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Synthesis and Characterization of Advanced Metal-Organic Frameworks (MOFs)

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ABSTRACT

Objective: *This study aims to summarize, compare, and discuss the structure, synthesis techniques, and novel applications of Metal-Organic Frameworks (MOFs) as sensing materials. Specifically, it focuses on their use in sensors for detecting pharmaceuticals, pesticides, heavy metals, food additives, and other contaminants. Additionally, the study explores the antibacterial applications of MOFs due to their unique physical properties.* ***Methods:*** *The solvothermal process for synthesizing MOF-199 was investigated by varying the ethanol-to-water solvent ratio (1:1 to 1:2), solvothermal temperatures (85°C to 100°C), and synthesis times (24 to 48 hours). Characterization of the synthesized materials was conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area analysis to assess the structure, surface area, and pore characteristics.* ***Results:*** *The results indicate that MOF-199 synthesized under the optimal conditions (100°C for 48 hours with a 1:1 ethanol-to-water ratio) exhibited a specific volume of 0.693 cm³/g, a pore volume of 11.8 Å, a BET surface area of 5518 m²/g, and crystallinity of 103%. These properties are crucial for enhancing the performance of MOFs in electrochemical sensing applications.* ***Novelty:*** *This paper provides a detailed overview of the antibacterial applications of MOFs and their nanocomposite forms, offering new insights into their potential for sensing a wide range of chemicals and their enhanced selectivity for electrochemical analysis. The study introduces the solvothermal synthesis of MOF-199 and presents optimized parameters for its production, contributing to the development of more sensitive, cost-effective, and versatile electrochemical sensors for detecting contaminants.*

INTRODUCTION

Metal-organic frameworks, also known as MOFs, are porous, crystalline organic-inorganic hybrids composed of a regular pattern of positively charged metal ions surrounded by organic "linker" molecules. Metal ions form nodes that connect the linker arms, resulting in a repeating, cage-like structure. MOFs have a very large internal surface area due to their hollow structure.

Researchers developed MOFs with a surface area of over 7,800 square meters per gram. To put this in context, a teaspoon of this stuff (about a gram of hard material) would cover an entire football field [1].

MOFs show outstanding structural diversity when compared to other porous materials, including homogenous pore topologies, atomic-level structural homogeneity, changeable porosity, a wide range of lattice topology, geometry, dimensions, and chemical activity. This allows researchers to efficiently manipulate the framework's topology, porosity, and functionality.

The particular design and tunability of MOFs—crystalline porous materials comprising of nonorganic and organic parts in a rigid periodic lattice structure—are not readily attainable in standard porous materials, such as completely inanimate zeolites [2].

A drawing of a metal-organic framework (MOF). Metal ions and organic ligands combine to form MOFs, which are very porous and have a large surface area. Depending on the metal ions and organic molecules utilized, different MOF structures can be created. Scientists may build MOFs from various metal atoms and organic ligands to selectively adsorb certain gasses into carefully tailored pockets inside the structure. Thus, MOFs have a high potential for effective integration and investigation in a wide range of sensing applications. MOFs may be constructed arbitrarily, similar to Lego bricks, and outperform every previously known class of materials in terms of flexibility. Outperform any previously known material class in terms of flexibility [3].

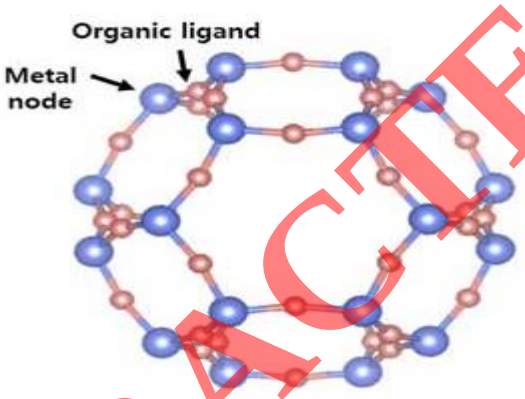

Figure 1. Origanic ligand and metal node.

The combined effects of shapes and contents determine the physicochemical characteristics of materials, and MOFs are intriguing examples of how the distinctive structure of hollow-structured materials may bring a number of benefits. Some examples include shorter mass and charge transmission lengths, a microreactor environment, a better surface-to-volume ratio, low density, and increased loading capabilities. As a result, materials scientists and chemists have long been interested in developing hollow structures for industrial use [4]. Scientists have long struggled to develop porous or hollow-structured materials with predictable, especially complicated, shapes and compositions. MOFs are crystalline hybrid materials made from organic and inorganic compounds by molecular self-assembly [4].

Objectives of the study is study and know the mean of MOFS, know the importance of MOFS, study synthesis and characteristics of MOFS, study application of MOFS

Importance of MOFS

Over the last few years, much study has been conducted on various synthesis methods and the characterization of highly porous materials with massive interior surface areas. These materials' structural structure holds promise for a range of applications, including chemical separation, chemical sensing, catalysis, gas storage, light-harvesting ion exchange, and drug delivery. One of the most prominent research

reasons for MOFs is their exceptional porosity, which defines them as unique porous solids with features that outperform those of common and standard porous materials. MOFs are described as very porous materials that suit advanced needs in modern technologies because of their regular, rigid/flexible designability and diversity in structure and characteristics [5].

Compared to standard inorganic permeable substances and activated carbons, there are numerous methods for coordinating varied inorganic salts to support metal nodes and organic molecules, resulting in very porous structures. This is seen in the large number of research published on this type of chemical during the previous two decades. In addition to the adsorption capabilities and the properties of both inorganic and organic components, MOFs have some distinct features that may be effectively used in industries such as lighting and magnetism [6].

