PROJECT REPORT

On

UPCYCLING PET WASTE INTO METAL-ORGANIC FRAMEWORKS FOR WATER TREATMENT APPLICATIONS

Submitted by

AMALA AJAY ,(AB22CHE002)

In partial fulfillment for the award of the

Bachelor's Degree in Chemistry

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM

2024-2025

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH
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ERNAKULAM

B.Sc. CHEMISTRY PROJECT REPORT

Name : **AMALA AJAY**
Register Number : **AB22CHE002**
Year of Work : **2024-2025**

This is to certify that the project "**UPCYCLING PET WASTE INTOMETAL-ORGANIC FRAMEWORKS FOR WATER TREATMENT APPLICATIONS**" is the work done by **AMALA AJAY.**

Dr. Saritha Chandran A.
Head of the Department

DEPARTMENT OF CHEMISTRY

Mr.Linto Anto
Staff-member in charge

Submitted to the Examination of Bachelor's Degree in Chemistry

Date: ……………………

Examiners: Rejani George …… 30/04/25

: …… Linto Anto …… 30/04/25

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH
ST. TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM

CERTIFICATE

This is to certify that the project work entitled "**UPCYCLING PET WASTE INTO METAL-ORGANIC FRAMEWORKS FOR WATER TREATMENT APPLICATIONS**" is the work done by **AMALA AJAY** under my guidance in the partial fulfilment of the award of the Degree of Bachelor of Science in Chemistry at St. Teresa's College (Autonomous), Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

Mr. LINTO ANTO
(Project Guide)
Assistant Professor
Department of Chemistry and
Centre for Research
St. Teresa's College, Ernakulam

DECLARATION

I hereby declare that the project work entitled **"UPCYCLING PET WASTE INTO METAL-ORGANIC FRAMEWORKS FOR WATER TREATMENT APPLICATIONS"** submitted to Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of **Mr. LINTO ANTO, ASSISTANT PROFESSOR,** Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the Degree of Bachelor of Science in Chemistry.

AMALA AJAY

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ABINA MICHAEL

AMALA AJAY

FIDA HIDAYATH

NANDANA A ANIL

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Chapter 1

Introduction

One of the main concerns the world has been facing for a long time is plastic pollution. Plastic pollution is the accumulation of plastic objects and particle including plastic bottles, bags and micro beads in the Earth's environment that adversely affects humans, wildlife and their habitat. In 1907 the invention of Bakelite brought about a revolution in materials by introducing truly synthetic plastic resins into world commerce [1] . In 1950, plastic production was around 2 million tons, and it was boosted to 368 million tons in 2019. Plastic consumption has thus increased about 180 times from 1950 to 2018. The worldwide plastic production is calculated to be 400.3 million tons in 2022. Plastic production is thus expected to increase exponentially hereafter.[2] Plastic pollution has become a catastrophic issue which is threatening ecosystem, wildlife and human health alike.

Plastic is widely known as a synthetic polymer developed by polymerization of monomers extracted from petrochemicals and combined with other chemicals. Monomers are the repeating units of long-chain polymers that are held together by covalent bonds.[2] Plastics are inexpensive and durable, making them very adaptable for different uses due to which manufacturers choose to use plastic over other materials. Today, however, the average consumer comes into daily contact with all kinds of plastic materials that have been developed specifically to defeat natural decay processes. Since synthetic plastics are largely non-biodegradable, they tend to persist in natural environments. Moreover, many lightweight single-use plastic products and packaging materials, are not deposited in containers for subsequent removal to landfills or recycling centres. Instead, they are improperly disposed of at or near the location where they end their usefulness to the consumer. Indeed, landscapes littered by plastic packaging have become common in many parts of the world. The causes and effects of plastic pollution are truly worldwide.

Given the global scale of plastic pollution, the cost of removing plastics from the environment would be tremendous. Most solutions to the problem of plastic pollution, therefore focus on preventing improper disposal or even on limiting the use of certain plastic items in the first place. Fines for littering have proved difficult to enforce, but various fees or outright bans on foamed food containers and plastic shopping bags are now common, as are deposits redeemed by taking beverage bottles to recycling centers. Recycling plastics is an effective way to decrease plastic pollution.

One of the main plastic pollutants is PET plastics. Polyethylene terephthalate or PET is the most common thermoplastic polymer resin of the polyester family and is used in fibers for clothing, containers for liquids and foods is only partially recycled, with an estimated recycling rate of just 28.4% in 2019. Depolymerization of PET through hydrolysis can be considered as the most basic method for PET recovery. The basic components of PET polymerization are terephthalic acid (TPA) and ethylene glycol (EG) monomers.[3]

With our project we are using suitable techniques to isolate tetrephthalic acid and further we use it for the preparation of MOF (Metal organic framework) with suitable metal. We further investigate on the properties and application of the synthesized MOF with suitable experiments.

1.1 METAL ORGANIC FRAMEWORKS (MOFs)

Metal-organic frameworks (MOFs) represent a new category of highly ordered porous crystalline hybrid materials created through the coordination of metal-containing nodes (ions or clusters) and multifunctional organic ligands. Porous materials, including porous ceramics, zeolites, activated charcoals, porous metals, polymer foams, and porous glass, are utilized in various ways in our everyday lives. Thanks to their well-known properties and extensive applications, the field of porous materials especially nanoporous materials has experienced rapid development over the past two decades. From the recently developed porous materials (MOFs) stand out from traditional porous materials due to their high porosity and thermal stability. MOFs are a promising choice in a number of application areas, including catalysis, gas storage/separation, energy storage/conversion, sensors, drug delivery, bio-imaging, and more, thanks to their extensive array of exceptional qualities. One special feature of MOF chemistry is the ability to modify topologically varied crystal structures according to research interests. Yaghi and Li's 1990 research in the area of porous coordination polymers marked the beginning of MOF materials history.[4]

In general, there are several methods for creating MOFs with interesting characteristics and a variety of crystal structures. Slow diffusion, hydrothermal (solvothermal), electrochemical mechanochemical, microwave assisted heating and ultrasound are some of the different synthetic techniques that can be used to create MOFs.

