COMPARATIVE STUDY OF MAGNESIUM BASED METAL- ORGANIC FRAMEWORKS SYNTHESIZED BY GREEN METHOD

Abstract

The importance of porous framework materials has attracted the researchers in the past few decades which has application in various fields. This is due to the presence of ultra-high surface area, regular porosity and abundance of functional groups. A novel porous magnesium based metal-organic frameworks were synthesized by adding with and without the flower and leaf extract of clitoria ternatea. The Mg-MOFs were synthesized by irradiating with microwaves. The functional group determination of the MOFs were done using FTIR analysis. The crystalline size was done by PXRD analysis. The nano size characterization was done by using TEM analysis. From the following characterization, it was found that by adding the plant extracts, the crystalline size of MOFs were reducing. The crystalline sizes were calculated for Mg-MOF(alone), Mg-MOF (flower) and Mg-MOF (leaf) and were found as 51.79nm, 28.91 nm and 28.52 nm. The TEM analysis of three MOFs were done and confirmed that the prepared MOFs were nanisized and the SAED pattern of Mg-MOF (alone) showed poly-crystalline nature and Mg-MOF with flower and leaf extract changed to single-crystalline nature. Thus the results confirms about the successful synthesis of muti-functional MOFs by green method.

Keywords: Metal-Organic Frameworks; FT-IR; PXRD; TEM; SAED; Clitoria ternatea

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I. INTRODUCTION

Development and synthesis of metal-organic frameworks in the field of co-ordination chemistry and crystal engineering have been of great interest because of their intriguing variety of architectures. Carboxylic acid is commonly used ligand because it contains different coordinating groups. The carboxylic acid act in different modes in metal-ion coordination as bidentate bridging, bidentate chelating, tridentate chelating-bridging or monodentate. Many approaches have been used to synthesize metal-organic frameworks. Most MOF synthesis are liquid-phase syntheses, where separate metal salt and ligand solution are mixed together or solvent is added to a mixture of solid salt and ligand in a reaction vial. The common methods are solvothermal methods, microwave-assisted synthesis, electro-chemical synthesis, mechano-chemical synthesis and sono-chemical synthesis. Metal organic frameworks find potential applications in various fields such as gas storage, gas separation, catalysis, luminescent materials, sensing materials, bioimaging etc.

Zn, Co, Zr, and other d- and f-block elements are typically the primary metals used in MOF formation. These elements have good topological, chemical, and physical properties excellent performance across a range of applications [1]. Compared to d-block components, magnesium metal is more desirable due to its abundant earth resources and capacity for sustainable recycling. However, there haven't been many reported studies on Mg MOFs up to this point. The usage of plant extracts in the preperation of MOFs are being utilizing since the plant extracts act as a reducing agents [2] . The plant components contains electron donating groups like amines, phenols, akenes alkaloids, flavanoids etc. These components can reduce the MOF structure and thus make it as a good electrical conductivity species. Even they can affect the pore size of the MOFs.

So the present study was about the microwave assisted synthesis of magnesium based metal-organic frameworks by adding with and without the flower and leaf extract of Clitoria ternatea (butterfly pea plant). The ligand used was 1,4-benzenedicarboxylic acid. The prepared MOFs were characterized using different techniques and found that the MOFs has muti-functional applications.

II. MATERIALS AND METHODS

All the chemicals and reagents which were used in the present study was of A. R grade. $MgSO_4.H_2O$ and benzene dicarboxylic acid (BDC) were of Merck A. R grade. Methanol used was of SRL, India. The flowers and leaves of Clitoria ternatea were collected from near by located places.

1. **Preparation of Plant Extracts:** The flower and leaf extracts were prepared by collecting plant materials, 5g each of the flowers and leaves were washed and dried. After that 30ml of methanol was added and were digested by passing microwave irradiation at a power of 450w for 15 minutes. The so formed liquids were cooled, decanted and filtered to obtained the flower and leaf extracts.

2. **Preparation of MOFs:** Initially magnesium based metal-organic framework was prepared by adding 0.1 mol of each MgSO4.7H20 and BDC. The mixture was pulverized by using a pestle and mortar to form powdered mixture. The solvent used for mixing was methanol (30ml) to make a paste. This paste was then transferred to a conical flask and sealed. This was then subjected to microwave irradiation at a power of 450W for 15 minutes. A white colored solution was obtained which was filtered, washed using methanol and dried to obtain the Mg based MOF.