Properties and Synthesis of MOFS

Improved MOF activation approaches have recently been reported that do not collapse the framework or block the channels. MOFs have a crystal structure that includes metal ion centers and organic coordination ligands. There are about 10,000 papers in the literature that contain synthesized and verified MOF structures.

MOFs exhibit unique properties such as remarkably large surface area (up to 6000 m2/g), reactive microstructure, uniform but reactive micropores (0.5 to 2), extremely large plasma volume (about 90% of free volume), completely bare and exposed organic sites, and abundant compositions. MOFs have also been found as excellent catalytic frameworks created particularly for mobile precursors due to their Johnson structure and overall surface area. Furthermore, these materials may be designed to be extremely technical about certain chemicals [7].

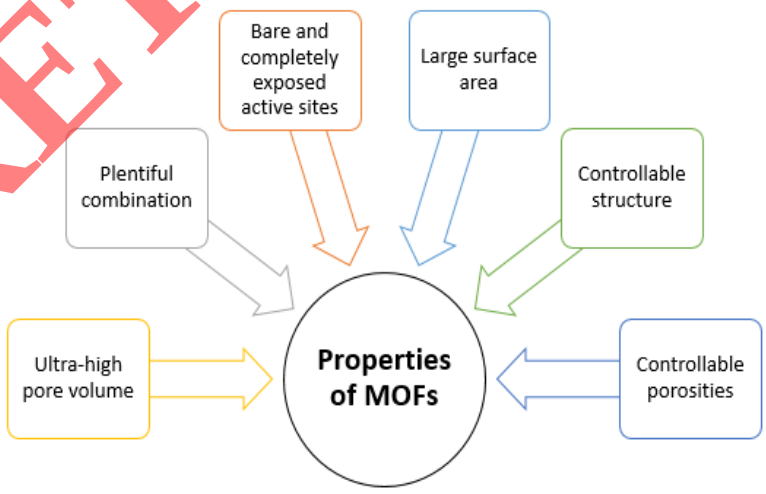

Figure 2. Shows the properties of MOFs.

The MOFs criteria are optional for infrastructure, morphological features, and crystalline nature. As a result, it is critical to select a synthesis technique that maximizes

the physical and chemical advantages of the acquired components. Health and environmental coverage are particularly important in large-scale acquisitions. Access to the MOFs frameworks and attributes is possible through a variety of channels. These techniques include slow, reflux, electrochemical, hydrothermal, sonochemical, deposition, and clear film [8].

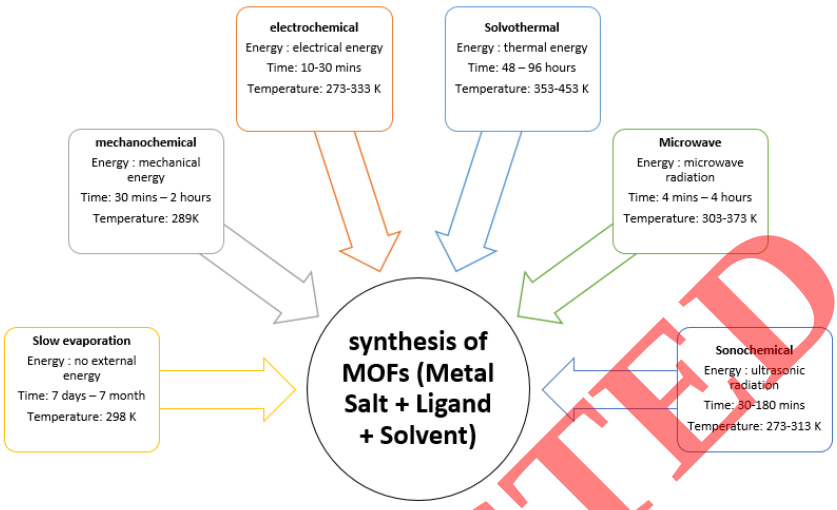

Figure 3. Shows the synthesis of MOFs.

Figure 3 highlights the many techniques and synthesis conditions typically utilized for MOF formation as described in the literature. The standard approach is normally carried out in the liquid phase, combining the organic ligand, metal SBU, and solvent for a set amount of time. The reaction product is filtered and evaporated to get pure MOF. The most common approach for producing MOFs is hydrothermal/solvent-thermal synthesis using standard electrical heating at a regulated temperature. Solvent-thermal reactions often include the use of highly soluble organic solvents such as dimethylformamide, diethylformamide, acetonitrile, acetone, ethanol, or methanol. Solvent mixes can be used to circumvent issues caused by the varying solubility of the initial reagents. Solvent-thermal synthesis may be done at various temperatures.

Glass vials can be utilized at low temperatures, but beyond 130 °C, the synthesis is typically carried out in a small-volume Teflon-lined autoclave. The hydrothermal synthesis of MOFs is a more ecologically friendly technique that substitutes organic solvents with water. Because of the low cost and environmental friendliness of water, there have been several attempts to synthesize MOFs. Carboxylate-based MOFs, for example, have been synthesized using organic salts (rather than their homogeneous organic ligands) as an anionic linker source, Thus, the dissolution and deprotonating processes essential for MOF production are considerably favored in aqueous solution.

However, these syntheses typically require long reaction times to achieve perfect crystallization, and alternative synthesis methods such as microwave-assisted synthesis, electrochemical synthesis, sonochemical synthesis, mechanical synthesis, and spray-drying synthesis have been investigated to accelerate crystallization and obtain more

uniform crystals with smaller sizes. These approaches aim to synthesize MOFs in less time and with better quality. The choice of solvent is critical in liquid phase processes and is determined by a variety of factors, including redox potential, reactivity, solubility, and stability, among others. The type of solvent also influences the reaction's thermodynamic and activation energies. In addition to the liquid phase, some research has concentrated on solid-state MOF synthesis [9].