Example of MOF includes Cu-MOF, Zn-MOF, and Mn-MOF.

Applications of MOF includes gas storage and delivery, drug delivery, rechargeable batteries, adsorption properties, supercapacitors, separation membranes, catalysis, sensing.

No	Designation	Formula	Abbreviation interpretation
1	MOF-74	Zn_2DOT	Metal Organic Framework
2	MOF-101	$Cu_2(BDC\text{-}Br)_2(H_2O)_2$	
3	MOF-177	$Zn_4O(BTB)_2$	
4	MOF-235	$[Fe_3O(BDC)_3(DMF)_3][FeCl_4].(DMF)_3$	
5	MOF-253	$Al(OH)(BPYDC)$	

Table 1.1 Examples of typical MOF names and their composition

1.2 METHODS FOR SYNTHESIS OF MOF

A variety of MOF synthesis techniques have been documented, including microwave, electrochemical, mechanochemical, sonochemical, plus conventional synthesis (including solvothermal). MOFs are frequently crystallized from a solution. Unreacted remnants of the original chemicals clog the pores, particularly with water and organic solvents. Dense structures are more stable thermodynamically.

Thus, the synthesis of inorganic units and the encapsulation of foreign molecules into the porous structure are crucial for the creation of MOFs. Purification and activation of MOFs after post synthetic treatment is a crucial step. Purification is essential for MOF catalytic applications because reaction byproduct contaminants can mimic catalytic activity and significantly reduce adsorption potential. Purification often entails a solvent treatment, frequently at a high temperature. A material's activation necessitates pore emptying, which is frequently a challenging process because heating inclusions out of a porous structure can cause the framework to collapse, particularly if the framework and guest molecules are bonded by strong bonds or if high temperatures are needed to remove the inclusions. MOF activation can be made simpler using a variety of techniques.[5]

There are two types of traditional synthesis: solvothermal and non-solvothermal.

1.2.1 SOLVOTHERMAL SYNTHESIS

The solvothermal method has been widely used for the preparation of MOFs. This technique is employed due to its simplicity, convenience of usage, crystallinity, and high yield. In this approach, metal salts and organic ligands are stirred in protic or aprotic organic solvents which contain the formamide functionality. Aprotic solvents include DEF, DMF, NMP, DMSO, DMA, acetonitrile, and toluene. Protic solvents are methanol, ethanol, and mixed solvents. To keep away from the issues associated with the distinct solubility of the initial components, mixtures of solvents can be used. If water is used as a solvent in MOF synthesis, it is referred as the hydrothermal method. This mixture is poured into the closed vessel at elevated pressure and temperature for several hours or a day. Glass vials are used at low temperature, and a Teflon-lined stainless-steel autoclave is used for high temperature (>400 K) in the reaction. Then, the closed vessel is heated at a temperature greater than the aprotic or protic solvent’s boiling point to bring about higher pressure. The chief parameter of this reaction mixture is the temperature, and there are two temperature ranges, i.e., the reaction taking place in a closed vessel above the solvent's boiling point under autogenous pressure referred to as a solvothermal reaction, and a nonsolvothermal reaction happens below or at the boiling point of the solvent under ambient pressure. Due to the high pressure, the solvent is heated above its boiling point and the salt will melt, which then aids the reaction. In addition, to acquire a large crystal with a high internal surface area, slow crystallization from a solution is required.[4]

1.2.2 NON-SOLVOTHERMAL SYNTHESIS

1.2.2.1 MICROWAVE SYNTHESIS

With frequencies ranging from 300 to 300,000 MHz, microwaves (MW) are a kind of electromagnetic radiation. Only the electrical component of radiation of the two usually affects the production of compounds. In typical organic compounds, the maximum MW energy (0.037 kcal mol71) is not enough to cleave chemical bonds. The heating results from two different kinds of MW impacts on a material: those on free ions and polar molecules. Polar molecules and ions attempt to line up with the alternating field in both situations. When an electrolyte solution generates electric current, resistance causes warmth to occur. Hydrogen bonds are what give polar molecules, like water, their resistance. Rapid heating alone cannot account for the observed rise in reaction rates, despite the fact that numerous tests have shown that microwave treatment effectively shortens the synthesis duration. MW irradiation provide energy to break through the activation energy barrier but does not alter the activation energy, which is a constant for every reaction. Consequently, compared to the conventionally heated system, the reaction is finished faster. Another significant element that contributes to the rise in reaction rate and yield is noteworthy. The solvent selection is a crucial step in any MOF production. The solvent must meet new, particular requirements while using microwave radiation. In addition to absorbing microwave energy, the solvent should have the capacity to transform electromagnetic energy into thermal energy. The dielectric loss tangent is employed to evaluate this capability. Another unique characteristic of microwave heating is that it raises a solvent's boiling point somewhat more than traditional heating does; that is, once the boiling point is reached, the solvent typically remains in the metastable state and does not boil. The fact that a solution can only boil when it comes into touch with its vapor helps to explain this phenomena. Similar contacts are typically generated on the defects of glass (or another material of a vessel) that cannot be wetted with the solvent, in addition to the upper boundary with air. Thus, on these imperfections, interfaces between liquid solvent and vapor emerge, and it is in these locations that the first signs of boiling bubbles appear. But while heated in a microwave, the vessel walls.[4]

1.2.2.2 ELECTROCHEMICAL SYNTHESIS

The fundamental concept of the electrochemical synthesis of MOFs is that metal ions are added as a consequence of an electrochemical process rather than from a solution of the appropriate salt or as a byproduct of the metal's reaction with an acid. Specifically, the anode dissolves to provide metal ions to the reaction mixture that contains dissolved linker molecules and an electrolyte. This enables the start of a continuous process and prevents anions from forming throughout the reaction, both of which are necessary to produce comparatively significant amounts of MOFs.

