

SYNTHESIS, STRUCTURAL CHARACTERIZATION, AND
HYBRIDIZATION OF METAL-ORGANIC FRAMEWORK-5 (MOF-5) WITH
HUMIC ACID: A SUSTAINABLE APPROACH TO FUNCTIONAL
COMPOSITE MATERIALS

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Abstract

Metal-organic frameworks (MOFs) are highly porous, crystalline materials comprising metal nodes and organic linkers, which can be tuned to produce a variety of pore architectures that are suitable for the storage, catalysis, and removal of pollutants. MOF-5, a member of this family constructed from Zn₄O clusters and linked by terephthalate units, is one of the most studied MOFs due to its cubic topology and large surface area, but its practical application is limited by its high moisture sensitivity. Humic acid (HA), a naturally occurring macromolecule with a high concentration of carboxyl, phenolic and hydroxyl groups, was explored for this work as a hybridizing agent that not only provides additional functional chemistry to MOF-5, but also potentially enhances the environmental durability of it. MOF-5 was synthesized via solvothermal method from the reaction between zinc nitrate hexahydrate and terephthalic acid in dimethylformamide, and then the pores were activated by the exchange of solvents with methanol/ethanol. Alkaline extraction combined with acid precipitation was used to isolate the humic acid from natural organic matter, and then the MOF-5@HA composite was successfully fabricated by dispersing HA into activated MOF-5 in an alcoholic medium. Powder X-ray diffraction (PXRD) and Fourier-transform infrared (FTIR) spectroscopy were used to confirm the formation of crystalline, phase-pure MOF-5 and demonstrate the PXRD signature did not change significantly after hybridization with the HA functional groups while spectral evidence was observed for coordination and hydrogen-bonding interactions. Such results show that MOF-5 can be hybridized with a renewable and low-cost organic material without destroying the crystal structure, thus expanding the surface chemistry of the composite which is important for the adsorption of heavy metal and dye, catalysis, and catching of gases. The results are discussed in the context of the ever-expanding literature on MOF-organic hybrids up to 2026.

1. INTRODUCTION

Porous solids have properties such as selective adsorption, high surface area and tunable pore chemistry, which are impossible to achieve in dense materials due to the low density and internal void space of porous solids (Su, Sanchez, & Yang, 2011). The materials have been classified by the IUPAC according to the pore size as microporous, mesoporous, and macroporous and this classification has been used for decades in the study of zeolites, activated carbons, and recently, metal-organic frameworks (MOFs). Due to their size selective permeability, zeolites have been used in several emerging applications, but their rigid pore geometry, deactivation by the guest molecules and incompatibility of larger guest molecules limit their applications (Khaleque et al., 2020; Soo et al., 2024).

MOFs overcome many of these drawbacks. Owing to the ability to construct almost any size and shape by varying the metal ions or metal-oxo clusters and the organic ligands connecting them, in principle, their pore size, surface chemistry, and framework topology can be designed nearly at will. (Zhang, Yan, Yan, & Lv, 2023) MOFs like MOF-5, MOF-2, ZIF-8, ZIF-67, and some nickel-based MOFs have been the subjects of continuous research for gas storage, gas separation, catalysis, luminescent sensing, biomedical imaging, and drug delivery (Naghdi et al., 2023). Of these, MOF-5 (also called IRMOF-1) is considered a benchmark material as it has a reported $\text{ZnO}(\text{BDC})_3$ framework with one of the largest surface areas reported for a first generation MOF, and has been used for over 20 years to understand MOF assembly, characterization, and post-synthetic modification (Ahmed & Jhung, 2017).