RESEARCH METHOD

Synthesis Method

Mechanochemical Synthesis

Is a technique for producing mechanically strong metal-organic frameworks (MOFs) without the use of solvents, resulting in physical and chemical changes in the reactants.

Application: metallurgy and metal processing, but it is currently gaining appeal in other chemical domains such as inorganic chemistry and medicines.

Process: The reactant particles are ground or milled, allowing chemical reactions to take place with few or no solvents, Either mechanical grinding or automated ball mills take the role of conventional thermal melting techniques.

Advantages: This solvent-free method lowers waste and enables the use of less soluble precursors such as metal oxides and hydroxides. It is eco-friendly and can lower production costs.

Challenges: The biggest disadvantage is the low production rate, which makes scaling difficult.

Mechanochemical Synthesis Methods

a. Solvent-free grinding (SFG) uses no solvents at all.
b. Liquid-assisted- grinding (LAG) is a faster and more flexible method that increases reagent mobility by using small amounts of liquid.
c. Ion liquid assisted grinder (ILAG): Uses a small amount of fluid and salts to improve structure, but may hinder X-ray diffraction study of single crystals.

Benefits of Ion-Liquid-Assisted Grinding: Introducing modest quantities of solvent increases the mechanochemical processes and can alter the structural consequences, showing effectiveness in the selected synthesis of multilayer organometallic compounds. [10].

Solvo Thermal Method

This method is most commonly employed in the fabrication of metal-organic frameworks (MOFs) and zeolites. It allows products to self-assemble from soluble starting components.

Operating conditions

The process works in a pressure vessel at temperatures ranging from 80 to 260 °C under self-pressurization, with the rate of cooling after the reaction influencing the end product.

Reaction timeframes

Both hydrothermal and diffusion processes sometimes need extensive reaction times, ranging from several days to many weeks [11].

Diffusion method (slow evaporate)

This method involves progressively bringing various species into contact to encourage crystal formation.

Techniques: **Liquid solvent diffusion**

Entails forming 2 layers of varying densities, 1 containing a solvents that produces precipitation and the other encapsulating the product. A liquid layer separates them, and crystals form at the contact when the precipitated solvent diffuses into the opposite layer.

Physical barriers

This method employs two vials of varying diameters to aid in the progressive diffusion of the reactants.

Gels

Can operate as a medium, slowing diffusion and preventing widespread precipitation during crystallization.

Results

This process of diffusion is same to provide single crystals appropriate for X-ray diffraction (XRD), giving it an edge over numerous or non-crystalline products, particularly those that dissolve poorly [12].

Microwave method

This approach employs microwave-assisted techniques to manufacture metal oxides with tiny particles, resulting in the formation of metal nanocrystals.

Process

Microwaves can be used to heat the solution for an hour or longer, however, this approach has not yet been widely employed to make crystalline metal-organic frameworks (MOFs).

Advantages

It enables high-speed synthesis while maintaining exact control over the form and size of the resultant particles.

Disadvantages

One significant downside is the tendency to generate amorphous materials. However, it can help with consistent seeding conditions, comparable to single-shot X-ray analysis.

Solvent Evaporation Conditions

Well-saturated solutions and a temperature-dependent increase in solubility are necessary for successful crystal development, which results in crystal formation as the chilling process proceeds [11].

Electrochemical method

This process produces metal-organic framework (MOF) powders on an industrial scale and has various benefits over melt thermal synthesis.

Advantages

a. Prevents the use of metal salt anions, such as nitrates.
b. Facilitates faster synthesis by operating at lower reaction temperatures.
c. Limits mass crystallization by producing metal ions near the support surface, which reduces the creation of undesired crystals during film formation.

Thermal considerations

Lower temperatures assist in preventing thermal cracking after cooling, which is a typical issue in melt thermal techniques because of mismatches in thermal expansion coefficients between support structures and MOF.

Control of parameters

In comparison to melt thermal approaches, the electrochemical method provides for more precise management of synthesis parameters via voltage modifications and specialized signal applications [13].

Sonochemistry Method

This method studies the chemical reactions that occur when strong ultrasound waves are supplied to a reaction mixture at rates that vary from 20 kHz to 10 MHz.

Mechanism

Micro-jets and cavitation produced by ultrasonic waves can disperse tiny particle aggregates and erode, activate, and clean solid surfaces. Chemical reactions that generate radicals and excited molecules can occur in cavities during extreme circumstances, at interfaces under intermediate conditions, or in a bulk medium with high shear stresses.

Advantages

Sonochemistry is widely employed in the creation of organic and nanomaterials because it improves reactant solubility. Its objectives include quick, energy-efficient, ecologically friendly, and room-temperature functioning of MOF.

Comparison of metal-organic frameworks (MOFs) fabrication: Different metal-organic frameworks (MOFs) fabrication methods produce products with different porosities and surface areas [13].

Mechanochemical versus thermal methods

Studies show that mechanochemical methods, such as those used to synthesize MOF-74, produce similar porosity to thermal methods while avoiding toxic solvents and reducing waste, which is critical for sustainability. Another study showed that the mechanical synthesis of IRMOF-3 maintained high porosity and crystallinity, suggesting that the organic binder significantly influences the properties of the MOF.

Characterization of MOFs

A range of chemical and physical approaches are required to characterize MOFs to evaluate their properties, such as texture, structure, homogeneity, electrical and optical capabilities, and water stability - all of which are important for water treatment via adsorption.