Protic solvents are employed to stop metal cations from accumulating on the cathode, although in this instance, hydrogen could be released in due course of this process. The electrochemical method was used for the first time to synthesize MOFs (HKUST-1) in 2005. As the dissolving anode, copper sheets 5 mm thick were used; the sheets were dipped in a solution of BTC in methanol together with copper cathodes. Within 150 min after applying voltage, a green-blue precipitate was deposited. A somewhat modified method was proposed by Hartmann. They compared the hydrothermal, conventional non-hydrothermal and electrochemical methods of synthesis of HKUST-1. All methods gave the Cu phase with comparable surface areas and pore volumes. It should be especially noted that this method affords both powders and films. For example, a thin layer of HKUST-1 was electrochemically deposited on copper mesh was used as anode. [4]

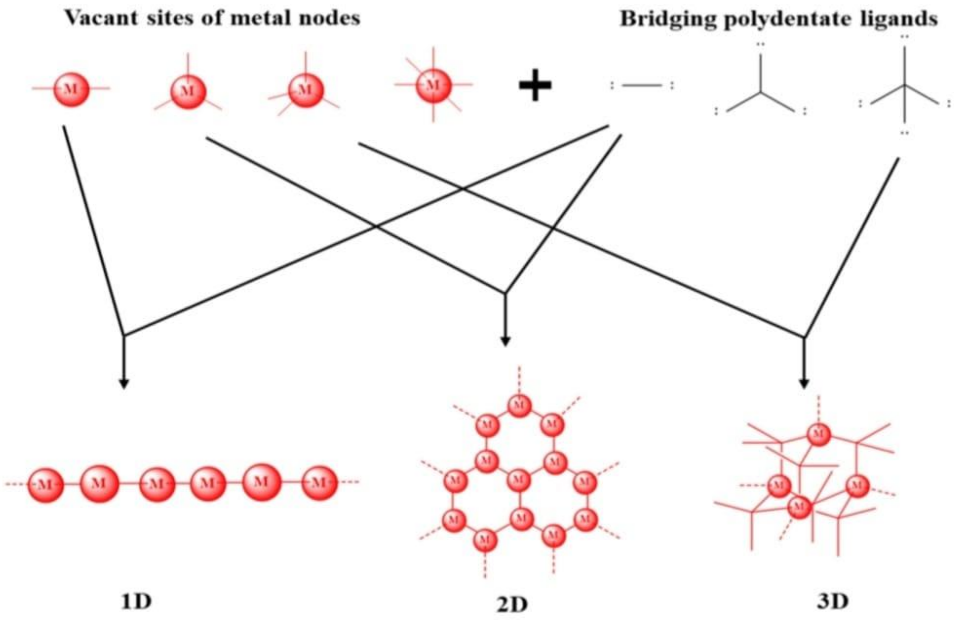

Fig1.1.MOFs with various metal nodes and organic linkers.

1.3 BIMETALLIC MOF

The Bimetallic MOFs (BMOFs) are formed by introducing second metal in MOF structure, with a purpose to enhance the existing properties of a MOF. The heterojunctions developed using BMOFs having mixed-metal ions could utilize the synergistic effects of the two atoms. Due to the addition of secondary metal nodes in a MOFs or its derivative, several defects are expected to increase, giving rise to increased porosity. Electrical conductivity between electrodes and electrolyte surfaces is also expected to increase because of the enhanced electronic coupling between the metal nodes. BMOF could possess different morphology from the parent MOF but in most cases, it retains the crystal structure of the MOF. Depending upon how the metal ions are distributed, the BMOF structures can be either of ‘solid solution’ type or ‘core- shell’ type.[6]

Post-synthesis modification (PSM) is used to synthesize solid solution BMOFs in which metal ions are having homogeneous distributions throughout the crystal while core-shell BMOFs, which have chemically different MOF shell from the MOF core, are synthesized using one-pot synthesis. Due to their advanced structure, BMOFs can be used as self-template or sacrificial template for the fabrication of porous homo-Bimetallic materials, such as porous carbon materials, Bimetallic sulphides and Bimetallic oxides. The new assemblies have generally a large surface areas maintaining the structural characteristics of the parent MOFs. Large surface areas can diffuse Nano sized subunits, and sufficient active sites that enhances their performances to be utilized in many applications.

Moreover, Bimetallic MOFs can be used as precursors/templates for the synthesis of a variety of nanostructured materials, including carbon composites, metal compounds, and MOF composites. By selecting appropriate Bimetallic MOFs and controlling the post-treatment process (*e.g.*, pyrolysis, hydrolysis, and hydrothermal treatment), the compositions and structures of the afforded nanomaterial's can be controlled [7]. Bimetallic MOF-derived nanomaterials exhibit exposed active sites and high stability and conductivity, which can benefit their applications in the catalysis of more challenging reactions under harsh conditions and electrochemical energy storage and conversion.

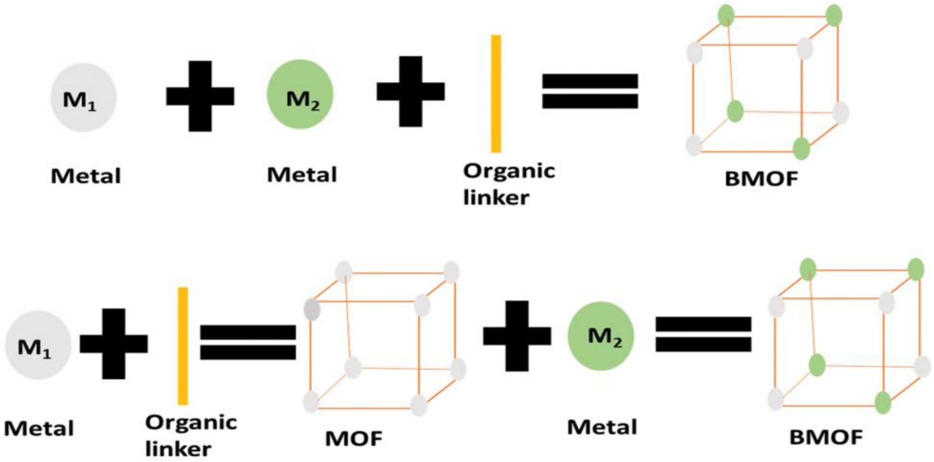

Fig1.2.Systematic synthesis of Bimetallic MOFs

1.4 Fe-Al BIMETALLIC MOF

Fe-Al Bimetallic metal-organic framework (MOF) possess two different metal ions, Iron and Aluminium as nodes in their molecular framework. The main aim of modifying a Bimetallic MOF from a monometallic MOF is to make MOFs having more active sites and a wider application range. They are prepared either by using a hydrothermal reaction system in the presence of Fe and Al metal precursors with various molar ratios [8] or with a simple one-step solvothermal method. [9]