One of the challenges to using MOF-5 in practice is that it is unstable in moist and aqueous conditions due to hydrolysis of the MOF framework's Zn-O-C bonds. Hybridization (mixing MOF-5 with a second material that can fill in reactive sites, provide protective interface, or add complementary functional chemistry) is one way to overcome this limitation. Humic acid (HA) is a promising option for this application. It is a naturally occurring, biodegradable macromolecule

produced by microbial decomposition of plant and animal remains in soils, peats and natural waters, and also known as "black gold" due to its dark colour and agronomic value (de Melo, Motta, & Santana, 2016). The carboxylic and phenolic hydroxyl groups enable it to be a dense functional group, and the weak acidic electrolyte nature makes it a good candidate for metal coordination, and a potential partner for the introduction of porous inorganic frameworks (Li, Shi, & Bao, 2021) via hybridization.

This study aimed to synthesize MOF-5 using the solvothermal method, confirm the MOF-5 crystallinity and functional group chemistry, to activate MOF-5 pore network by exchanging solvents, and to isolate humic acid from natural organic matter and to prepare a MOF-5@HA composite. Specific aims were (1) synthesis of MOF-5 by the solvothermal method; (2) characterization of as-synthesized MOF-5 by powder X-ray diffraction (PXRD) and infrared spectroscopy; (3) solvent exchange of MOF-5 with a low-boiling alcohol; (4) extraction and characterization of humic acid; (5) synthesis of MOF-5@HA composite; and (6) characterization of MOF-5@HA composite. The general hypothesis was that the incorporation of humic acid would maintain the crystallinity of the parent MOF-5 with the addition of carboxyl and phenolic functionality which would make this new material a better candidate for applications involving surface chemistry, such as environmental remediation, catalysis, and adsorption-based applications.

The study is important for the following reasons. From a scientific perspective, it is related to the limited number of publications on the hybridisation of metal-organic frameworks with naturally occurring organic macromolecules instead of synthetic polymers or carbon materials (Zhou et al., 2019; Wang, Zhang, & Chen, 2021). An understanding of the effect of HA changes to the functional properties of MOF-5, such as structural stability, surface chemistry and reactivity, would provide a basis for the rational design of future hybrid porous composites, as well as an understanding of how much of the

performance enhancement can be attributed to the actual chemical coordination of the HA and MOF5 components, and how much to physical adsorption of the HA component onto the surface of the MOF5 component. From environment point of view, MOF-HA composites are attractive because of the combination of chelating functionalities of HA with the large surface area of MOF-5 can be explored for heavy metal, dye, and other pollutant removal from water, in a synergistic manner (Li, Wang, & Chen, 2020; Naseem, Khalid, & Rasheed, 2022). Humic acid is naturally abundant and biodegradable, and has already been widely used as a low-cost amendment for agriculture, making the use of this substance as a hybridizing agent an attractive option for developing materials for environmental remediation from renewable, non-synthetic feedstocks instead of using petrochemical-derived polymers. In practice, the use of both MOF-5 precursors and humic acid in low cost and universal access, it is possible that the successful hybridization will guide the design of low-cost, sustainable adsorbents and catalyst supports (Zhang, Sun, & Liu, 2021; Sun, Zhao, & Wu, 2022). Combined, these scientific, environmental and practical motivations make the present study a fundamental investigation of MOF-5/HA interaction chemistry, as well as a preliminary step toward application-oriented hybrid material design.

2. LITERATURE REVIEW

2.1 Metal–Organic Frameworks and MOF-5

MOFs are coordination polymers constructed from metal ions and/or metal-oxo clusters connected together with multidentate organic ligands to form extended, generally three-dimensional, crystalline structures. The framework has been one of the most studied MOFs since its discovery in 1999 (Li, Eddaoudi, O'Keeffe, & Yaghi, 1999) because of its exceptionally high surface area (as reported later, 2,900–3,800 m²/g, but in the original paper, it was estimated at more than 2,000 m²/g) as well as its relative simplicity of solvothermal synthesis (Rowsell & Yaghi, 2004) and its well-defined cubic

topology. Comprehensive reviews by Furukawa, Cordova, O'Keeffe, and Yaghi (2013) and by Zhou, Long, and Yaghi (2012) place MOF-5 in the context of design ideas for the isorecticular MOF family, and highlight the ongoing significance of MOF-5 for gas storage and separation. The wide variety of metal node and ligand chemistries that can be used to build MOFs demonstrates the versatility of the structure, with other examples such as HKUST-1 (Chui et al., 1999), UiO-66 (Cavka et al., 2008), MIL-101 (Ferey et al., 2005), ZIF-8 (Park et al., 2006), and NU-1000 (Farha et al., 2012) showing that MOFs can have different stability profiles and application niches, ranging from CO₂ capture to photocatalysis and biosensing (Kreno et al., 2012).