Techniques Used

The key characterization approaches are**:**

a. Surface morphology and form changes based on mineral ratios are examined using transmission electron microscopy called (TEM) and scanning electron microscopy called (SEM).
b. X-ray photoelectron spectroscopy called (XPS) validates effective synthesis and investigates surface chemistry.
c. FTIR detects functional groups by detecting absorption bands at certain wavelengths related to O-C-O, C=C, and C=O vibrations.
d. XRD is used to measure the crystal structure of MOFs.

Importance of structure: The shape and structure of produced MOFs impact their performance, and varied forms result from factors such as doped metal molar ratios [12].

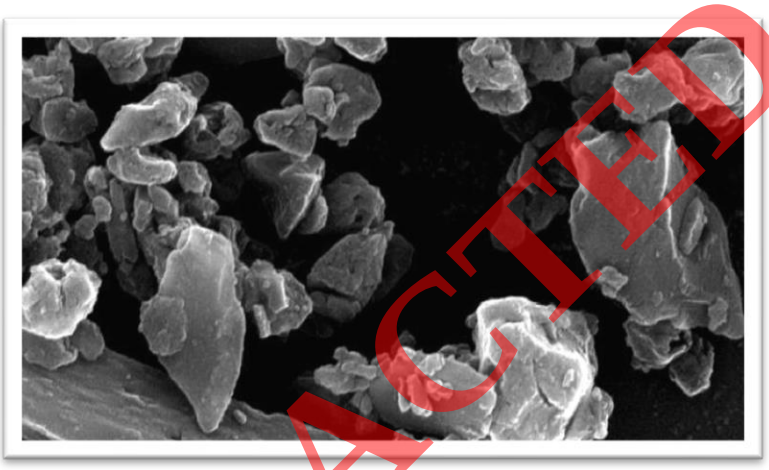

Figure 4. Scanning electron microscopy photo of the synthesized MOFs of iron-nickel.

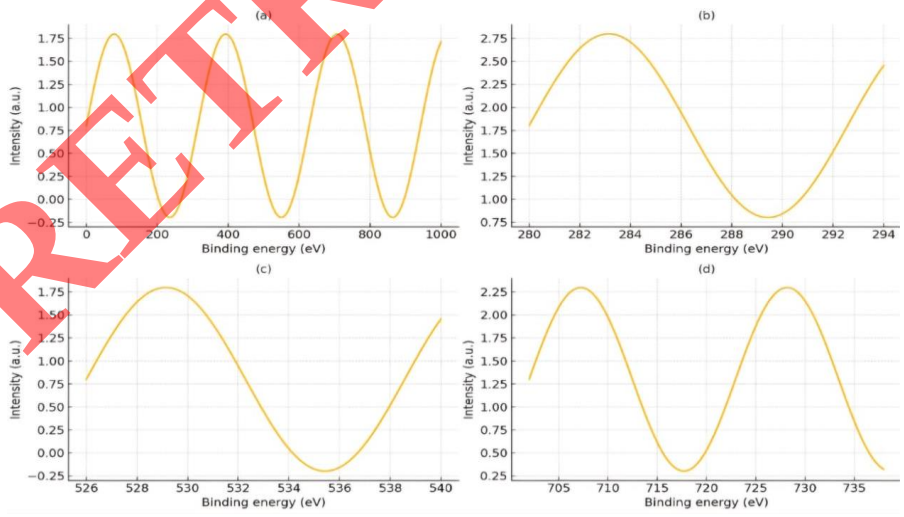

Figure 5. Fe-MOFs XPS spectra.

MOFs Activation & purification

MOF synthesis has made significant strides and improvements over the years, with other important areas receiving less attention. Two important aspects that require serious thought are MOF activation and purification. These stages are crucial to the application and manufacturing processes. A technical comparison of many contemporary

purification and activation approaches is attempted in this section of the review paper. In these methods, which are the latter stages of MOF synthesis, trapped solvents and/or organic binders that have not yet interacted with the material are frequently ejected, producing frameworks with a comparatively large surface area and persistent porosity. Insufficient purification and activation, frequently connected to framework collapse, are linked to the low observed pore volume and surface area, Although theoretical numbers are not required for experimental surface area, they do offer information about the material's potential for optimization. Additionally, it's crucial to choose or develop activation methods that prevent the framework's structural collapse, which might lead to a partial or complete loss of porosity This study's methodologies (Figure 6) include solvents exchange activation, freeze drying activation, supercritical carbon dioxide (ScCO2) activation, and conventional or calcining activation. And chemical activation (acid treatments) [14].

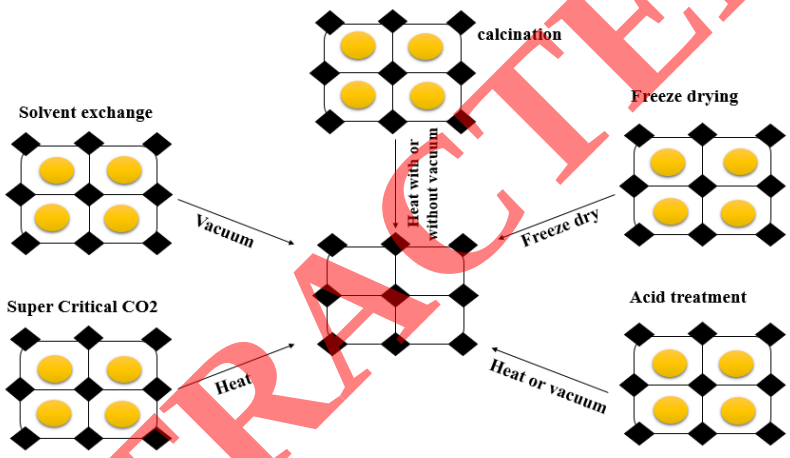

Figure 6. Activation and refinement methods of MOFs.