The microwave-assisted solvothermal/hydrothermal (MW-ST/MW HT) method allows the control of shape and produces MOFs with self-assembly.[10]

1.4.1 PROPERTIES OF Fe – Al BIMETALLIC MOF

The catalytic process is considered as an excellent approach for handling the environmental pollution at the large-scale. The rapid recombination of the electron/hole pair stagnates the photo catalytic process and may even create unexpected secondary pollutions. Hence, post-synthetic modification of porous Metal-Organic Framework (MOFs) is an expeditious pathway to improve the functions of MOFs. Mixing metal into MOFs structure was selected as the optimal pathway because the presence of different metal ions generates a hetero junction, which contributed to the band gap reduction. The incorporation of aluminium ionic into MIL–88B (Fe) might improve photo catalytic activity by granting the Bimetallic with increased conductivity and stability[10]**.** General properties of MOFs (e.g., thermal and chemical stabilities, porous structures, high surface area) along with the properties of the bimetals enhance other properties like dye degradation. . Fe–Al BDC was used for the photo degradation of various water-soluble hazardous dyes (e.g., RhB, [9-(2-carboxyphenyl)-6 (diethyl amino) xanthen-3-ylidene]-diethylazanium chloride, and MB, 3,7-bis (dimethyl amino)-phenothiazine-5-ium chloride) using solar irradiation and the efficient chemisorption of F in a different pHrange (pH2–11).[11]

1.5 CHARCTERIZATION TECHNIQUES

1.5.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR):

Infrared (IR) spectroscopy, particularly Fourier Transform Infrared Spectroscopy (FT-IR), is a widely used technique for chemical analysis in laboratories. It provides valuable insights into molecular vibrations, enables the identification of functional groups within a molecule, making it a powerful tool for recognizing the chemical composition of a compound.

The method is based on the absorption of infrared light by a sample, resulting in a spectrum that displays absorbance or transmittance intensity against frequency (wave number). Each peak in the IR spectrum corresponds to specific molecular vibrations, allowing for the identification of functional groups. As such, the IR spectrum acts as a unique fingerprint for unknown compounds, which can be compared with standard reference spectra for structural identification.

IR spectroscopy is versatile and can be used to analyze both organic compounds and inorganic materials, such as minerals and metals. Additionally, it can be applied to liquids and solids at atmospheric pressure. [12]

1.5.2 UV VISIBLE ABSORPTION SPECTROPHOTOMETER:

UV visible spectrometry is an analytical method that is based on Beer-Lambert law. The sample to be analyzed is passed through electromagnetic radiations in the UV -visible region (200nm- 800nm)[13]. As a result, the molecules absorb energy causing transitions of electrons in the molecule. This results in the absorption spectra. The absorption spectra of a sample are indicative of its colour within the visible spectrum.

This technique has several applications such as drug development, structural analysis of organic compounds, determination of molecular weight, and impurity detection. UV spectroscopy enables both qualitative and quantitative analyses to be performed efficiently.

1.5.3 X- RAY DIFFRACTION (XRD):

X ray diffraction technique is used for characterizing crystalline materials. It provides information regarding the structure and arrangement of atoms within the compound. X-ray diffraction peaks result from the constructive interference of a monochromatic X-ray beam scattered at particular angles by the lattice planes in a sample. The intensities of these peaks reflect the arrangement of atoms within the lattice. As a result, the X-ray diffraction pattern serves as a fingerprint for the periodic atomic arrangement present in a material.[14]

1.5.4 SCANNING ELECTRON MICROSCOPE (SEM):

SEM (Scanning Electron Microscope) is a versatile advanced instrument that is employed to observe the surface phenomena of the materials. SEM is based on the principle that primary electrons from the source transfer energy to the electrons of the sample material. This energy causes emission of secondary electrons, which are then collected from each point of the sample to form an image.

SEM data gives information regarding the morphology, composition, topography and crystallography of the sample. Thus, it is a multipurpose instrument used to analyze different materials with high resolution.[15]

Chapter 2

Materials and Methods

This chapter gives a brief description of the materials and experimental procedures adopted for the present investigation.

2.1 MATERIALS REQUIRED

- Pieces of plastic taken from PET bottles
- Ethanol
- Sodium Hydroxide pellets (Nice Chemicals Pvt Ltd, Kerala)
- Sodium dodecyl sulphate (SDS) (SD Fine Chemicals Ltd, Mumbai)
- Aluminium Nitrate ($Al(NO_3)_3.9H_2O$) (Nice Chemicals Pvt Ltd, Kerala)
- Ferric Nitrate ($Fe(NO_3)_3.9H_2O$) (Nice Chemicals Pvt Ltd, Kerala)
- N,N-Dimethylformamide (DMF) (Nice Chemicals Pvt Ltd, Kerala)

All chemical reagents were of analytical grade and used directly without further purification.

