

## Metal-Organic Frameworks on Cotton-Linen Blend for Hydrophobicity

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### ARTICLE INFO

#### Article history:

Received 12 May 2024

Accepted 21 May 2024

Available online 05 June 2024

#### Keywords:

CL blended Fabric;

Metal Organic Frameworks;

Hydrophobic.

### ABSTRACT

Cotton Linen (CL) blended fabrics, extensively utilized in clothing, household items, and various applications, face limitations due to their inherent hydrophilicity, restricting their expansion into diverse fields. The emergence of multifunctional textiles has garnered attention, and the utilization of metal-organic framework materials in application development presents novel prospects for crafting versatile fabrics. This study focuses on creating a multifunctional composite, ZIF-8 CL blended fabric, boasting elevated hydrophobic properties through the incorporation of CL blended fabric as the foundational material. The experimentation involves compounding the fabric with ZIF-8, investigating the impact of different proportioning methods on the composite material. Characterization through SEM and other tests explores the influence of finishing conditions on the hydrophobic effect. The stability of hydrophobic CL blended fabrics is assessed via tests, including washing resistance, abrasion resistance, and exposure to chemical reagents. Results indicate that the PMHS fabric, post-hydrophobic protection and finishing, exhibits remarkable self-cleaning capabilities against water-based pollutants like mud, coffee and textile dye. The fabric displays excellent anti-sludge performance and demonstrates robust wear resistance. Moreover, it exhibits high stability under treatment conditions involving acid, alkali, and organic solvents. The findings contribute valuable insights and strategies for the future evolution of textile materials.

### 1. Introduction

Metal-organic frameworks (MOFs) show significant potential for a wide range of uses due to their impressive characteristics, such as a substantial specific surface area, robust stability, and the ability to be chemically tailored [1]. In 2019, Zhang and colleagues [2] introduced a heat-pressing technique for the direct synthesis of MOFs on fabric surfaces. During the same year, Farha and co-workers [3] described a method for coating fibers with an MOF-808 framework incorporating zirconium as a metal component through a dipping process. Additionally, Zhao and colleagues [4] applied Metal Organic Frameworks into textile materials using poly-acrylic acid (PAA) as a binding agent. These investigations lay a solid foundation in supporting the development of MOF fabric composites. The majority of reported MOF fabric composites, exhibited exceptional performance in various applications, such as testing [5], dye wastewater treatment [6], and the creation of self-cleaning surfaces [7].

Yingying Yang, in a previous study [8], applied Zeolitic Imidazolate Framework-67 onto pure cotton fabric, then subjected it to a PDMS coating treatment. Even after undergoing both rubbing and washing, the cotton fabric with (Zeolitic Imidazolate Framework-67) still displayed a vibrant purple hue on the fabric surface. Hence, this proved the effectiveness of coating PDMS resulting in enhancing metal organic framework's fabric composites. Although, it's worth noting that PDMS typically necessitates the use of THF as a solvent [9], which poses significant health risks during the application process. Additionally, the amalgamation of PDMS with its curing agent may result in the development of a denser coating, impacting the texture of the material. In contrast, Polymethylhydrosiloxane (PMHS) has a relatively milder impact [10]. Chen and colleagues [11] demonstrated this by creating a coating of PMHS with ZnO on bamboo surfaces, resulting in effective hydrophobic modification and a substantial enhancement in the bamboo's resistance to mold. It's important to mention, though, that the methods for applying this treatment typically involve

silica-sol processes, which can be intricate [12]. In essence, the aforementioned research endeavors aim to establish highly hydrophobic surfaces for the protection of various materials. Currently, there exist two approaches for creating superhydrophobic surfaces. The first involves generating a textured structure on materials with low surface energy, while the second entails chemically modifying rough surfaces [13].

In this research, a remarkably resilient fabric composite was developed from cotton-linen blended fabric through the incorporation of ZIF-8 and PMHS with enhanced hydrophobic properties. The stability of the hydrophobic CL blended fabrics is evaluated by different treatment conditions like abrasion resistance, chemical inertness, washing resistance and effects of volume ratio of PMHS to C<sub>3</sub>H<sub>8</sub>O on surface (WCA) of coated fabric. The effects of different pollutants on treated CL blended fabric are investigated. Additionally, the stability under treatment conditions involving acid, alkali, and organic solvents is examined.