Calcination

The technique of calcination involves applying heat and vacuum to the pores of the structures to eliminate undesirable particles and trapped solvent molecules. The methods used to activate zeolites and carbon are comparable to those used to activate MOFs. It has effectively turned on the MOFs UiO-66 [$Zr_6(O)_4(OH)(bdc)_{12}$] and Cr-MIL-101 [$Cr_3F(H_2O)_2(bdc)_3$] (bdc = benzene dicarboxylate). The corresponding surface areas of UiO-66 and Cr-MIL-101 are 1070 and 4100 m^2/g. Because MIL-101 and UiO-66 have exceptional chemical and thermal stability, they may be activated using conventional methods. Nevertheless, while achieving complete porosity for these frameworks is crucial, the activation approach's use is limited by the complete loss of crystallinity and porosity during the activation process. Most MOFs lose porosity and crystallinity as a solvent moves from the liquid state to the gaseous state barrier in their pores, Pore pressure, in addition to surface tension, is incompatible with the coordination bonding energies in most MOFs. To make the most of the vast surface area of most MOFs, several activation techniques are required [15].

Activation by solvent exchange

This method involves a gentler activation under vacuum when a high-boiling-point solvent, such as DMF, is converted to a lower-boiling-point solvent, such as trichloromethane. Liquids with a low boiling point have less intermolecular interactions, therefore surface tension and capillary forces decrease during activation. Yaghi and colleagues were the first to activate MOFs using this process when they synthesized MOF-5 -IRMOF-1, $Zn_4O(BDC)_3$, in DMF-chlorobenzene. Change $CHCl_3$ to DMF-chlorobenzene to keep the structure intact, then activate it. The solvent exchange resulted in a microporous framework with a Langmuir surface area of about 2900 (m^2/g). Hupps and coworkers conducted more research on IRMOFs utilizing solvent exchange and conventional activation. While IRMOF-16 showed negligible nitrogen adsorption, activated IRMOF-3 had an outside area of 10 (m^2/g). Even though greater surface areas were predicted for IRMOF-3 and IRMOF-16 based on computational projections, the surface areas of IRMOF-3 and IRMOF-16 increased to 1800 (m^2/g) and 470 (m^2/g), respectively, when DMF was substituted with $CHCl_3$ or THF. Thus, while solvent exchange activation enhances porosity, it can also generate materials that are less porosity-rich than computations and single-crystal structure predictions would imply [15].

Freeze-drying activation

Several research teams have employed this approach to activate MOFs of various capacities. In this procedure, a new solvent replaces the guest after many freeze-thaw cycles, and colleagues used this technique to activate two equilateral copper paddle-wheel-based frameworks $Cu_2(L)(H_2O)_2$ (L = methane-tetra)(p-benzoic acid). After replacing the guest solvent molecules with benzene, the sample was stored in benzene. The substance was frozen at 0 degrees Celsius and then heated three times to room temperature. Following freeze-thaw cycles, the samples were vacuumed at pressures and temperatures lower than the solvent's triple point. Finally, by avoiding the liquid phase, benzene sublimation overcame capillary forces and surface tension. Compared to solvent exchange activation, freeze-drying of equilateral MOFs $Cu_2(L)(H_2O)_2$ yielded much higher SBET values. It was also found that the XRD pattern of the guest solvent sample differed from that of the freeze-dried benzene samples. Benzene was sublimated by heating the mixture under low pressure [16].

Activation of MOFs using supercritical carbon dioxide (ScCO2)

The use of ScCO2 refer to (supercritical carbon dioxide) to Activated MOFs might potentially be viewed as an extension of solvent exchange, wherein ScCO2 takes the place of an essential solvent, such as THF or CHCl3, for DMF. Activation using ScCO2 is a less harmful approach than solvent exchange activation and conventional activation, both of which can result in framework collapse. This is subtly done by using ScCO2 for MOF activation, which bypasses the liquid-to-gas phase transition of the guest solvent molecules and passes straight through a supercritical phase, thereby avoiding the drawbacks of surface tension and capillary forces. They are 0.6, 22.0, 22.1, 23.0, 27.8, 34.4,

and 42.9 dynes/cm for liquid CO2, EtOH refers to ethanol, MeOH refers to methanol, acetone, DCM refers to dichloromethane, N, N-dimethylformamide (DMF), DMSO refers to dimethyl sulfoxide, and water, respectively. When IRMOF-3 was activated with ScCO2, the SBET surface area increased by 258 times in comparison to conventional calcination and by 1.6 times in comparison to solvent exchange. The popularity of ScCO2 for activating MOF materials may be due to its inexpensive cost and ease of scaling up [12].

Chemical Activation (Acid Treatment) MOFs

May also be chemically activated (treated with acid). The guest solvent molecules containing neutral species are the focus of the two activation techniques mentioned above. However, simple heating is unable to free the coordination site of the unloaded chemical when the solvent particles possess a charge (ionic) or have a high boiling point. This is because these molecules have little volatility and are not volatile (unlike ions) (Mondloch et al., 2019). As a result, when solvent molecules such as benzoic acid or ionic species are integrated into the framework during synthesis (occasionally as modifiers), chemical treatment may be the best course of action. However, significant amounts are required to regulate and accelerate the nucleation and development of MOFs. Many of the conjugated bases connected to various types of metal nodes inside the framework, which are typically observed in the production of modified MOFs, may also be effectively removed by acid treatments of MOFs. This method's requirement for thermal activation even after acid treatment is a major drawback, making it inappropriate for heat-sensitive MOFs. The material must also be suitably chemically stable to reduce hydrolysis and structural collapse during acid treatment [17].