Although MOF-5 has an excellent porosity, it is chemically unstable in water: the presence of water causes the Zn–O–C coordination bond to be broken, resulting in the loss of crystallinity and the destruction of the pore network (Britt, Tranchemontagne, & Yaghi, 2008). The weak point has inspired extensive studies for post-synthetic modification, surface functionalization, and polymer, carbon material and biomolecule hybridizations to retain the porosity of MOF-5 while enhancing its moisture resistance (Zhang, Li, & Wu, 2018).

The composition and reactivity of humic acid.

Humic acid is one of three major fractions of humic substances (HS) (along with fulvic acid and humin) which originate from the long-term microbial and chemical transformation of plant and animal residues in soils, peat, lignite, and aquatic sediments (Stevenson, 1994). HA is not a single defined compound, but a supramolecular assembly of aromatic and aliphatic parts, stabilized through weak non-covalent interactions like hydrogen bonding, π - π stacking and hydrophobic association (Piccolo, 2002). It possesses high chelating ability for metal cations (Zn²⁺, Cu²⁺, Pb²⁺, Fe³⁺) due to its carboxyl, phenolic hydroxyl, carbonyl and quinone groups (Tipping, 2002), and its aromatic domains have π -stacking and van der Waals forces with the ability to bind hydrophobic organic contaminants. All of these properties have

been exploited in agriculture for a long time as a conditioner for soil and for the more recent use as a functional modifier for engineered materials (Chen, Xu, & Zhao, 2017; Senesi, Miano, & Brunetti, 2003).

2.3 Mechanisms and Strategies for MOF-5/Humic Acid Hybridization

Multiple possible interaction mechanisms exist to connect MOF-5 and HA: (i) coordination bonding between deprotonated carboxylates of HA and the open or accessible Zn²⁺ sites on the MOF-5 surface; (ii) hydrogen bonding between hydroxyl groups of HA and oxygen atoms of the MOF-5 framework; (iii) electrostatic attraction of deprotonated carboxylates of HA to locally positive Zn²⁺ sites on the MOF-5 surface (pH-dependent); and (iv) π - π stacking between the aromatic rings of HA and the benzene rings of the MOF-5 terephthalate linker. The interactions between the HA and the mineral are expected to take place mainly at the external surfaces and pore mouths, and not at the internal pore space in the mineral, so that a moderate HA loading may be expected to maintain the internal pore space of the mineral while providing additional chemically active adsorption sites (Wang, Li, & Zhou, 2019). Two synthetic approaches for MOF-organic hybridization have been reported: in-situ incorporation of the organic component during the crystallization of MOFs and post-synthetic hybridization, which involves contacting pre-formed crystals of MOFs with an organic solution under controlled conditions. In-situ methods may disrupt nucleation processes and are inefficient at producing amorphous or poorly crystalline MOFs in cases of high organic loading, while post-synthetic methods are based on surface adsorption and complexation, and generally produce more crystalline MOFs (Dahlan, Keat, Aziz, & Hung, 2023). Although there are few precedents for MOF-5/HA composites specifically, it is clear that natural macromolecules can be successfully introduced into MOF frameworks to enhance their functional versatility and aqueous stability (Zhao, Liu, & Sun, 2019).

The importance of the environment and the gaps that remain.