2.2 EXPERIMENTAL METHODS

2.2.1 PREPARATION OF TEREPHTHALIC ACID

Colourless post- consumer PET waste bottles obtained from household waste recycling bins were used as the reactant material. All the labels and caps were first removed, and the waste PET bottles were washed and dried and cut into small pieces.3g of fragments of plastic, 100ml ethanol, 14g NaOH and 1g SDS were taken in a round bottom flask and refluxed for 3-4hrs.It is then filtered using Whatman No.1 filter paper and 50% H_2SO_4 is added to the filtrate and acidified till the pH turns 3. The white precipitate thus formed is filtered and kept in the Muffle furnace for 3-4hrs to dry.[16]

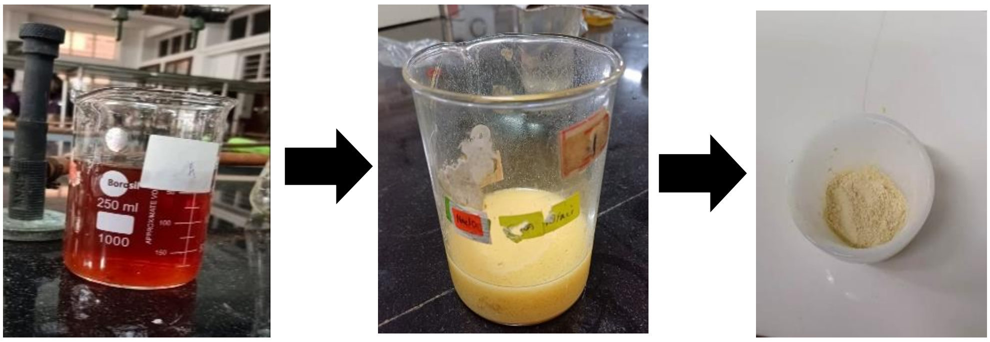

Fig2.1 *Synthesis of Terephthalic Acid*

2.2.2 PREPARATION OF Fe-Al BIMETALLIC MOF

The Bimetallic Fe-Al MOF was prepared using a mixture of $Fe(NO_3)_3.9H_2O$ (Ferrous Nitrate), $Al(NO_3)_3.9H_2O$ (Aluminium Nitrate), Terephthalic Acid and N,N-Dimethylformamide (DMF). 0.27g of Aluminium Nitrate, 0.27 g of ferrous nitrate and 0.199g of TPA were taken in a 45mL of DMF into a 50mL Teflon-lined stainless steel autoclave and reacted at 180°C for 12 hrs. After cooling down, the solid was filtered using Whatman followed by drying in a muffle furnace at 120° for 4hrs to obtain the final product.[9]

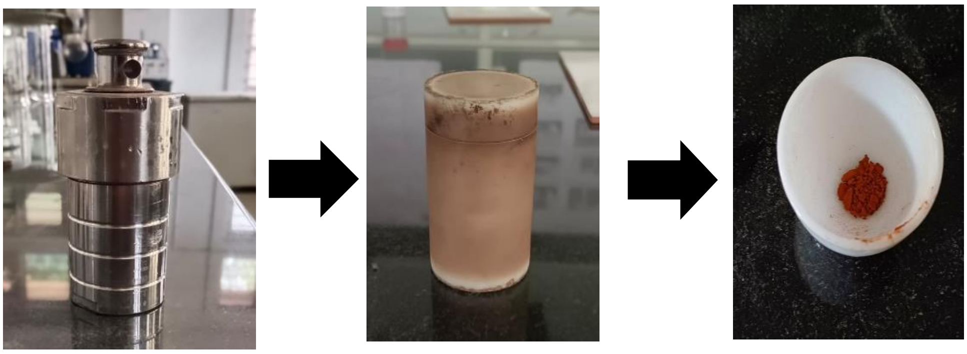

Fig 2.2 *Fe-Al Bimetallic MOF*

2.3 CHARACTERIZATION

2.3.1 INFRARED-RED SPECTROMETRY (IR)

The IR spectrum of synthesized particles were recorded using Fourier Transform Infra-Red spectrometer, Thermo Nicolet iS50 4000cm^{-1} to 400cm^{-1}.

2.3.2 SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDX)

SEM -EDX were taken using Jeol 6390LA/ OXFORD XMX N spectrometer with Accelerating voltage: 0.5 to 30 k, Filament: Tungsten, Magnification x 300000, EDAX resolution 136 eV, EDAX detector area 30 mm2 and Elemental Mapping.

2.3.3 X- RAY DIFFRACTION (XRD)

The X-ray pattern was recorded using Bruker D8 Advance.

2.4 ADSORPTION STUDIES USING METHYLENE BLUE AS MODEL DYE

About 0.1g methylene blue was taken and made up to 100ml using distilled water.10 ml of this solution was pipetted out into a beaker. The pipetted solution was made upto 100ml using distilled water to make 10ppm Methylene Blue solution. To 10ml of the above solution, 0.01g of Fe-Al bimetallic MOF was added and kept for adsorption studies for 1 hour. The solution obtained after adding the MOF as well as the coloured solution of Methylene Blue was given for UV spectroscopy.

Chapter 3

Results and discussion

3.1 CHARACTERIZATION OF TPA AND Fe-Al BMOF

3.1.1 INFRARED SPECTROSCOPY (IR)

Figure 3.1 shows the IR spectrum of synthesized terephthalic acid, respectively.