Methodology

One of the stable MOFs that can be made with the solvothermal method is MOF-199, which is made with Cu2+ as the metallic and 1,3,5-benzene dicarboxylate BTC as the organic linker. During the process of water adsorption, the structure of MOFs containing zinc frequently collapses due to their high attraction for moisture. On the other hand, MOFs that include copper are frequently more stable. The metal, copper, serves as a joint in MOF-199's metal-organic frameworks, while the anchor is provided by 1,3,5-benzene dicarboxylate molecules. The metal sites' partial positive charges improve MOF-199's adsorption capabilities. MOF-199's unit cell has a cubic symmetry, with tiny octagonal cages and huge cavities for structural support.

MOF-199 Synthesis

The overall procedure for the thermal preparation synthesis of MOF-199 was based on Schlichte's work, in which 24 milliliters of a 1:1 ethanol: water solvent were used to dissolve 0.42 grams of BTC. Following 10 minutes of mixing, a clear solution was obtained. Following that, 0.875 g of $Cu(NO_3)_2$ was added, and the mixture was carefully agitated for another ten minutes. When the combination was entirely dissolved, it formed a blue solution. Following that, the blue mixture was transferred to a 50 mL Teflon-lined stainless steel pressure vessel. To accomplish crystallization, the reactor was heated to

100°C for a set amount of time (Table 1). Following the reaction, the reactor was allowed to cool to normal temperature before collecting blue powder. After that, the blue powder was filtered and washed with 60 mL of a 1:1 water-ethanol combination. Ultimately, the blue powder was stored in vials at 60 °C after being activated under vacuum for 21 hours using a rotary evaporator [18].

Table 1. Shows prepared samples of the synthesis of MOFs-199.

No. of samples	Time (h)	Temp. (˚C)	Ethanol: water ratio
1	24	25	1:1
2	24	84	1:1
3	24	100	1:1
4	30	100	1:1
5	48	100	1:1
6	48	100	2:1

The physical and chemical properties were examined with X-ray scattering microscopy (XRD, Bruker), Belleville surface areas (BET), and scanning electron microscopy (SEM). The nitrogen adsorption equation at 77 K (using Quantachrome Novawin to determine the total pore volumes) with degree of crystallinity of the MOFs was ascertained by dividing the synthesized MOF 199's total peak intensities by the standard MOF-199's total peak intensities [19].

RESULTS AND DISCUSSION

Through the use of scanning electron microscopy (SEM), the morphology of MOF-199 in each sample was examined. According to the SEM images, increasing the reaction time to 48 hours resulted in reduced octahedral crystallization at 140 °C, crystal deformation, and diameter shrinkage. SEM images of the crystal phase of the chosen synthetic MOF-199 samples are shown in Figure 6. The decrease in yield is directly linked to the change in MOF-199's morphology with a longer reaction time, indicating that MOF-199 has redissolved as a result of the longer reaction time. The octahedral shape of the crystal phase became less noticeable as the reaction time rose, according to the SEM images of MOF-199 crystals [20].

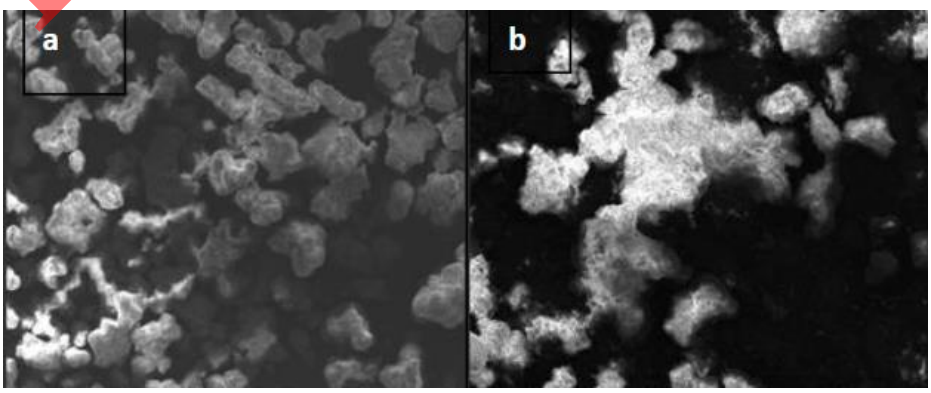

Figure 7. An SEM photo of the crystal shown in the selected synthesized MOF.

MOF-199's crystalline shape is frequently visible in its XRD pattern, It has unique peaks at 2θ = 6.5°, 9.5°, 11.5°, and 13.4°. The MOF-199 powder XRD patterns seen in Figures 7-9 were in line with the material's typical XRD pattern, which exhibits exceptional crystallinity. The impact of raising the solvent temperature (25–100 °C) while keeping other parameters constant (ethanol: water ratio 1:1, synthesis time of 24 hours) on the MOF-199 framework's structure is shown in Figure 9. The MOF-199 phase was not pure at a synthesis temperature of 25 °C; characteristic peaks were seen (see Figure 7.a). By adjusting the solvent temperature, different MOF-199 samples showed altered peak intensities. When evaluating these results with the rate of crystallinity of MOFs (see Table 2), it is crucial to notice that raising the solvothermal temperature to 100°C enhanced the degree of crystallinity of the created MOF-199 samples. Figure 9 indicates that 100 °C is the ideal temperature for the sample to have high crystallinity; thus, this temperature will be chosen, and the impact of reaction time at this temperature will be ascertained next" The impact of changing the reaction period (24, 30, and 48 hours) at a water-to-ethane ratio of 1:1 and a solvothermal synthesis temperature of 100 °C is shown in Figure 8. With peaks at 2θ ≈ 6.5 °C, 9.5 °C, 11.5 °C, and 13.4 °C, MOF-199 is produced even after 18 hours. The intensity of the peaks increased when the solvothermal synthesis period was extended to 48 hours, suggesting that by The quality of crystals, Table 2 demonstrates that within this range, crystallinity increases [21].