In the context of water treatment, HA modified MOFs are especially attractive due to the ability of HA's chelating groups to bind heavy metals, its aromatic domains to adsorb organic dyes and pharmaceuticals, and the high surface area and controllable porosity of the parent MOF (Naseem et al., 2022). However, the experimental information on MOF-5/humic acid composites was still limited at the time this work was initiated, most of the information was drawn from studies on other MOF-organic matter composites or from HA-MO interaction with metal oxides. Compounding this gap, HA is compositionally heterogeneous and source-dependent, making it difficult to repeat the results of studies (Fragouli, Roulia, & Vassiliadis, 2023; Vikram, Sagar, Gangwar, Husain, & Narayan Kewat, 2022). The present study seeks to bridge part of this gap in the synthesis, characterization and hybridisation of MOF-5 with HA under controlled conditions in the laboratory and the subsequent interpretation of the structural and spectroscopic evidence, both in terms of classical and in terms of recent literature.

3. MATERIALS AND METHODS

3.1 Materials and Reagents

The zinc source used was zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] while terephthalic acid (C₈H₆O₄) was used as the organic linker for the synthesis of MOF-5. The reaction was carried out in N,N-dimethylformamide (DMF) as a reaction medium. Methanol and ethanol were used for post-synthetic solvent exchange. Humic acid was extracted from the natural organic matter using sodium hydroxide (NaOH) and acid precipitation using hydrochloric acid (HCl).

3.2 The synthesis of MOF-5 using the Solvothermal Method

The syntheses were performed in a fume hood. Zinc nitrate hexahydrate (2.97 g) was dissolved in 100 mL of DMF, while the terephthalic acid (1.0 g) was dissolved in 50 mL of DMF with mild heating. Both solutions were mixed together in a

Teflon-lined autoclave and stirred to homogeneity. The sealed autoclave was heated at 100-120 °C for 24 h to provide solvothermal formation of MOF-5 crystals, which were then cooled slowly to room temperature. The product was filtered off under reduced pressure, washed with fresh DMF and then with ethanol to wash away unreacted precursors and the remaining solvent, and then dried under reduced pressure at 100 °C for 12 h. The dried powder was kept in a desiccator to avoid moisture absorption (McKinstry et al., 2016).

3.3 Solvent Exchange of MOF-5

Residual DMF was removed with the help of a lower boiling alcohol, either methanol (b.p. 64.7 °C) or ethanol (b.p. 78.4 °C) to remove the DMF and open up the pores. The crystals of MOF were soaked into the selected solvent for 1-2 h with intermittent shaking, and solvent was changed three to five times to ensure the removal of DMF. The activated crystals were then dried under vacuum at room temperature or up to 70 °C to avoid thermal degradation (Andres, Ortiz, & Ramirez, 2021).

Humic acid was extracted and characterized using the following procedure:

Ten to Twenty g of natural organic matter (NOM) were stirred in 100 mL of 0.1 M NaOH for 24 hours at room temperature, insoluble materials were filtered out, and the filtered solution was used. Humic acid was precipitated from filtrate by adding HCl dropwise until the pH of the filtrate reached 1-2 and was settled, filtered or centrifuged (3,000-4,000 rpm, 15-20 min), washed with distilled water several times to remove salt and dried at 50-60 °C (Fatima, Nazir, & Iqbal, 2021).

3.5 Formation of the MOF-5@HA Composite.

The activated but dried MOF-5 crystals were seeded in methanol or ethanol, and the humic acid was introduced at a ratio of ~ 10-20% (w/w) to MOF-5. The mixture was stirred at room temperature for several hours to allow HA to adsorb with the MOF-5 surfaces and – potentially – to enter the pore network to some extent. Excess unbound HA and residual solvent were removed by a final solvent exchange process, prior to drying under vacuum (Dahlan et al., 2023).

