovedeep Sahota, Dr. Dharmender Jangra, Dr. Nardev Bajaj, Dr. Rajinder Deol, Dr. Manpreet Singh, Dr. Avinash, Dr. Sanchayan, Dr. Anil, Dr. Sajan, Dr. Shubham Vashishtha, Dr. Vickey Nandal, Dr. Nimish Joseph, Dr. Ajay Lodhi, Dr. Vinay Kumar, Mr. Dheerajpal, Mr. Abhinav, Mr. Avishek, Mr. Divgian Sidhu, Mr. Himanshu, Mr. Prashant, Mr. Jasmeet, Mr. Amritpal, Mr. Tapinder, Mr. Dalvir, Mr. Chamkaur, Mr. Racchpal, Mr. Gurpreet, Mr. Lalit Anjum, Dr. Himanshu Maharana, Mr. Navneet, Dr. Ravi, Mr. Raghav, Mr. Gaurav, and Ms. Harpreet. Their moral support, engaging discussions, and shared knowledge significantly enriched my research experience. I cherish the memories created with them during this research journey. Their positivity and uplifting spirits have been the driving force behind my perseverance.

I am also very grateful to former senior members of the SMITA Research Lab, including Dr. Bhavana Sharma, Dr. Deepika Gupta, Dr. Kamlesh Panwar, Dr. Kiran Yadav, Dr. Raghav Mehra, Dr. Varun Arora, Dr. Jagan Meena, Dr. Neeta Kumari, Dr. Rashmi Agrawal, and Ms. Surabhi. Their generosity in dedicating their time, knowledge, and skills to instruct me in laboratory instruments and techniques has been immeasurable. Their consistent presence and unfaltering motivation have played a pivotal role in shaping my research journey. I am also deeply thankful to the present members of the SMITA Research Lab, such as Mrs. Gurneet Kaur, Mr. Karan Chandrakar, Ms. Kiran Rana, Mr. Pranay Ahuja, Mr. Akhilesh Sharma, Mr. Gopal Kumar, Mr. Suraj, Mr. Ankit Shankar, Mrs. Nayana J Nair, Mr. Ram Agrawal, and Dr. Charu Agrawal. Their enthusiasm and dedication to rigorous experimentation were inspiring. A special thanks go to my lab members and friends, Mr. Rajesh Kumar

and Mr. Jogender, for their consistent support during this journey. I am also grateful to the former lab staff of the SMITA lab, Mr. Praveen and Mr. Arvind, for their valuable support and assistance for various lab-related tasks.

I am genuinely speechless in expressing my profound gratitude to my entire family for their unwavering support and unselfish sacrifices during my educational pursuit. I want to extend special thanks to my parents, Mr. Mahinder Singh Jhinjer and Mrs. Naresh Rani Jhinjer, whose encouragement and inspiration made it possible for me to complete this thesis. Their love and support have been the foundation upon which I built my aspirations.

Finally, I want to acknowledge the invaluable contributions of anonymous reviewers and researchers whose work has been a constant source of inspiration and knowledge for this thesis. To all the individuals mentioned above and to those whose names may have been inadvertently excluded, please know that your support has been deeply valued and cherished. I want to sum up by quoting the famous line of Majrooh Sultanpuri.

मैं अकेला ही चला था जानिब-ए-मंज़िल मगर
लोग साथ आते गए और कारवाँ बनता गया

With sincere appreciation

Hardeep Singh Jhinjer

ABSTRACT

Textile substrates with additional qualities, functions, or capacities beyond their core textile features are known as functional textiles. Multifunctional textiles are gaining attention due to their ability to fulfill multiple applications, like hydrophobicity, hydrophilicity, flame-retardancy, microbial inhibition, and odor adsorption, etc.. Different nanomaterials, polymers, carbon materials, and inorganic and organic compounds are being reported to impart various functionalities to textile substrates.

The rapid growth of industrialization, global warming, and modern lifestyle are responsible for the emergence of many environmental hazards. The presence of pollutants, volatile organic compounds (VOCs), and malodors in the ambient air degrades the quality of life. Similarly, UV radiation from the Sun and microbial infections also seriously threaten human health. Further, the problem of fabric malodors is very challenging as many unpleasant smells are caused by the biotransformation of non-odorous chemicals (called "odor precursors") by certain microorganisms. Most smells emanating from the human body are examples of this biotransformation. Similarly, the increased levels of particulate matter, nitrous oxides, sulfur oxides, carbon oxides, and other toxic VOCs are of major concern for air pollution. These pollutants have adverse effects on human health. The presence of a small amount of these VOCs in the air can cause unpleasant odors and toxicity. Also, long-term exposure to these pollutants/odors, even at levels of a few parts per million, can cause life-threatening respiratory diseases, like asthma, eye and throat irritations, and even cancer. Therefore, developing innovative, multifunctional smart textiles is essential to mitigate the adverse effects of these hazards.