## 2. Experimental

### 2.1. Materials

Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), Poly-Methyl-Hydro-Siloxane (PMHS) pre-polymer and 2-Methyl-Imidazole (MIM) bought from Aladdin reagent Co. Ltd. (Shanghai, China). Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was bought from Tianjin Damao Chemical Reagent Factory, OP-10 Emulsifier was bought from Tianjin Mading Technology Co., Ltd, Anhydrous methanol (CH<sub>3</sub>OH) was bought from Tianjin Jiangtian Chemical Co., Ltd, Isopropyl alcohol (C<sub>3</sub>H<sub>8</sub>O) was bought from Tianjin Kaires Fine Chemical Co., Ltd and the original CL blended fabric (20x14/54x52) procured from Wujiang-Weijia Textile Company, Ltd.

### 2.2. Instruments

Ultrasonic Cleaner (KQ-100DA) bought from Kunshan Ultrasonic Instrument Co, Ltd, Padder (RAPID) bought from Xiamen Ruibi Precision Machinery Co., Ltd, Optical Contact Angle Measuring Instrument (DSA-100) bought from KRUSS, Germany, Precision Electronic Balance (TLE203E/02) bought from Shanghai Mettler Toledo Instrument Co., Ltd and Electro Thermal Drying Oven (101-1AB) bought from Tianjin Fuer Technology Co., Ltd.

### 2.3. Synthesis of ZIF-8 via Solvo-thermal growth [14]

#### 2.3.1. Carboxymethylation of cotton linen (CM-CL) fabric

The initial stage of the process involved treating the cotton linen (CL) blended fabric with a combination of

sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and OP-10. This treatment was aimed at preparing the fabric for subsequent modifications. Following this preparatory step, carboxymethylation was carried out to introduce carboxymethyl groups onto the fabric. At ambient temperature, the CL blended fabric is immersed in a solution containing caustic soda and ethanol, maintaining a mass ratio of fabric to solution at 1:30 (weight/volume). The treatment is conducted at 60 °C for 30 minutes. Subsequently, the fabric is transferred to a solution of isopropanol and water, to which sodium chloroacetate is introduced, initiating a reaction held at a specified temperature for a determined duration. Finally, the treated CL blended fabric undergoes a 10-minute immersion in a glacial acetic acid solution with a concentration of 2g/L, followed by rinsing with water and drying at 100 °C, resulting in the production of carboxymethyl cotton linen blended fabric (CM-CL). There by achieving a degree of substitution (DS) of around 0.0225. This modification is crucial for imparting desired properties to the fabric for further processing.

#### 2.3.2. Preparation of ZIF-8 @Cotton linen composite material

The method for producing ZIF-8 @Cotton linen blended (ZCL) fabric is detailed in Fig. 1, illustrating a series of steps to transform the cotton linen (CL) blended fabric into ZCL. Initially, the fabric was submerged in a solution of zinc nitrate hexahydrate dissolved in methanol for a duration of 10 minutes. The fabric was carefully rolled during immersion to ensure thorough absorption of the solution. Following this, the fabric underwent a drying process at a temperature of 50°C for a duration of 10 minutes to remove excess solvent and facilitate the next stage of modification.

Subsequently, the fabric was subjected to a comparable treatment with methanol containing 2-methylimidazole. This additional modification step is essential for further functionalizing the fabric surface. The process was repeated three times to ensure adequate modification, with each repetition involving immersion in the methanolic solution, followed by drying. After each cycle, the fabric was thoroughly washed with methanol to remove any residual reagents or byproducts.

Finally, after the completion of all modification steps, the fabric was dried again to yield the final ZCL fabric. This meticulous process ensures that the fabric retains its desired properties while incorporating the necessary modifications to achieve the desired characteristics for various applications.