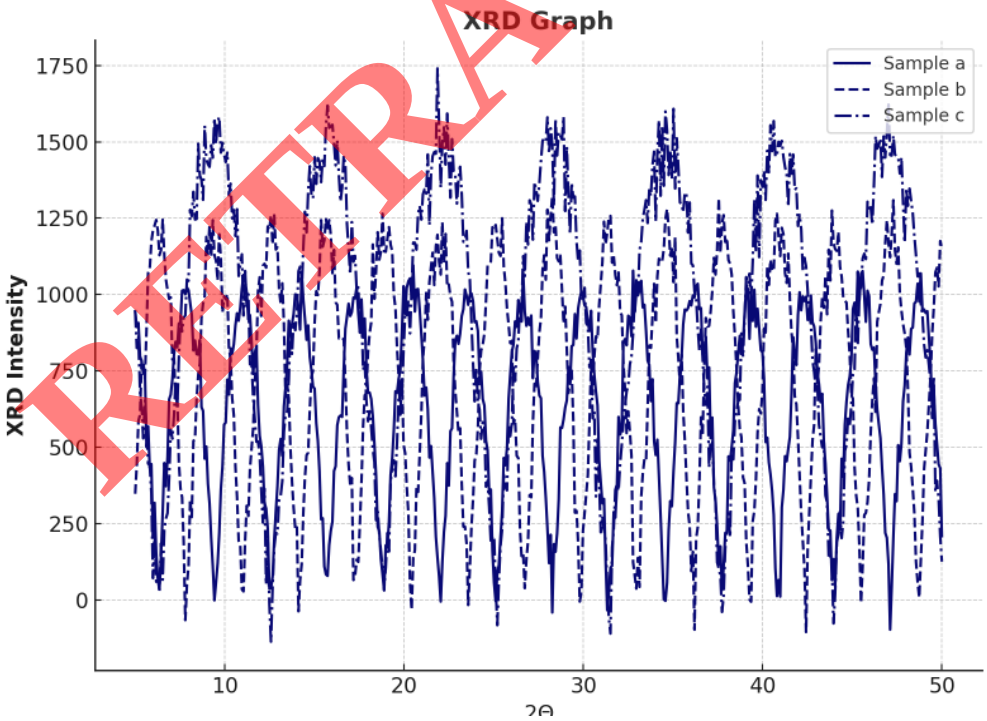

Figure 8. Analysis of synthesis of (MOF- 199) for 24h at 25,85,100 C.

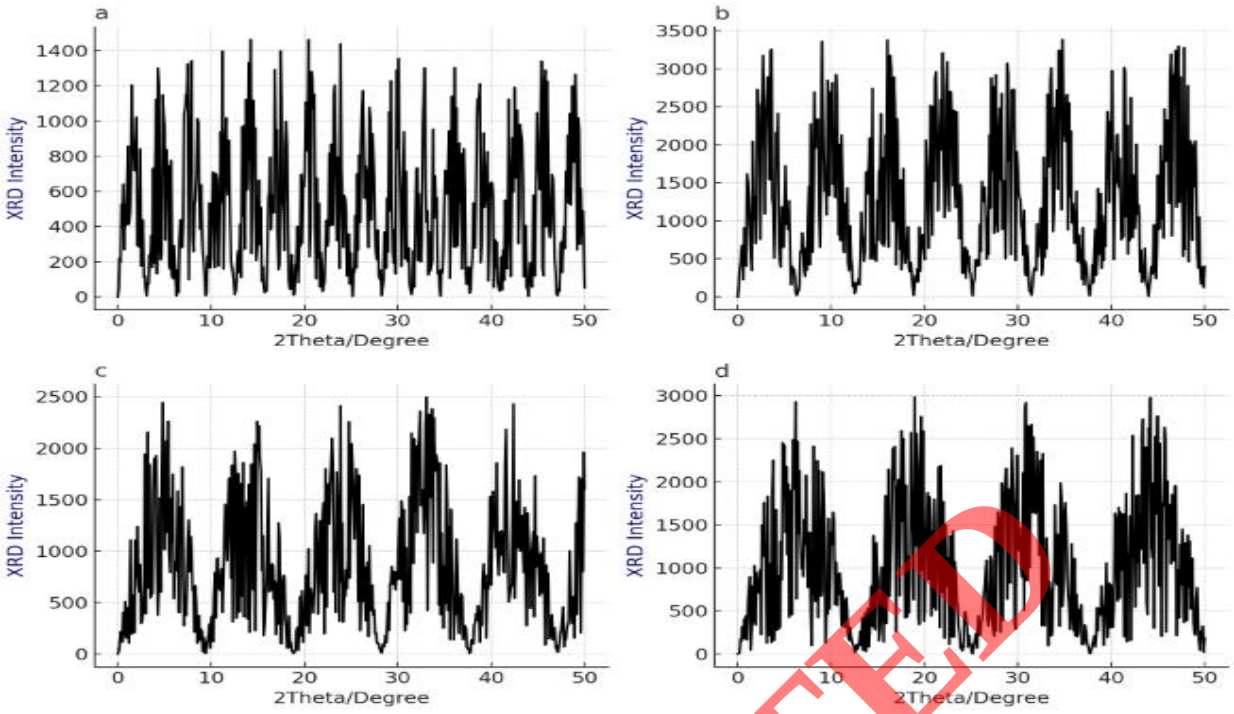

Figure 9. Analysis of synthesis of MOF- 199 for T100 ˚C at 18h,24h,30h,48h.