Metal-Organic Frameworks (MOFs) are an emerging class of materials that can be potential candidates for developing innovative, multifunctional, and smart textiles to mitigate the adverse effects of the above-discussed hazards. MOFs consist of two components: organic and inorganic. The organic part is known as bridging ligands or linkers. On the other hand, the inorganic elements are metal ions or clusters.

MOFs have gained importance due to their high adsorption capacities and open metal sites. Natural fiber-based textiles also seem to be very promising substrates for MOFs to expand their different applications. Among the various MOFs, MOF-5, MOF-199, ZIF-8, and ZIF-67 are relatively easier to synthesize and are widely studied in the literature for their different applications.

In this study, a facile and rapid approach for in-situ surface functionalization of the cellulosic textiles with MOF-5, MOF-199, ZIF-8, and ZIF-67 MOF structures. The carboxymethylation was performed to facilitate the growth/attachment of MOFs on the cotton fabric. The in-situ process was found to be facile, rapid, and commercially viable. All the MOF structures were grown on the fabric by in-situ technique. It was also found that carboxymethylation and deprotonation of the linker are essential for rapid growth, high add-on, and high wash durability. FESEM analysis revealed the morphology of different MOF crystals. MOF-5 crystals showed flake-type morphology, the MOF-199 crystals showed octahedral morphology, the ZIF-8 crystals were of distorted spherical shape, displaying indistinct hexagonal characteristics and the ZIF-67 crystals exhibited cubic and tetragonal shapes. FESEM analyses confirmed the uniform coverage of the fabric by MOF structures and the XRD studies confirmed the crystal structures of the grown MOFs. The chemical characteristics of the MOF-

functionalized cellulosic textiles were analyzed using ATR-FTIR and XPS techniques. Based on N₂ adsorption, the BET surface areas were calculated for the carboxymethylated and all MOF-functionalized cotton fabrics. The modified fabrics showed significantly high surface areas as compared to the pristine fabric. The BET surface area was the highest for ZIF-8@CMC at 77.78 m²/g, followed by ZIF-67@CMC fabric at 57.64 m²/g. Surprisingly, the surface areas of the MOF-5@CMC and MOF-199@CMC were just 1.43 m²/g and 4.03 m²/g, respectively. It was observed that there was no significant change in the strength and breaking elongation of the cotton fabrics after the MOF growth.

The MOF functionalized cotton fabrics were investigated for pollutant adsorption, malodor/VOCs adsorption, UV-blocking, and antimicrobial properties. The MOF functionalized fabrics showed rapid adsorption of significantly high amounts of three model aromatic pollutants: aniline, benzene, and styrene. Further, all the MOF functionalized textiles also showed adsorption of high amounts of malodor up to 1000 ppm. Interestingly, all the MOF functionalized samples showed nearly 99.9% antimicrobial activity against *E. coli* and *S. aureus*. Additionally, MOF-199@CMC and ZIF-67@CMC showed high UPF values of 238 and 149, respectively. A comparative study of these multifunctional fabrics in terms of ease of growth, surface area, wash durability, malodor adsorption capacity, UV-blocking properties, antimicrobial activities, and commercial viability has been reported. These MOF functionalized textiles can be used as highly effective protective textiles.

The study also demonstrates the development of a ZIF-8 NPs-based finish for polyester textiles for malodor adsorption and to prevent microbial growth. ZIF-8 NPs

with an average size of ~60 nm were synthesized by a water-based procedure at ambient temperature and applied in small concentrations on a PET fabric using a commercial polyurethane binder and crosslinker. The ZIF-8 functionalized polyester fabric (ZIF-8@PET Fabric) was characterized for its morphology and functionalities.

In comparison to the control PET fabric, the ZIF-8@PET fabric has a significantly higher surface area. The reported fabric exhibited outstanding wash durability, malodor adsorption, and antibacterial activity. The fabrics were found to adsorb high concentrations of three odor-causing model compounds, such as isovaleric acid, indole, and nonenal, and could effectively inhibit the bacterial growth of *E. coli* and *S. aureus*. Further, the fabric functionality was retained even after several wash cycles and could be reused repeatedly.