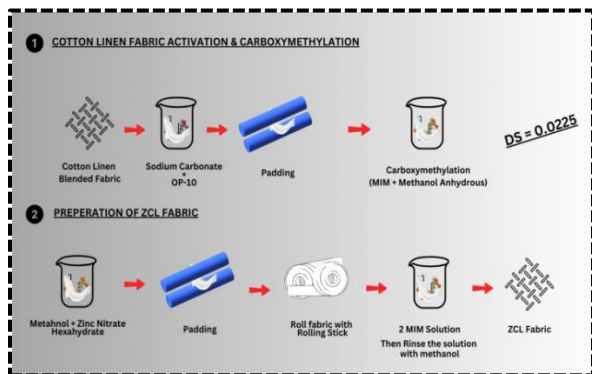


Fig. 1 Preparation of ZCL fabric

### 2.3.3. Preparation of ZCL/PMHS composite material

ZIF-8 alone contributes to the hydrophobicity, adsorption capacity, chemical stability, structural integrity, and selective permeability of the fabric, making it a versatile material for various applications while the inclusion of PMHS in conjunction with ZIF-8 enhances the hydrophobicity, durability, and self-cleaning properties of the fabric, resulting in a high-performance material suitable for various applications.

Hence, following the activation step, the activated fabric is subsequently immersed in a solution containing PMHS (poly-methyl-hydro-siloxane) and isopropyl alcohol at different concentrations. This immersion process aims to introduce the PMHS coating onto the fabric surface, possibly altering its properties based on the concentrations used. Initially, solutions of PMHS and isopropyl alcohol are prepared separately. PMHS is typically dissolved in a suitable solvent, which could be isopropyl alcohol or another compatible solvent. The concentration of PMHS and Isopropyl Alcohol in the solution is 1:1, 1:2, 1:3, 1:4, 1:5 respectively. The activated fabric is then immersed in the prepared solution ensuring that the fabric is thoroughly coated with the solution, allowing for uniform deposition of the PMHS coating.

Once the fabric has been adequately immersed in the PMHS and isopropyl alcohol solution, it is removed from the solution. Excess solution is allowed to drain off with the help of padding machine. After that, the fabric is left in drying machine at the temperature of 100 °C.

## 2.4. Analyses and measurement

### 2.4.1. Characterization

The scanning electron microscope (SEM, EDS, Hitachi S4800) was employed to examine the surface structure and elemental composition of various altered textiles.

### 2.4.2. Performance testing

#### a. Mechanical stability

The mechanical durability of CL blended fabric samples treated with ZCL/PMHS was assessed through abrasion tests using sandpaper at 20, 40, and 60-second intervals. Finally, the water contact angle on the fabric's surface was determined.

#### b. Chemical inertness

ZCL/PMHS textiles underwent immersion in different solvent solutions, including acetone, methanol, DMF, MMA, acetic acid and acetonitrile, each lasting for a duration of 24 hours. Further, also immersed in aqueous solutions with different pH levels, specifically (pH-2, pH-3, pH-5, pH-7, pH-9, pH-11, and pH-12), for a duration of 24 hours. Subsequently, the water contact angle (WCA) of the fabric surface was measured.

#### c. Laundering durability

In assessing the washing stability of MOF-induced CL blended fabric designed for oil-water separation, a series of experiments were conducted with varying washing durations of 5, 15, and 20 minutes while also the water contact angle was measured.

## 3. Results and discussion

### 3.1. Synthesis and characterization

ZCL fabric was produced by introducing carboxymethylated CL blended fabric into ZIF-8 in solvothermal. As depicted in Figure 2b, the ZCL fabric comprised zinc ions coordinated with both the carboxylate anions and hydroxyl groups of the CL blended fabric, along with 2-methylimidazole [15]. And the scanning electron microscopy (SEM) images verified the deposition of ZIF-8 nanoparticles on the fabric surface, as shown in Fig. 2(a2, b2). In contrast, the un-treated CL blended exhibited a noticeable groove and an almost smooth surface, as indicated in Fig. 2(a1). The remarkably rapid nucleation rate in the solvent was responsible for generating ZIF-8 particles of diminutive size, approximately 50 nm. These small nanoparticles proved ideal for establishing nanoscale surface roughness, serving as the foundation for creating hydrophobic surfaces in subsequent steps. The inherent hydrophilicity of the initial CL blended fabric, attributed to the strong attraction of hydroxyl groups on its surface, made it prone to staining by water contaminants. However, following the incorporation of ZIF-8, the fabric's contact angle substantially increased to 116.4°.

The ZIF-8 nanoparticles constitute a micro/nano-scale rough structure, and with PMHS membrane modification, this layered micro/nano structure increases roughness, reduces surface energy, providing favorable conditions for the hydrophobic performance of the PMHS

fabric, resulting in a very high contact angle of 138.7 °C on the surface of the ZCL/PMHS fabric.