3.6 Characterization Techniques

To determine the crystallinity and the phase purity, powder X-ray diffraction (PXRD) pattern was recorded using Cu K α radiation (λ = 1.5406 Å) in 2 θ in the range of 5–50°, with a step size of 0.02° and scan rate of 1°/min. Fourier-transform infrared (FTIR) spectra were measured in the mid-IR region (4000–400 cm^{–1}) with 32 scans averaged per sample, and 4 cm^{–1} resolution, in order to identify functional groups and coordination bonding, using either KBr pellets or attenuated total reflectance (ATR) methodology. The two techniques were used to the MOF-5, humic acid, and MOF-5@HA composite so that it could be directly compared how the structure and spectroscopy of MOF-5 changed with hybridization.

4. RESULTS

The obtained product from the solvothermal reaction was a white crystalline powder that was identified as MOF-5 (Table 1) with the expected morphology. After drying the product was visually and structurally stable, meaning that the coordination structure was not lost during the drying process.

Table 1. Physical Outcome of MOF-5 Synthesis

Parameter	Observation
Product colour	White crystalline powder
Physical state	Fine solid crystals
Stability after drying	Stable; no visible degradation

The as-synthesized MOF-5 (Table 2) exhibited sharp well-resolved reflections that matched those reported previously by Li et al. (1999) and later refined by Rowsell and Yaghi (2005) with the reflections indexed to the (200), (220), (400), (420)

and (422) planes of the cubic MOF-5 lattice. The high crystallinity and lack of unassigned peaks suggest a highly crystalline and phase-pure product.

Table 2. PXRD Reflections of As-Synthesized MOF-5

2 θ (°)	Peak Character	Crystal Plane
6.8	Sharp	(200)
9.6	Sharp	(220)
13.7	Sharp	(400)
15.4	Present	(420)
18.8	Present	(422)

FTIR analysis of MOF-5 confirmed the presence of bands corresponding to a successful coordination between Zn and carboxylate, such as C-H stretching of the aromatic linker at 3000–3100 cm^{-1} , C=O stretching of carboxylate at 1650–1700 cm^{-1} , symmetric/asymmetric

COO[−] stretching in the range of 1400–1550 cm^{-1} , and Zn–O framework vibrations in the range of 500–700 cm^{-1} (Table 3). These assignments are consistent with those reported previously for MOF-5 vibrational spectroscopy (Rowsell & Yaghi, 2004; McKinstry et al., 2016).

Table 3. FTIR Band Assignments for MOF-5

Wavenumber (cm^{-1})	Functional Group / Assignment
3000–3100	C–H stretching (aromatic linker)
1650–1700	C=O stretching (coordinated carboxylate)
1400–1550	COO [−] symmetric/asymmetric stretching
500–700	Zn–O vibration

The as-synthesized, DMF-laden material was found to be somewhat less accessible to pores than the solvent exchanged material (methanol/ethanol), but essentially no change in the overall PXRD

pattern of the material was observed upon activation (Table 4), suggesting that the overall crystallinity of the framework was retained.

Table 4. Effect of Solvent Exchange on MOF-5 Pore Activation

Parameter	Before Exchange (DMF)	After Exchange (MeOH/EtOH)
Solvent occupying pores	DMF	Methanol/Ethanol
Volatility	Low	High
Porosity	Partially blocked	Increased

Framework activation	Incomplete	Improved
The humic acid extracted from natural organic material was found in the form of dark brown amorphous solid. It exhibited in its FTIR spectrum (Table 5) the functional-group signature commonly found in humic substances ~ broad O-		H stretching, carboxyl C=O stretching, aromatic C=C stretching, and phenolic C-O stretching ~ and in its PXRD pattern (Table 6) only broad and diffuse scattering, indicating its non-crystalline, amorphous nature (Stevenson, 1994).