सार

अपने मूल कपड़ा विशेषताओं से परे अतिरिक्त गुणों, कार्यों या क्षमताओं वाले कपड़ा सब्सट्रेट को कार्यात्मक वस्त्र के रूप में जाना जाता है। बहुक्रियाशील वस्त्र कई अनुप्रयोगों को पूरा करने की अपनी क्षमता के कारण ध्यान आकर्षित कर रहे हैं, जैसे कि हाइड्रोफोबिसिटी, हाइड्रोफिलिसिटी, फ्लेम-रिटार्डेंसी, माइक्रोबियल अवरोध, गंध सोखना, आदि। साहित्य में विभिन्न नैनोमटेरियल्स, पॉलिमर, कार्बन सामग्री, अकार्बनिक और कार्बनिक यौगिकों से कार्यात्मक कपड़ा बनाया गया है।

औद्योगीकरण का तेजी से विकास, ग्लोबल वार्मिंग और आधुनिक जीवनशैली कई पर्यावरणीय खतरों के उद्भव के लिए जिम्मेदार हैं। परिवेशी वायु में प्रदूषकों, वाष्पशील कार्बनिक यौगिकों (वीओसी/VOC) और दुर्गंध की उपस्थिति जीवन की गुणवत्ता को खराब कर देती है। इसी तरह, सूर्य से यूवी विकिरण और सूक्ष्मजीवी संक्रमण भी मानव स्वास्थ्य को गंभीर रूप से खतरे में डालते हैं। इसके अलावा, कपड़े की दुर्गंध की समस्या बहुत चुनौतीपूर्ण है क्योंकि कई अप्रिय गंध कुछ सूक्ष्मजीवों द्वारा गैर-गंधयुक्त रसायनों (जिन्हें "गंध अग्रदूत" कहा जाता है) के बायोट्रांसफॉर्मेशन के कारण होते हैं। मानव शरीर से निकलने वाली अधिकांश गंध इस बायोट्रांसफॉर्मेशन के उदाहरण हैं। इसी तरह वायु में, पार्टिकुलेट मैटर, नाइट्रस ऑक्साइड, सल्फर ऑक्साइड, कार्बन ऑक्साइड और अन्य जहरीले वीओसी के बढ़े हुए स्तर प्रमुख चिंता का विषय हैं। ये प्रदूषक मानव स्वास्थ्य पर प्रतिकूल प्रभाव डालते हैं। हवा में इन वीओसी की थोड़ी मात्रा की उपस्थिति अप्रिय गंध और विषाक्तता पैदा कर सकती है। इसके अलावा, इन प्रदूषकों/गंधों के लंबे समय तक संपर्क में रहने से, यहां तक कि प्रति मिलियन कुछ भागों के स्तर पर भी, अस्थमा, आंख और गले में जलन और यहां तक कि कैंसर जैसी जानलेवा श्वसन संबंधी बीमारियां हो सकती हैं। इसलिए, इन खतरों के प्रतिकूल प्रभावों को कम करने के लिए नवीन, बहुक्रियाशील स्मार्ट टेक्स्टाइल विकसित करना आवश्यक है।

मेटल-ऑर्गेनिक फ्रेमवर्क (एमओएफ/MOF) सामग्रियों का एक उभरता हुआ वर्ग है जो उपरोक्त चर्चा किए गए खतरों के प्रतिकूल प्रभावों को कम करने के लिए अभिनव, बहुक्रियाशील और स्मार्ट वस्त्र विकसित करने के लिए संभावित उम्मीदवार हो सकते हैं। MOF में दो घटक होते हैं: कार्बनिक और अकार्बनिक। कार्बनिक भाग को ब्रिजिंग लिगेण्ड्स या लिंकर्स के रूप में जाना जाता है। दूसरी ओर, अकार्बनिक तत्व धातु आयन या क्लस्टर हैं।

MOF को उनकी उच्च सोखने की क्षमता और खुली धातु साइटों के कारण महत्व प्राप्त हुआ है। प्राकृतिक फाइबर-आधारित वस्त्र भी MOF के लिए अपने विभिन्न अनुप्रयोगों का विस्तार करने के लिए बहुत आशाजनक सब्सट्रेट प्रतीत होते हैं। विभिन्न MOF में से, MOF-5, MOF-199, ZIF-8, और ZIF-67 को संश्लेषित करना अपेक्षाकृत आसान है और उनके विभिन्न अनुप्रयोगों के लिए साहित्य में व्यापक रूप से अध्ययन किया गया है।