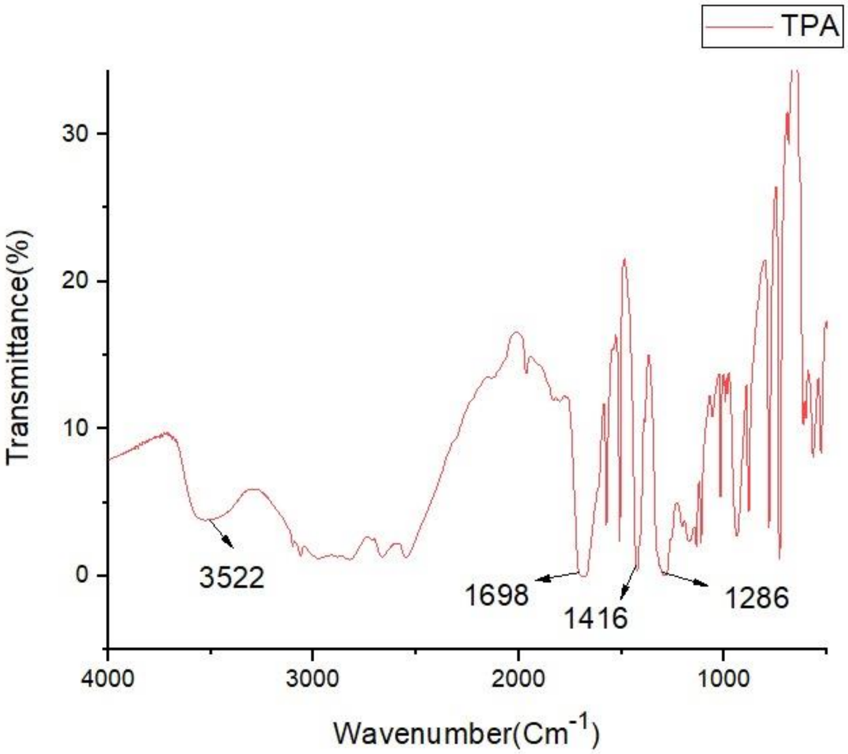

Fig 3.1 IR spectrum of the Terephthalic acid (TPA)

In the FTIR spectra, covering the range of 400-4000cm^{-1}, crucial information about its functional groups is revealed. Notably, a peak at 3522cm $^{-1}$ indicate the presence of O-H stretching vibration of the carboxylic acid , 1698cm corresponds to C=O stretching vibration of the carbonyl group , 1416cm shows bending vibration of methylene group and 1286cm shows C-O stretch of carboxylic acid. These details insights from the FTIR spectra provide a comprehensive understanding of the structural characteristics and functional groups present in the Terephthalic Acid.

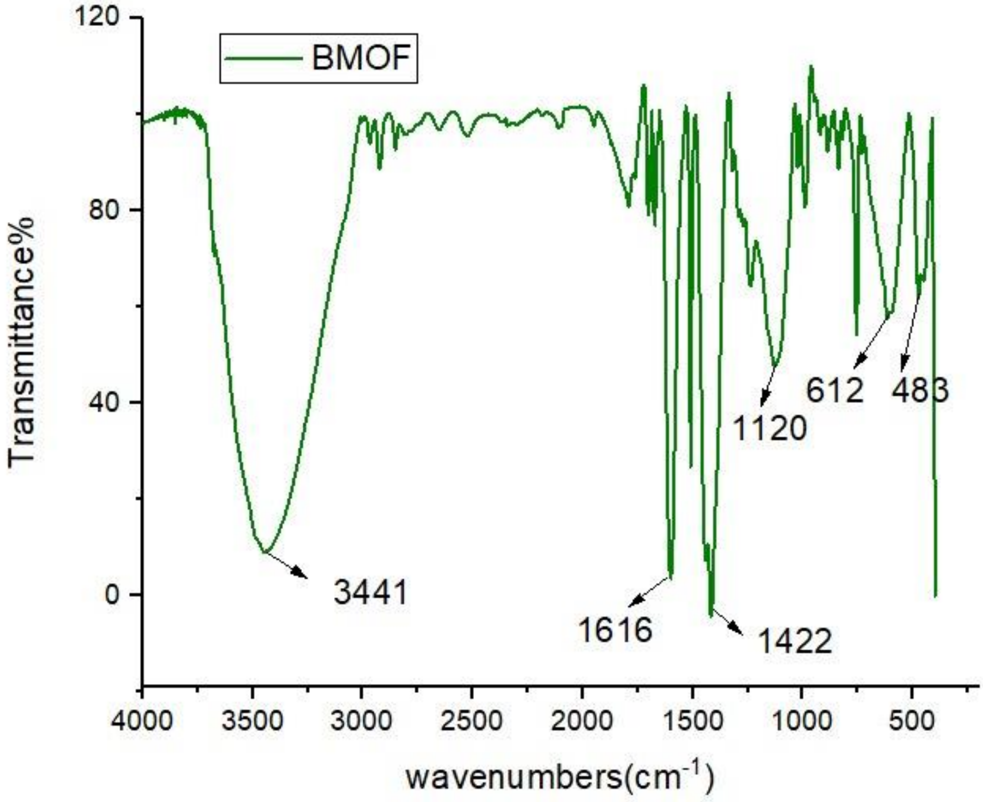

Fig 3.2 IR spectrum of Fe-Al MOF (BMOF)

The IR spectrum of Fe-Al MOF (fig 3.2) shows the peak at a 483 cm^{-1} which was corresponding to the vibrations of Al-O bond. The peak at 612 cm^{-1}corresponds to the Fe-O vibrations. The peak at 3411 cm^{-1} corresponding to the stretching of O-H group.