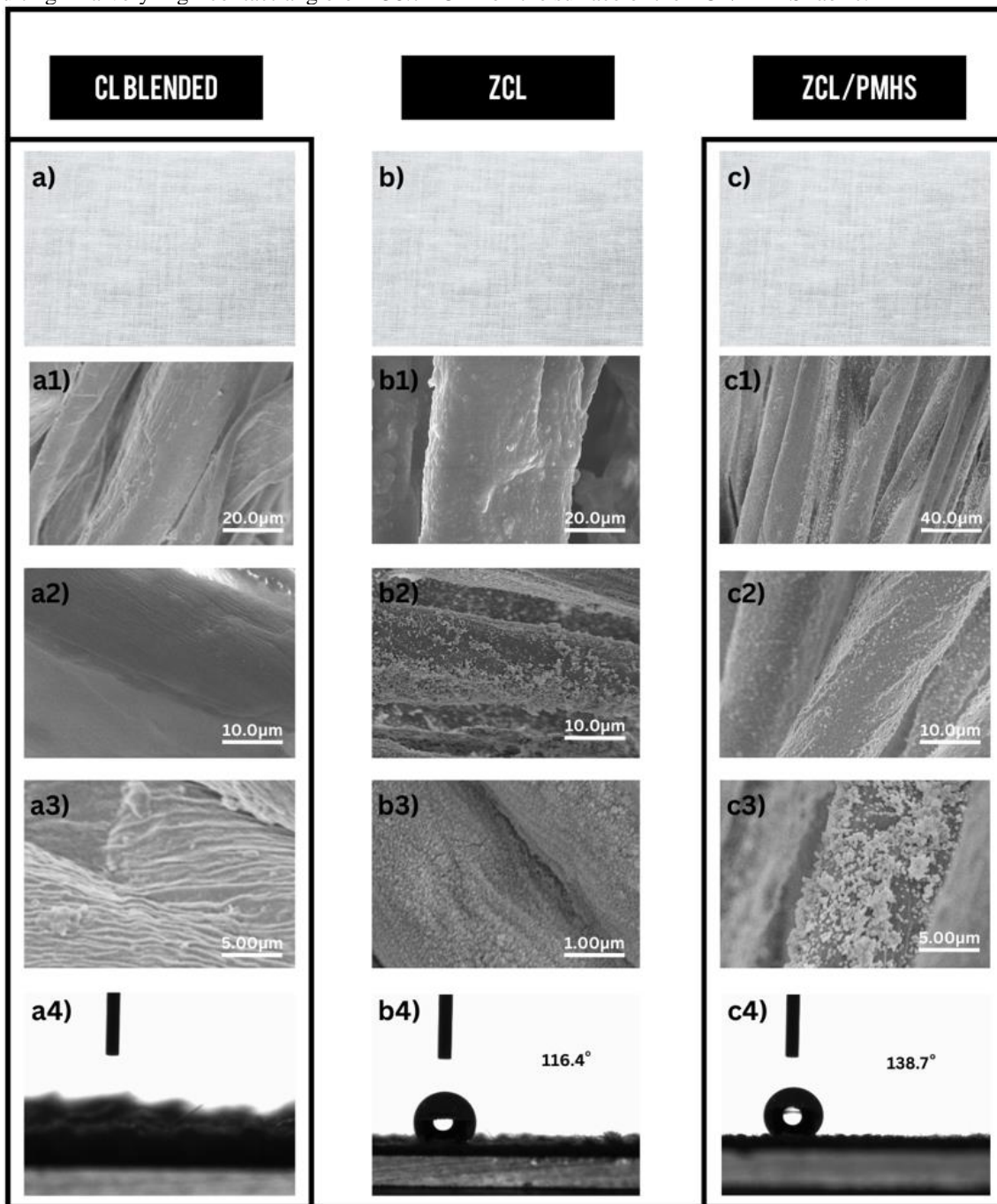


Fig. 2 SEM Microscope Images, WCA of different fabrics, (a)CL, (b)ZCL, (c) ZCL/PMHS.