Table 5. FTIR Band Assignments for Humic Acid

Wavenumber (cm ⁻¹)	Functional Group
3400	O-H stretching
1700	C=O stretching (carboxyl)
1600	Aromatic C=C stretching
1200-1300	Phenolic C-O stretching

Table 6. PXRD Characteristics of Humic Acid

Property	Observation
Peak character	Broad, diffuse
Crystallinity	Low
Overall structure	Amorphous

Successful HA incorporation was indicated by a slight change in colour from white to light brown after the composite was formed. As seen in Table 7, the MOF-5 @ HA composite also showed the characteristic reflections of MOF-5 with a slight decrease in peak intensity and a slight increase in background amorphous scattering that was also seen in the PXRD of the bulk composite, confirming that the MOF-5 lattice was not

destroyed during the process of hybridization. FTIR spectra of the composite (Table 8) revealed the presence of an intensified O-H stretching band, a shifted C=O band, broadening of COO- bands and a slight shift of the Zn-O vibration region, all indicating the interactions of the HA functional groups with the MOF-5 framework, which include hydrogen-bonding and coordination interactions.

Table 7. PXRD Results of the MOF-5@HA Composite

Feature	Observation	Interpretation
MOF-5 peaks	Retained	Framework preserved
Peak intensity	Slightly reduced	HA incorporation
Background	Slightly amorphous	Presence of HA

Table 8. FTIR Results of the MOF-5@HA Composite

Wavenumber (cm ⁻¹)	Change Observed	Interpretation
3400	Increased intensity	HA hydroxyl groups present
1700	Shifted	Zn-HA carboxylate interaction
1400-1550	Broadened	Complexation
500-700	Slight shift	Zn-O environment affected

The MOF-5@HA composite can be thought of as a hybrid material, combining the crystalline high surface area properties of MOF-5 with the

amorphous functional chemistry of HA as summarized in Table 9.

Table 9. Comparative Summary of MOF-5, Humic Acid, and the MOF-5@HA Composite

Property	MOF-5	Humic Acid	MOF-5@HA Composite
Appearance	White crystalline powder	Dark brown amorphous solid	Light brown solid
Crystallinity (PXRD)	High, sharp reflections	Low; broad, diffuse peaks	Retained MOF-5 peaks, slightly reduced intensity
Dominant functional groups (FTIR)	COO ⁻ , Zn-O	O-H, C=O, aromatic C=C, phenolic C-O	Combined MOF-5 and HA bands with shifts
Structural character	Rigid, ordered framework	Flexible, supramolecular	Ordered framework with HA surface functionality

The diffraction evidence combined with the spectroscopic data confirms that (a) MOF-5 was successfully synthesized with the same intended crystal structure and coordination of the Zn with carboxylate groups, (b) the pore network was opened up during the solvent exchange without losing the crystal structure, (c) the humic acid was extracted without altering its crystal structure, but with its functionality intact, and (d) hybrid MOF-5 maintained its framework while gaining the additional surface chemistry provided by the humic acid.

5. DISCUSSION

Both the PXRD and FTIR results obtained here support the description of MOF-5 by Li et al.

(1999) and subsequent structural refinements by Rowsell and Yaghi (2004, 2005), namely that the sharp reflections at low 2θ values and the characteristic Zn-O and carboxylate FTIR bands both reflect a well-ordered, phase-pure cubic framework. The ability of DMF to act as a solvent and as a structure-directing agent and the increase in pore accessibility after exchange with methanol/ethanol are consistent with the results obtained by Andres and co-authors on activation of MOF pore networks using low-boiling alcohols (2021).

It is well-documented that MOF-5 is moisture sensitive, which is why this study was motivated by the idea to hybridize MOF-5. A research group published its findings on ScienceDirect's open-

access materials collection, finding that after MOF-5 was left in ambient moisture for just one week, the main reflections seen in its PXRD disappeared into the background noise, thus verifying that the unprotected framework collapses rapidly (Lal, Singh, Singhal, Kumar, & Gahlot, 2024). Further reviews of the published research for ways to mitigate this drawback of MOF include hydrophobic surface coatings, substitution of ligands with more hydrophobic linkers, and the formation of composites with polymers or carbon materials; in this case, the surface coating is amorphous carbon, and the MOF-5 framework shows greater stability in water than without it. (Lal et al., 2024) Another large-scale machine-learning study of water stability of MOFs, based on over 900 MOFs with experimentally reported water stability, similarly identifies MOF-5 type frameworks with weak metal-carboxylate bonds and no stabilizing functionalization as water unstable, further supporting the need for hybridizations like the one studied here (Terrones, Wilmer, & Snurr, 2024).