इस अध्ययन में MOF-5, MOF-199, ZIF-8, और ZIF-67 MOF संरचनाओं का सूती वस्त्रों के ऊपर इन-सीटू विकास किया गया है। सूती कपड़े पर MOF के विकास/लगाव को सुविधाजनक बनाने के लिए कार्बोक्सिमिथाइलेशन किया गया था। इन-सीटू प्रक्रिया को सुविधाजनक, तीव्र और व्यावसायिक रूप से व्यवहार्य पाया गया। सभी MOF संरचनाएं इन-सीटू तकनीक द्वारा कपड़े पर विकसित की गईं। यह भी पाया गया कि कार्बोक्सिमिथाइलेशन और लिंकर का डिप्रोटोनेशन, उच्च एड-ऑन और उच्च धुलाई स्थायित्व के लिए आवश्यक है। FESEM विश्लेषण से विभिन्न MOF क्रिस्टल की आकृति विज्ञान का पता चला। MOF-5 क्रिस्टल ने परत-प्रकार की आकृति विज्ञान दिखाया, MOF-199 क्रिस्टल ने अष्टफलकीय आकृति विज्ञान दिखाया, ZIF-8 क्रिस्टल विकृत गोलाकार आकार के थे, जो अस्पष्ट हेक्सागोनल विशेषताओं को प्रदर्शित करते थे, और ZIF-67 क्रिस्टल घन और चतुष्कोणीय आकार प्रदर्शित करते थे। FESEM विश्लेषण ने MOF संरचनाओं द्वारा कपड़े की एक समान कवरेज की पुष्टि की, XRD अध्ययनों ने विकसित MOF की क्रिस्टल संरचनाओं की पुष्टि की। MOF-फंक्शनल सेल्युलॉसिक वस्त्रों की रासायनिक विशेषताओं का विश्लेषण ATR-FTIR और XPS तकनीकों का उपयोग करके किया गया था। नाइट्रोजन (N_2) सोखना के आधार पर, कार्बोक्सिमिथाइलेटेड और सभी MOF-फंक्शनल सूती कपड़ों के लिए BET सतह क्षेत्रों की गणना की गई। संशोधित कपड़ों में प्राचीन कपड़ों की तुलना में काफी ऊंचे सतह क्षेत्र दिखाई दिए। ZIF-8 फंक्शनल फैब्रिक के लिए BET सतह क्षेत्र सबसे अधिक $77.78 \text{ m}^2/\text{g}$ था, इसके बाद ZIF-67 फंक्शनल फैब्रिक का $57.64 \text{ m}^2/\text{g}$ था। आश्चर्यजनक रूप से, MOF-5 फंक्शनल फैब्रिक और MOF-199 फंक्शनल फैब्रिक का सतह क्षेत्र क्रमशः केवल $1.43 \text{ m}^2/\text{g}$ और $4.03 \text{ m}^2/\text{g}$ था। यह देखा गया कि MOF वृद्धि के बाद सूती कपड़ों की मजबूती और टूटने वाले बढ़ाव में कोई महत्वपूर्ण बदलाव नहीं हुआ।

MOF-फंक्शनल सूती कपड़ों की जांच प्रदूषक सोखना, दुर्गंध/VOC सोखना, यूवी-अवरोधन और जीवाणुरोधी गुणों के लिए की गई। MOF-फंक्शनल सूती कपड़ों ने तीन मॉडल प्रदूषकों की काफी उच्च मात्रा का तेजी से अवशोषण दिखाया: एनिलिन, बेंजीन और स्टाइरीन। इसके

अलावा, सभी MOF-फंक्शनल वस्त्रों में 1000 ppm तक उच्च मात्रा में दुर्गंध का सोखना भी देखा गया। दिलचस्प बात यह है कि सभी MOF-फंक्शनल सूती कपड़ों के नमूनों ने *E. coli* और *S. aureus* के खिलाफ लगभग 99.9% जीवाणुरोधी गतिविधि दिखाई। इसके अतिरिक्त, MOF-199-फंक्शनल फैब्रिक और ZIF-67-फंक्शनल फैब्रिक ने क्रमशः 238 और 149 के उच्च UPF मान दिखाए। विकास में आसानी, सतह क्षेत्र, धोने के स्थायित्व, दुर्गंध सोखने की क्षमता, यूवी-अवरुद्ध गुणों, जीवाणुरोधी गतिविधियों और व्यावसायिक व्यवहार्यता के संदर्भ में इन बहुक्रियाशील कपड़ों का तुलनात्मक अध्ययन बताया गया है। इन MOF-फंक्शनल वस्त्रों का उपयोग अत्यधिक प्रभावी सुरक्षात्मक वस्त्रों के रूप में किया जा सकता है।