### 3.2. Durability of ZCL/PMHS fabric

The abrasion resistance assessment involved using sandpaper, as depicted in Fig. 3a. The abrasion procedure was conducted for durations of 20, 40, and 60 seconds. Consequently, it was noted that as the duration increased, the water contact angle (WCA) on the ZCL/PMHS fabric surface dropped below 130° due to the extensive damage caused by the sandpaper, as illustrated in Fig. 3a.

Chemical inertness on ZCL/PMHS fabric assessed, using various solvents and chemical agents of different

pH. ZCL/PMHS fabric after immersed in varying pH solutions for 24 hours, different pH levels impacted on the WCA of ZCL fabric is depicted in the Fig. 3b. Upon submerging the PMHS fabric in different chemical solvents as shown in Fig. 3c for the same duration WCA was observed on the surface of fabric that decreased notably when immersed in acetonitrile and acetic acid. This decrease can be attributed primarily to the strong acidic and alkaline nature of acetic acid and acetonitrile,

which lead to the disintegration of the ZIF-8 structure in the acidic solution, resulting in fabric damage.

The study examined how the contact angle of ZCL fabric in washing changed when the fabric was submerged for different durations, specifically at 5, 15, and 20-minute intervals as shown in Fig. 3d. As the duration of washing increased, there was a noticeable reduction in the contact angle, which had the consequence of decreasing the fabric's hydrophobic properties.

By testing the surface water contact angle of fabrics under different finishing conditions, the effects of various coating treatments on the performance of PMHS fabrics were analyzed. As shown in Fig. 3e, the influence of the volume ratio of PMHS to isopropanol (C<sub>3</sub>H<sub>8</sub>O) on the surface water contact angle of the samples was investigated. With the increase in the volume ratio of PMHS to C<sub>3</sub>H<sub>8</sub>O, the solvent content of PMHS decreased, which was unfavorable for PMHS film formation, resulting in a gradual decrease in the fabric's surface water contact angle. Therefore, based on the experimental results, a volume ratio of 1:4 for PMHS to C<sub>3</sub>H<sub>8</sub>O was chosen.

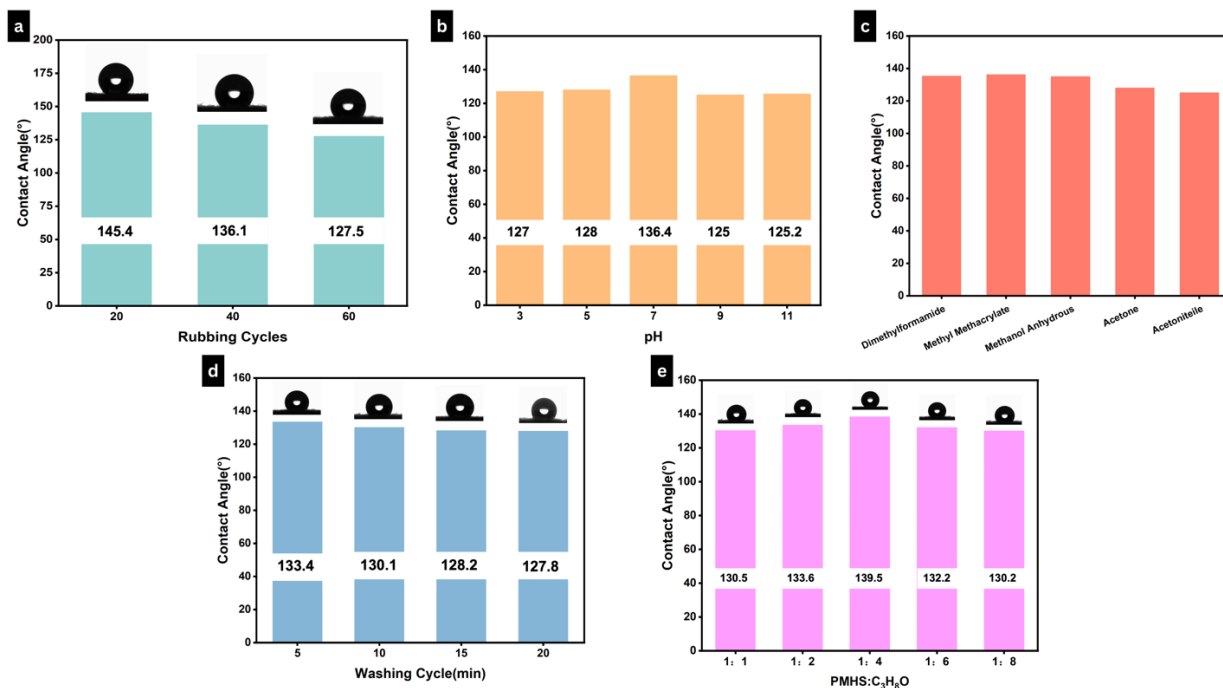


Fig. 3 WCA changes (a) 20, 40 and 60 min of friction (b) Effect of pH after immersing for 24 hours (c) Immersing in different chemical reagents (d) Effect of washing (e) Effect of volume ratio of PMHS to C<sub>3</sub>H<sub>8</sub>O