   The same procedure was used for preparing other two MOFs namely, Mg-MOF with the flower extract and Mg-MOF with the leaf extract which was depicted in the previous part of this study. [3] The microwave oven used for this study was of Samsung MS2 3F301E made.

3. **Characterization of the prepared MOFs:** The prepared Mg MOFs were characterized using different techniques like FTIR, PXRD and TEM. The IR spectrum of the samples were recorded using SCHIMADZU DR 43 S Spectrometer using KBr pellets in the range of 400-5000 cm-1. PXRD analysis was recorded using Burker D8 Advance X-ray diffractometer. TEM images of the three MOFs were recorded by using a JEOL/JEM 2100, DST-SAIF, Cochin.

III. RESULTS AND DISCUSSION

1. **FT-IR Spectral Analysis:** IR spectra of Mg-MOF without adding plant extract was depicted in the figure 1. Metal-oxygen vibration band was confirmed by the presence of an absorption band at 751cm $^{-1}$. An absorption band in 1630cm $^{-1}$ denoting C=O(-COOH) stretching vibration due to the existence of terephthalic acid in the MOF. An absorption at 1100cm $^{-1}$ in Mg-MOF was due to the bending vibration of hydrolysis group bonded to metal ions. And an absorption band at 3450cm $^{-1}$ which denotes H-O-H stretching of carboxylic group.[4]

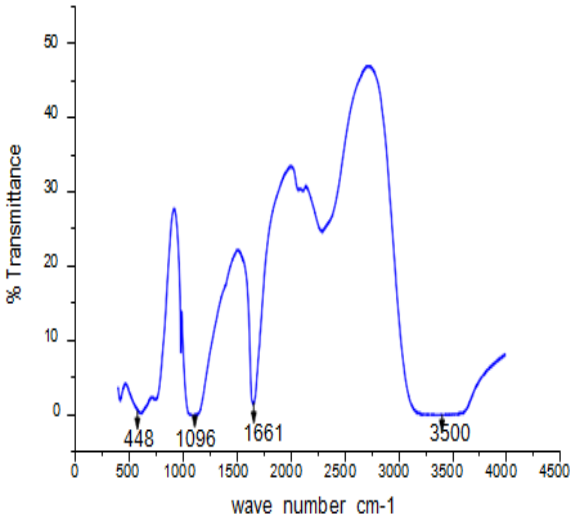

Figure 1: FT-IR Spectra of Mg-MOF alone

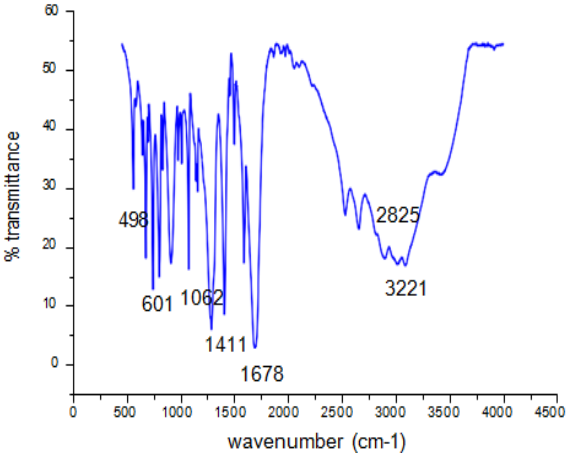

Figure 2: FT-IR Spectra of Mg-MOF (flower)

Figure 2 represents FTIR spectra of Mg-MOF prepared by using flower extract. A strong band formed at 1679 cm^{-1} was due to COOH stretching of benzene ring from the ligand, benzene dicarboxylic acid. The phenolic group from the flower extract was noticed at 3746 cm^{-1} . Another strong band formed at 1506cm^{-1} due to the -COO stretching of the ligand. The C=O stretching of the ligand was at 1108 cm^{-1}. The C-N stretching of aliphatic primary amine of flower extract. The -OH bending of COOH was at 974 cm^{-1}. Metal - ligand bond formation was at 582 cm^{-1}[3].