In addition, recent published literature related to the interaction between MOF and humic acid is also used to substantiate the choice of humic acid as a hybridizing agent. A recent 2024 study that directly examined the adsorption of humic acid onto a specific array of MOFs (UiO-66(Zr), MIL-100(Fe), ZIF-8 and an aluminium-fumarate framework) confirmed that HA is easily associated with the surface of MOFs via carboxyl- and hydroxyl-mediated interaction, and that this interaction is dependent on the solution pH and contact time (Mala, 2024), in line with the discussed pH-dependent electrostatic and coordination adsorption mechanisms for the present MOF-5@HA system. More directly relevant, a study from 2025 showed that the HA functionalization significantly improved the adsorption capacity of the composite compared to the unmodified MOF, with the authors claiming that this improvement was due to the increased surface functionality, density of active sites and specific surface energy of the composite after HA was added (Ahmadi, Rezaei, & Karimi, 2025). This result provides direct support to the

interpretation proposed here: the small decrease in MOF-5 PXRD intensity and the shifts in FTIR following HA loading were indicative of a productive, adsorption enhancing surface interaction rather than degradation of the MOF framework.

This study's results are placed in a larger design context in 2024 and 2025, in broader reviews of MOF composite chemistry. Pure MOFs are often too fragile, especially in aqueous and acidic/alkaline solutions, to be used as standalone materials for the removal of heavy-metal ions and are now regarded as an established approach to enhance the structural stability and adsorption efficiency in both acidic and alkaline conditions (Chen, Li, & Zhao, 2025). This review also classifies MOF hybrids based on target pollutants, with composites of MOFs with metal oxides being preferred for small polar molecules (such as CO₂, H₂O), and the hybrid composites with carbon or biomass for the adsorption of large molecule pollutants (such as organic dyes or antibiotics) via both physical and chemical adsorption (Chen et al., 2025). The MOF-5@HA composite studied in the present work belongs to the second category as HA represents a carbon-rich naturally derived macromolecule with a chemistry that is ideal for binding large and polar organic and metal-ion pollutants.

This is corroborated by a parallel line of 2024–2025 research on biomass- and organic-matter-derived MOF composites. An overview of biomass–MOF composites was discussed, which mostly contained hydroxyl and other functional groups on their surface that could anchor the growth of MOF or attach MOF by in-situ growth or layer-by-layer assembly, resulting in composites with good recyclability and long-term adsorption stability (Zhou, Xu, & Wei, 2024). Likewise, the review on MOF-based composites for organic effluent remediation in 2024 has focused on the integration of MOFs with functional or matrix materials, such as MOF-based hydrogels, aerogels, and their derivatives, which are now mainstream techniques to enhance flexibility, water stability, and maintain the high density of active sites and shape-selective adsorption properties of pristine

MOFs (Zhang, Liu, & Xu, 2024). The parallels confirm that the HA hybridization studied is not an ad hoc or a novel idea, but rather follows a design principle which has been attempted and proven to work successfully in the past.

A little caution should be used in the interpretation of the present spectroscopic and diffraction data. As mentioned in previous review on MOF-organic matter interactions (Wang et al., 2019), the separation of the contributions of chemically coordinated HA, hydrogen-bonded to framework oxygens, and physically adsorbed on the external crystal surface requires other techniques such as solid-state nuclear magnetic resonance or synchrotron-based X-ray techniques. Similarly, as this study did not employ nitrogen adsorption/desorption (BET) analysis and thermogravimetric analysis or electron microscopy, further direct quantification of surface-area change, thermal stability, and particle-level morphology after hybridization is also desired, in line with the recommendations of recent MOF-stability literature which provides the requirement of multi-technique validation of composite water stability under realistic, prolonged exposure conditions (Terrones et al., 2024).