### 3.3. Self-cleaning properties of the composite fabric

Investigation into Mud Water Immersion revealed the self-cleaning properties of ZCL/PMHS fabric through a dye immersion experiment, depicted in Fig. 4a. The fabric's hydrophobic nature facilitated pollutant removal without leaving residue, contrasting with immediate absorption seen in the original cotton-linen blend.

Similarly, the Dye immersion experiment illustrated the fabric's self-cleaning abilities, with pollutants rolling off the surface without residue, as shown in Fig. 4b. Additionally, a coffee stain experiment mirrored these results, confirming the fabric's effective self-cleaning capabilities depicted in Fig. 4c. This high hydrophobicity is crucial for household textiles and clothing, affirming the fabric's resistance to staining.

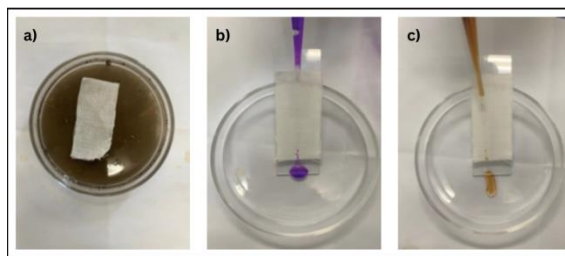


Fig. 4 (a) After 30 minutes mud immersion (b) Self-cleaning process of dye (c) Self-cleaning process of coffee stain

### Conclusion

This paper presents the development of a versatile composite material, ZIF-8 @cotton linen fabric, boasting significant hydrophobic properties. The base material, cotton linen fabric, was utilized to prepare this composite. Initially, carboxymethylated cotton linen fabric and ZIF-8 composite were synthesized to investigate the impact of varying ratios and composite methods on the resulting

material. Characterization via SEM was employed to assess its properties. The hydrophobic stability of the fabric was evaluated through abrasion resistance, resistance to washing, and chemical treatments.

ZIF-8 composites were synthesized via a solvothermal method. Results indicated that composites with a  $Zn^{+2}$  concentration of 50mM and a molar ratio of 2-methylimidazole to zinc nitrate hexahydrate of 8:1 exhibited higher adsorption rates on the fabric surface. Abrasion Impact on hydrophobicity provides concrete evidence of the adverse effects of abrasion on the hydrophobicity of ZCL/PMHS fabric, as demonstrated by the reduction in water contact angle below the critical threshold of 130°. This study provides valuable insights into the chemical inertness of ZCL/PMHS fabric, emphasizing its susceptibility to varying chemical environments. Practical implications include considerations for material selection and application contexts, particularly in industries where exposure to acidic or alkaline solutions is prevalent. For washing, the investigation elucidated a direct correlation between the duration of washing cycles and the decline in the contact angle of ZCL fabric, thereby influencing its hydrophobic characteristics. Subsequently dropping from 133.4° to 127.8° within 5-20 mins. For the selection of optimal volume ratio based on experimental data, a volume ratio of 1:4 for PMHS to  $C_3H_8O$  was identified as optimal, balancing solvent content and film formation to maintain desirable hydrophobic properties.

Through meticulous experimentation, this study reveals the remarkable self-cleaning attributes of PMHS fabric subsequent to hydrophobic protection and finishing procedures. Notably, the fabric exhibits efficacy in repelling water-based pollutants such as mud, coffee, and textile dye, showcasing its potential for applications necessitating cleanliness and stain resistance.

#### Declaration of Competing Interest

The authors assert that they do not possess any identifiable financial conflicts of interest or personal affiliations that might have seemed to exert an impact on the research presented in this paper.

#### Data Availability

Information will be accessible upon request.

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