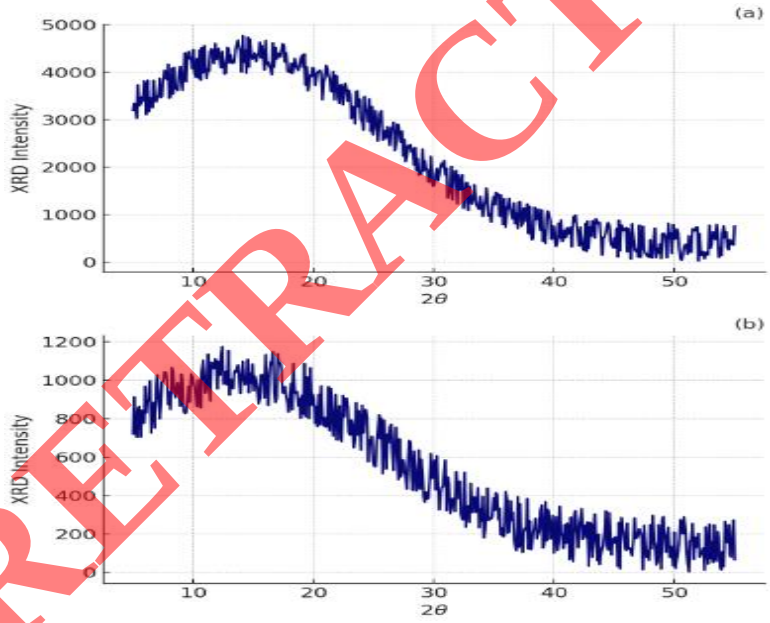

Figure 10. XRD of synthesis of (MOF-199) at 100°C, 48 h and ratio (ethanol: water 1:1), (ethanol: water1:2).

With all synthesis parameters held constant, Figure 10 illustrates the impact of the solvent's water concentration (1:1–1:2) for samples 5 and 6. The typical MOF-199 pattern may be seen in the diffractogram information regarding crystals formed with changing solvent volumes [22]. XRD patterns of the synthesized MOF-199 did not change when the water content was changed, however the intensity of the distinctive peaks did change significantly. At 1:1 ethanol: water, the unique peaks were more intense (Figure 10a) and had a greater surface area (Table 2). The water content rose at 1:2 ethanol: water, slowing the crystallization process since the basic components were at a lower concentration. As

a result, at the 1:1 ratio, a high degree of crystallization and a large surface area were obtained. Table 2 shows the results of crystallization using the second equation. The synthesized MOF-199 sample had the maximum crystallinity after 24 hours of isothermal

treatment at 85 °C. However, When comparing the crystallinity of MOF-199 and BET area values, MOF-199 at 100 °C for 48 hours has the highest surface area (5518 m^2/g) and a high crystallinity (103%) (Table 2). The surface area of the synthesized MOFs was determined using the BET approach with N_2 adsorption at 77 K. It has been shown that increasing surface area enhances catalyst activity. In terms of reaction time and temperature, the MOF-199 surface area values obtained (5518 m^2/g at 100 °C for 48 hours) exceeded Jiang's value (1247 m2/g at 100 °C for 13 hours). We can conclude that the synthesized MOF-199 in this investigation showed high relative crystallinity and was almost equivalent to the standard (Table 2). The optimal thermal solvent for MOF-199 synthesis under the selected operating settings is 100 °C, 48 hours, and a 1:1 ethanol-to-water ratio, as shown. The thermal solvent conditions are determined using the MOFs' .

No. of samples	Time (h)	Temp. (˚C)	Surface area m2/g	Crystallinity %
1	24	25	-	122
2	24	84	2679	106
3	24	100	2902	100
4	30	100	3635	100
5	48	100	5518	103
6	48	100	-	94

XRD patterns, which are similar to the standard MOF-199 XRD pattern with high crystallinity.

Table 2. Samples of crystallinity and Surface area.

CONCLUSION

Fundamental Finding : Over the past 20 years, substantial advancements have been made in the research and development of Metal-Organic Frameworks (MOFs), particularly in enhancing their functional capacities and identifying new structures. The synthesis, purification, and activation of MOFs are critical steps in determining their practical applicability. Without these steps, MOFs cannot be utilized effectively. The study highlights the technical methodologies for MOF synthesis and activation, emphasizing the balance between efficiency and sustainability. Techniques like supercritical CO_2 and freeze-drying are promising for overcoming challenges associated with traditional purification and activation methods. **Implication :** The findings underline the importance of refining MOF synthesis processes to ensure their viability for industrial applications, particularly in wastewater treatment. MOFs' unique properties, such as high surface area, thermal stability, and resistance to corrosion, make them suitable candidates for adsorption and filtration technologies. Their optimization

could lead to more sustainable solutions in environmental engineering and industrial processes. **Limitation :** The study identifies several limitations, including the high cost, time, and energy demands of conventional activation and purification techniques. Moreover, the structural stability of MOFs under high temperatures remains a challenge, potentially restricting their widespread application. Current alternatives, such as supercritical carbon dioxide, show promise but require further investigation to address scalability and economic feasibility. **Future Research :** Future studies should focus on developing cost-effective and energy-efficient synthesis and activation techniques. Research should also prioritize the scalability of advanced methods, like supercritical CO_2 activation, to industrial levels. Additionally, exploring MOFs with enhanced stability and functionality in extreme environmental conditions could broaden their applications beyond wastewater treatment to other industries such as gas storage, catalysis, and drug delivery.

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