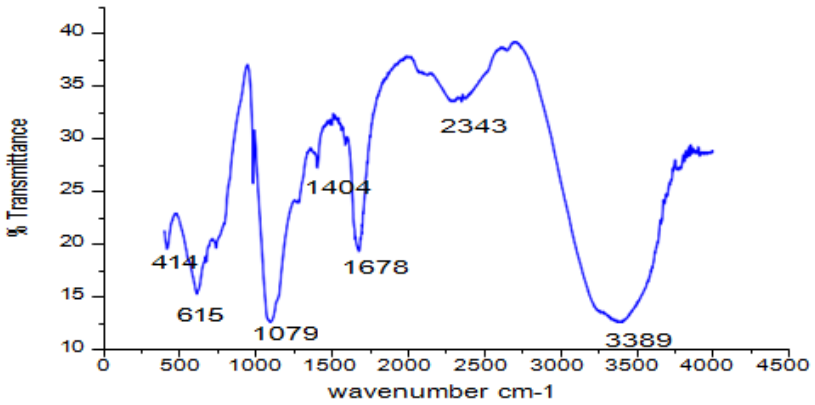

Figure 3: FTIR Spectra of Mg-MOF (leaf)

Figure 3 represents Mg-MOF with leaf extract. Metal coordinated to the ligand was depicted by the presence of an absorption band at 615 cm^{-1} [5]. The amine group from the leaf extract was confirmed from the formation of absorption band at 1404 cm^{-1}. An absorption band was observed at 1678 cm^{-1} in Mg-MOF with leaf extract indicating of -COOH stretching of benzene ring. And also, the band at 414 cm^{-1} indicated that the metal was bonded to carboxylic group of the ligand. The presence of phenolic group of leaf extract was at 3300-3500cm^{-1}. Table 1 represents the FTIR data of the three MOFs.

Table 1: FT-IR data of the prepared MOFs

samples	-OH stretching of COOH	-CH stretching of alkanes	-COOH stretching of benzene	Aromatic amines of plant extract	-CO stretching of COOH	Aliphatic bond of plant extract	Metal- ligand bond
Mg-MOF	3500	-	1661	-	1096	-	448
Mg-MOF (Flower)	3221	2825	1678	1403	1062	582	542
Mg-MOF (leaf)	3389	2343	1678	1404	1079	615	414

2. **Powdered XRD study:** Powdered XRD patterns of the prepared MOFs were shown in the figures 4, 5 and 6. Figure 4 represents the Mg-MOF prepared without adding plant extract. The high intensity diffraction peaks denotes the prepared MOF was crystalline nature. The diffraction peaks at 2 θ values confirmed the presence of nano particles of Mg-MOF. The 2 θ values of 18 ^{o} , 23 ^{0} , 28 ^{o} and 43^{0} confirmed the crystalline nature of

the compound [4]. The grain size was calculated according to the Debye-Scherrer equation. Thus the nano particle size of the MOF was of 51.79nm in size.

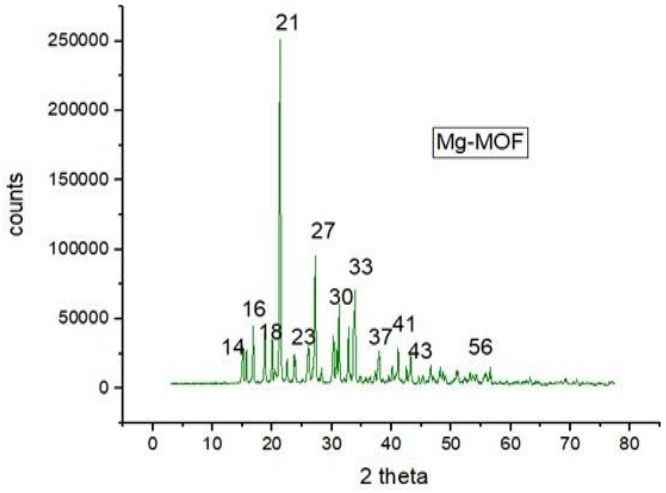

Figure 4: PXRD data of Mg-MOF

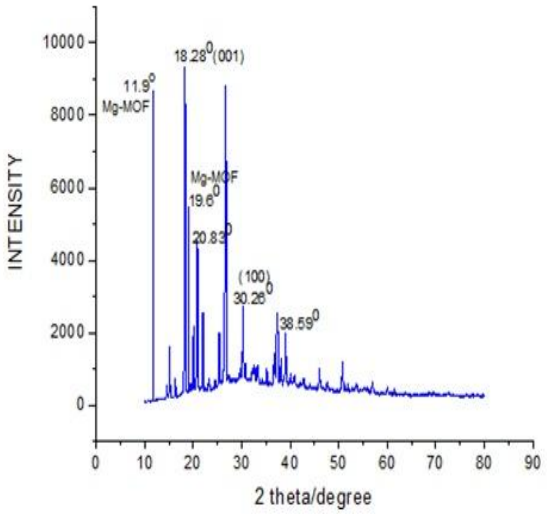

Figure 5: PXRD data of Mg-MOF (flower)