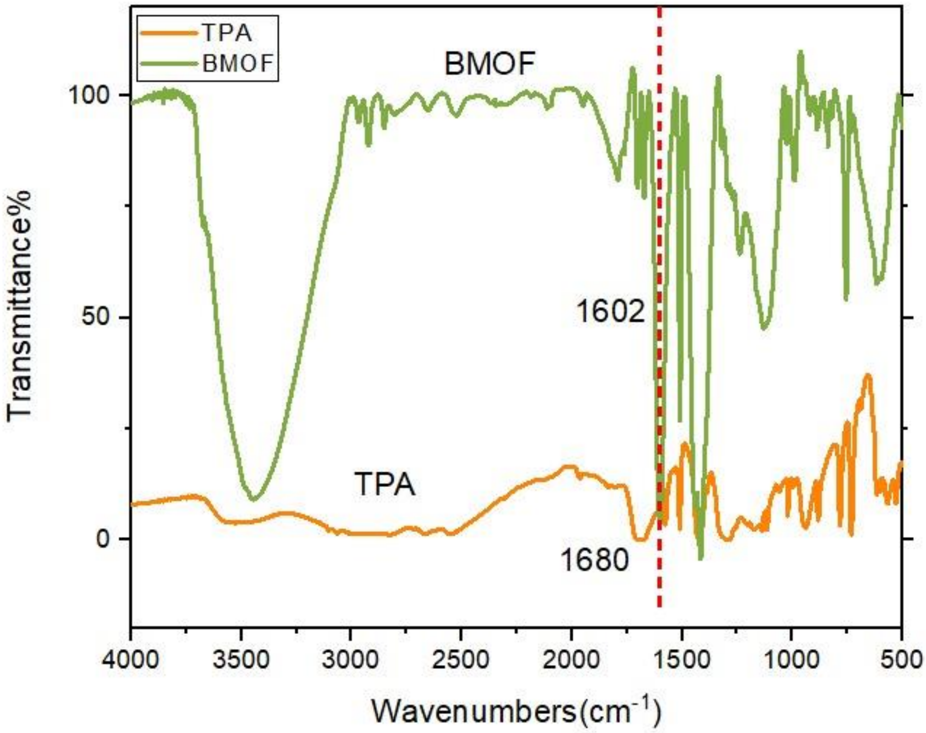

Fig 3.3 Comparison of IR spectrum of TPA and BMOF

When we compare the IR plotting of Bimetallic MOF and terephthalic acid the peak at 1680 cm^{-1} is the characteristic peak of the terephthalic acid which was absent in Bimetallic MOF instead it shows the peak at 1602 cm^{-1} which concludes that the ligand is binding to the metal.

3.1.2 SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDX)

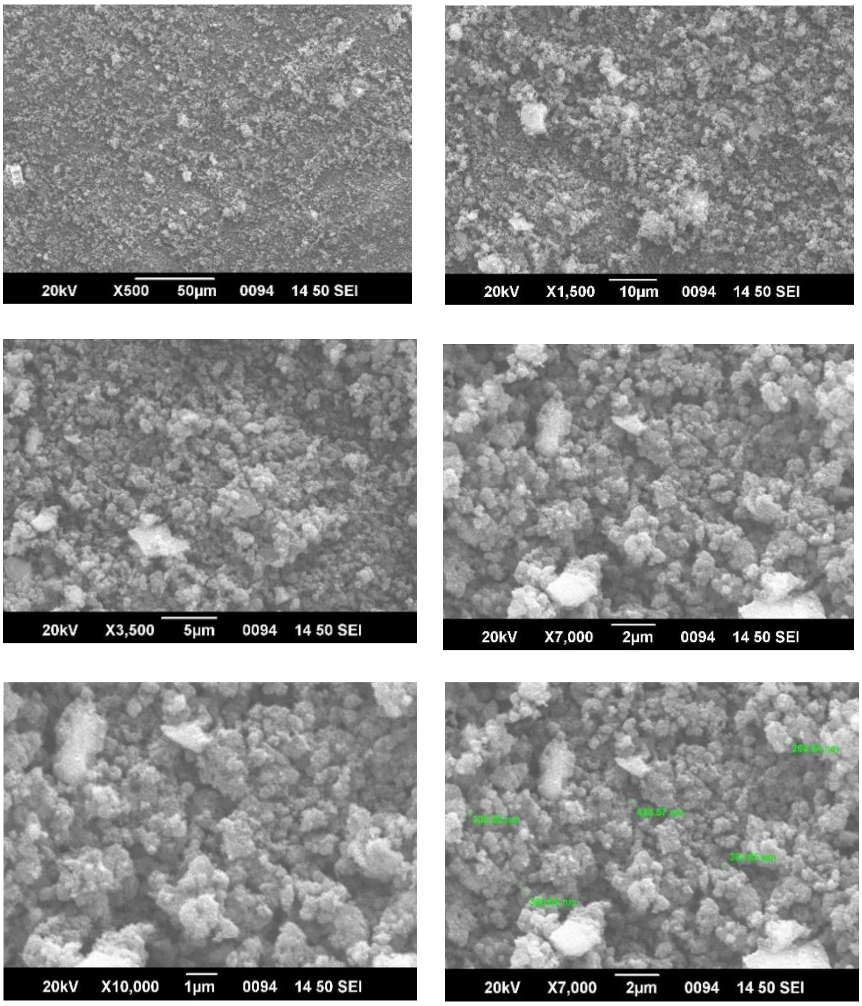

Fig 3.4 SEM images of BMOF (Different dimensions)

Scanning electron microscopy is a highly functional technique used to obtain high-resolution images and detailed surface information of sample. The surface morphologies of Fe-Al Bimetallic MOF at 500x to 7000x magnifications show their rough porous surface.