MOF-5 should also be viewed in the context of other framework design that is stable in water since 2024. A number of research groups have gone to great lengths to design MOF architectures with hierarchical porosity that are inherently highly water-stable, and have reported systems that remain water-stable after exposure to boiling water, a test far more severe than exposure to ambient humidity under which unmodified MOF-5 is known to be less water-stable and can degrade in days (Zhang, Liu, & Zhang, 2026). These are next generation frameworks which obtain their stability largely through internal modification, choosing metal nodes and ligands with intrinsic stronger coordination bonds, instead of external hybridization. The emergence of these hybrid materials highlights the fact that there are at least two alternative strategies to overcome the above limitation, namely external functional coating and internal framework redesign, and that these will be

favoured for the specific application depending on the importance of cost, ease of synthesis or stability in extreme environments. Applications that require moderate humidity resistance and increased pollutant-binding functionality, such as point-of-use water treatment or soil remediation, could benefit from the low cost and renewability of humic acid, and hybridization of an already well-understood and easily synthesized framework, like MOF-5, could be an attractive and pragmatic solution for these applications.

Despite these constraints, the agreement of the present results with the overall results of the 2023–2026 literature on stability of MOFs and MOF-organic hybridization is significant. The HA functionalization of MOF surfaces has been shown to retain MOF-5's major PXRD reflections, alongside the presence of new coordination and hydrogen-bonding interactions, which is consistent with a broad range of literature demonstrating the ability of natural organic macromolecules to functionalize MOF surfaces without destroying the parent crystalline lattice, and to improve adsorption capacity for metal ions and organic pollutants (Ahmadi et al., 2025; Mala, 2024; Zhou et al., 2024). This helped to verify the main hypothesis of the study, namely, that MOF-5 and humic acid can be mixed to create a hybrid material that will have a broader range of functional chemistry and, consequently, of potential applications for environmental remediation, catalysis, and adsorption technologies.

6. CONCLUSION & RECOMMENDATIONS

A solvothermal synthesis of MOF-5 was performed with success and it was confirmed by PXRD and FTIR to be a highly crystalline, phase-pure cubic framework having the expected Zn-carboxylate coordination chemistry. The pore network was activated by solvent exchange with methanol/ethanol without adversely affecting the crystallinity. Humic acid was also extracted from natural organic matter and found to be an amorphous solid with carboxyl, hydroxyl, and phenolic functional groups. The MOF-5@HA composites obtained by hybridization with humic

acid had a MOF-5 diffraction signature that was significantly retained and FTIR evidence suggested new coordination and hydrogen-bonding interactions between functional groups of the HA and the MOF-5 zinc nodes. The results obtained in this work, combined with more recent works on MOF water stability and MOF-organic hybridization, reinforce the idea that humic acid can be used to improve the functional chemistry of MOF-5, without destroying the MOF structure, and can be considered a viable low-cost and renewable material for this purpose.

The results of this study suggest some avenues for future study. First, the changes in surface area, thermal stability and particle morphology after hybridization should be quantified by nitrogen adsorption/desorption (BET), thermogravimetric analysis, and scanning or transmission electron microscopy techniques. Second, the specific pollutants – heavy metals, dyes, and pharmaceuticals – need to be tested for in terms of their practical adsorption performance as a function of pH, temperature, contact time, and initial pollutant concentrations. Third, the resistance of HA to hydrolytic degradation should be compared to that of MOF-5 by performing systematic stability tests under aqueous, acidic and basic conditions to see if there is a measurable benefit in MOF-5's hydrolytic stability with HA relative to without HA. Fourth, scale-up synthesis and regeneration studies would be carried out to determine the material's industrial feasibility. Lastly, comparative studies with other HA-functionalized MOFs, such as the aluminium-fumarate and zirconium-based MOFs recently reported in the literature, would be useful to determine if MOF-5 has specific advantages ~ or specific disadvantages ~ in being a platform for humic-acid hybridization as compared to more water stable MOFs.

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