Figure 5 represents the PXRD pattern of the Mg-MOF prepared using flower extract. The peaks at 2 theta value of 18.28^{o} (001), 3026^{o} (100) and 38.59^{o} (101) represents the crystalline nature. The peak at 20.83^{o} is due to the bio-molecule from the flower extract. [3] The peaks of Mg-MOF particles were at 11.9^{o} and 19.6^{o}. The grain size was calculated by Debye-Scherrer equation and found to be 28.9 nm.

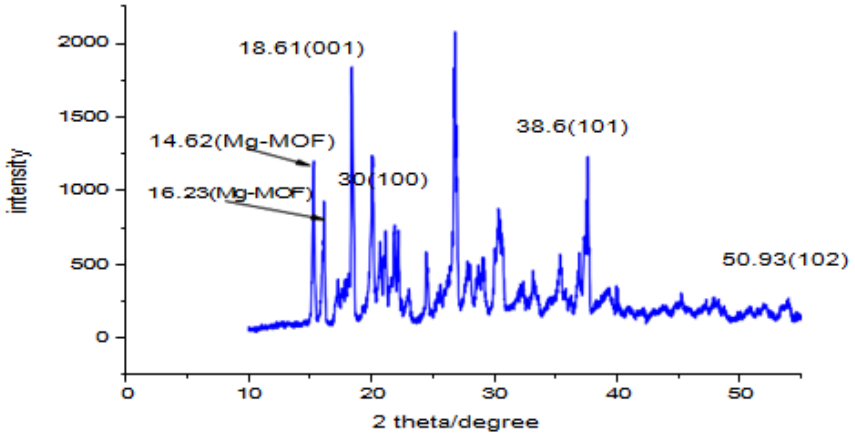

Figure 6: PXRD data of Mg-MOF (leaf)

Figure 6 represents the PXRD pattern of the Mg-MOF by adding leaf extract. The peaks at 2 θ values of 19 ^{o} (001), 28 ^{0} , 33 ^{o} (100), 38.25 ^{o} (101) and 50.93 ^{0} (102) confirmed the crystalline nature of the compound [6]. The grain size calculated based on Debye-Scherrer equation showed that the prepared MOF was of 28.52nm in size.

Thus it was confirmed that the grain size of the Mg-MOF prepared by without adding the plant extract was 51.79nm. And that the grain size of the Mg-MOF with flower extract was found to be 28.9nm and that of Mg-MOF with leaf extract was of 28.52nm. Thus by adding the plant extracts, the grain size was reduced.

3. **TEM analysis:** In the figure 7 represents the morphology of the Mg-MOF without the plant extract was evaluated by TEM analysis and selected area electron diffraction (SAED).