यह अध्ययन दुर्गंध सोखना और माइक्रोबियल विकास को रोकने के लिए पॉलिएस्टर वस्त्रों के लिए ZIF-8 NPs-आधारित फिनिश के विकास को भी दर्शाता है। ~60 nm के औसत आकार वाले ZIF-8 NPs को परिवेश के तापमान पर पानी आधारित प्रक्रिया द्वारा संश्लेषित किया गया था और एक वाणिज्यिक पॉलीयूरेथेन बाइंडर और क्रॉसलिंगर का उपयोग करके पीईटी/PET कपड़े पर छोटी सांद्रता में लागू किया गया था। ZIF-8 फंक्शनल पॉलिएस्टर फैब्रिक (ZIF-8@PET फैब्रिक) का विश्लेषण विभिन्न उपकरणों द्वारा किया गया।

मूल PET फैब्रिक की तुलना में, ZIF-8@PET फैब्रिक का सतह क्षेत्र काफी अधिक है। रिपोर्ट किए गए कपड़े ने उत्कृष्ट धुलाई स्थायित्व, दुर्गंध सोखना और जीवाणुरोधी गतिविधि का प्रदर्शन किया। यह पाया गया कि कपड़े तीन गंध पैदा करने वाले मॉडल यौगिकों, जैसे आइसोवालैरिक एसिड, इंडोल और नॉननल की उच्च सांद्रता को सोख लेते हैं, और *E. coli* और *S. aureus* के जीवाणु विकास को प्रभावी ढंग से रोक सकते हैं। इसके अलावा, कपड़े की कार्यक्षमता कई बार धोने के बाद भी बरकरार रहती है और इसे बार-बार दोबारा इस्तेमाल किया जा सकता है।

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/Abbreviation	Expanded Form/Term
°C	Degree Celsius
1D	One Dimension
2D	Two Dimension
3D	Three Dimension
AATCC	American Association of Textile Chemists and Colorists
aq.	Aqueous
Arb. Units	Arbitrary Units
ASTM	American Society for Testing and Materials
BDC	Benzenedicarboxylic Acid or Terephthalic Acid
BET	Brunauer, Emmett, and Teller
BTC	Benzenetricarboxylic Acid or Trimesic Acid
CC	Control Cotton
CeO ₂	Cerium Oxide
CM	Carboxymethylation
CMC	Carboxymethylated Cotton
CNFs	Cellulose Nanofibers
CVD	Chemical Vapor Deposition
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide

DS	Degree of Substitution
<i>E. coli</i>	<i>Escherichia Coli</i>
EDX	Energy Dispersive X-ray
EtOH	Ethanol
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier-Transform Infrared Spectroscopy
GCMS	Gas Chromatography-Mass Spectrometry
HKUST	Hong Kong University of Science and Technology
HRTEM	High-Resolution Transmission Electron Microscopy
IRMOFs	Isorecticular MOFs
ISO	International Organization for Standardization
M:L:T	Metal:Linker:TEA
MeOH	Methanol
MIL	Materials Institute Lavoisier
MOF-199@CMC	MOF-199 Functionalized CMC
MOF-5@CMC	MOF-5 Functionalized CMC
MOFs	Metal-Organic Frameworks
M	Molarity
N	Normality
nm	Nanometer
NMP	N-Methyl-2-pyrrolidone
NPs	Nanoparticles
PAN	Polyacrylonitrile
PCNs	Porous Coordination Networks
PCPs	Porous Coordination Polymers

PET	Poly(ethylene terephthalate)
PM	Particulate matter
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PVD	Physical Vapor Deposition
PVDF	Poly(vinylidene fluoride)
RGB	Red, Green, and Blue
<i>S. Aureus</i>	<i>Staphylococcus Aureus</i>
SBBs	Secondary Building Blocks
TEA	Triethylamine
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
TiO₂	Titanium Oxide
UiO	University of Oslo
um	Micrometer
UV	Ultraviolet
UV-visible	Ultraviolet-visible
VOCs	Volatile-Organic Compounds
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZIF-67@CMC	ZIF-67 Functionalized CMC
ZIF-8@CMC	ZIF-8 Functionalized CMC
ZIF-8@PET	ZIF-8 Functionalized PET
ZIFs	Zeolitic Imidazolate Frameworks
ZnO	Zinc Oxide