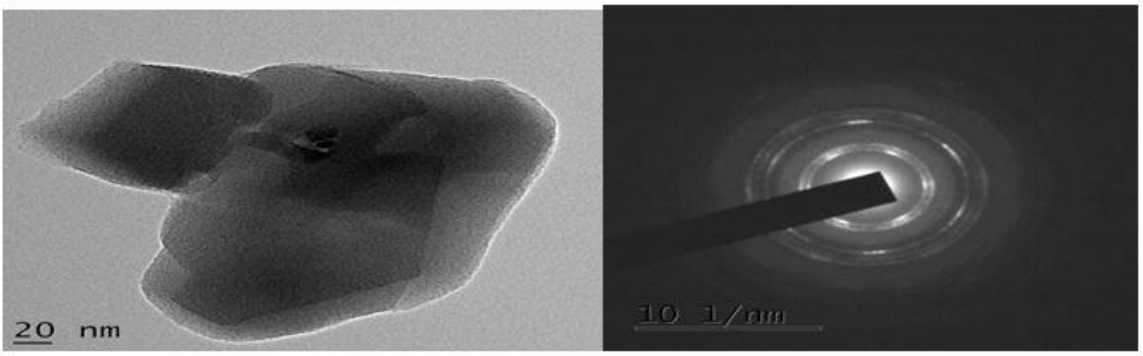

Figure 7: TEM images and SAED pattern of Mg-MOF

TEM images revels that the prepared MOF is nano-sized material. The prepared Mg-MOF was of irregular shape with average grain size of 20-45nm.[7] SAED pattern consisting of concentric bright rings which denotes that the prepared Mg-MOF was of poly- crystalline in nature. In figure 8 represents the TEM images and SAED pattern of Mg-MOF prepared by adding flower extract.

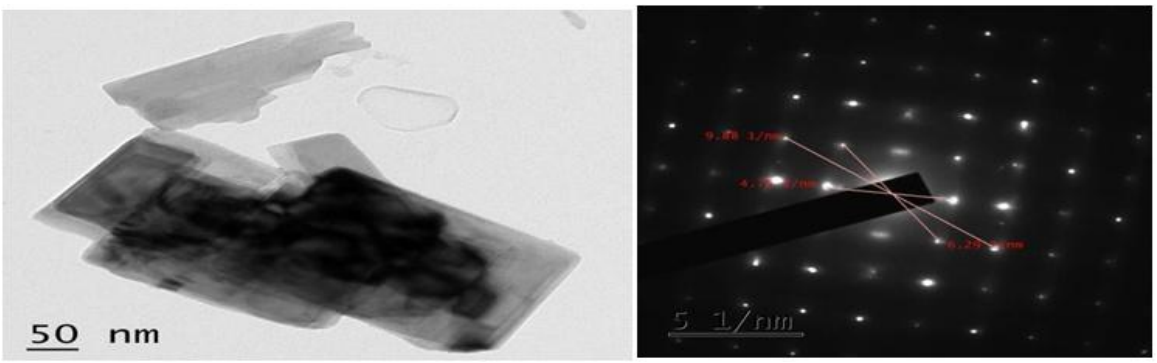

Figure 8: TEM images and SAED pattern of Mg-MOF (flower)

TEM images of the MOF represents rectangular shaped particles. And the SAED pattern represents equally space particles of single crystalline in nature. And the figure 9 represents TEM and SAED pattern of Mg-MOF prepared by adding leaf extract. TEM images represents spherical in size.

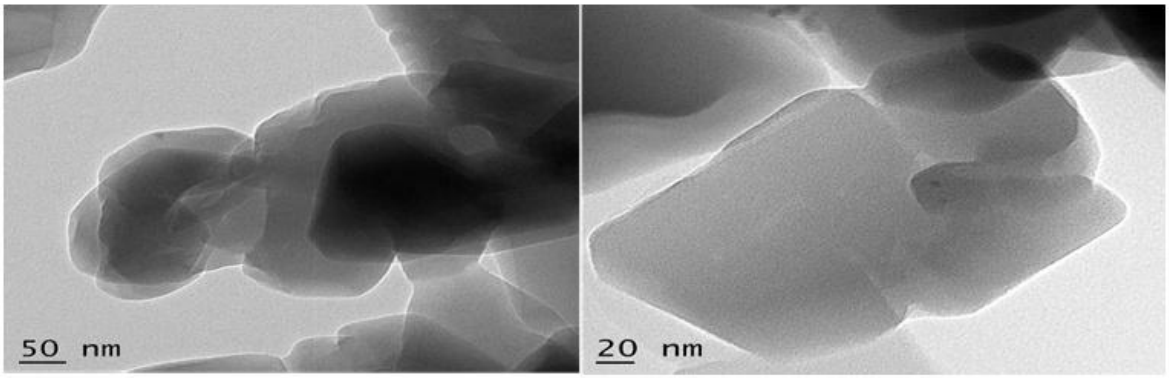

Figure 9: TEM images of Mg-MOF (leaf)

IV. CONCLUSION

The FTIR data indicated the bonding of the metal to carboxylic group of the ligand as well as with amino and phenolic group of the flower and leaf extract. The sharp peaks in the powder XRD patterns showed the crystalline nature of the synthesized MOFs. TEM shows the synthesized MOFs has nano structure. Thus the three different magnesium MOFs were synthesized and characterized successfully. The future aspects is to study about the electrochemical sensing capacity of MOFs.

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