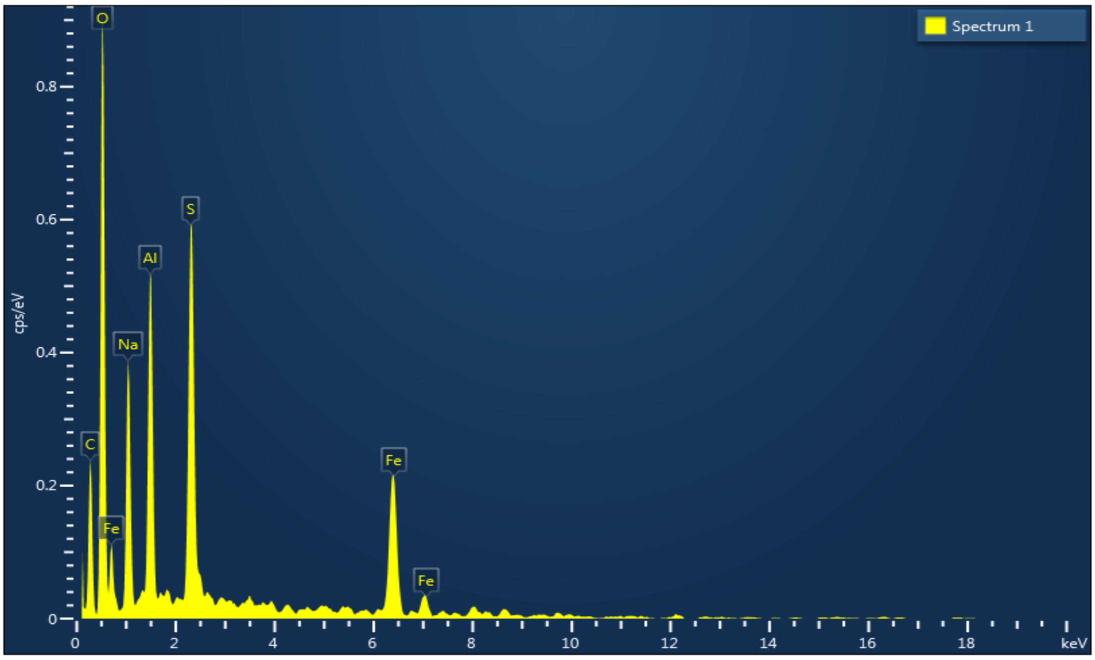

Fig 3.5 EDX spectrum of Fe-Al MOF

Element	Line Type	Weight%	Atomic%
O	K series	36.48	40.85
Na	K series	8.68	6.76
Al	K series	7.74	5.14
S	K series	8.35	4.67
Fe	K series	13.01	4.17

Table 3.1 Chemical composition of BMOF

The EDX analysis revealed the chemical composition of the BMOF having atomic percent of 40.85% for O, 5.14% for Al, 4.17% for Fe with 6.76% Na and 4.67% S as impurities.

3.1.3 X-RAY DIFFRACTION (XRD) ANALYSIS

The powder X-ray diffraction (XRD) patterns were carried out on Brucker AXS DB advance X-ray diffractometer. The prepared activated Bimetallic MOF was characterized by X-ray diffraction. Average size was calculated using Debye- Scherrer formula D=k λ/βCosθ, $where$ D is the crystalline size, λ is the wavelength of incident X-ray, β is the full width of half maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer's constant. Average size was calculated using Scherrer formula and was found to be 50.8856nm.

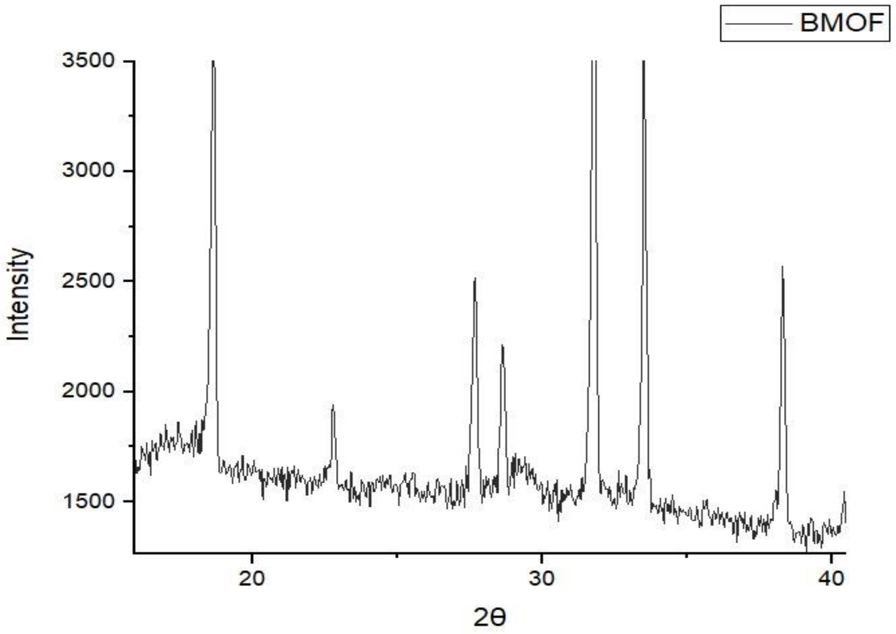

Fig 3.6 XRD graph of Bimetallic MOF

First peak

$D = K \lambda / \beta \text{Cos}\theta$

2θ =18.6566

2θ =18.6566× π/180

2θ =0.3256 radians

θ =0.1628 radians

β =0.1731

β =0.1731× π/180

β =0.0030

D =0.89× 1.5406 × 10-10 /0.0030× Cos (0.1628)

D =46.3169 nm

Second peak

$D = K \lambda / \beta \text{Cos}\theta$

2θ =31.765

2θ =31.765× π/180

2θ =0.5544 radians

θ =0.2772 radians

β =0.1699

β =0.1699× π/180

β =0.0030

D =0.89× 1.5406 × 10-10 /0.0030× Cos (0.2772)

D =47.5173 nm

Third peak

$D = K\lambda / \beta \mathrm{Cos}\theta$

$2\theta = 33.5094$

$2\theta = 33.5094 \times \pi/180$

$2\theta = 0.5848$ radians

$\theta = 0.2924$ radians

$\beta = 0.1353$

$\beta = 0.1353 \times \pi/180$

$\beta = 0.0024$

$D = 0.89 \times 1.5406 \times 10-10 / 0.0024 \times Cos\ (0.2924)$

$D = 59.6615$ nm

Fourth peak

$D = K\lambda / \beta \mathrm{Cos}\theta$

$2\theta = 38.2854$

$2\theta = 38.2854 \times \pi/180$

$2\theta = 0.6682$ radians

$\theta = 0.3341$ radians

$\beta = 0.1639$

$\beta = 0.1639 \times \pi/180$

$\beta = 0.0024$

$D = 0.89 \times 1.5406 \times 10-10 / 0.0024 \times Cos\ (0.3341)$

$D = 50.0466$ nm

Average size $D = (46.3169+47.5173+59.6615+50.0466)/4 = 50.8856$nm

3.2 APPLICATION

3.2.1 ADSORPTION OF METHYLENE BLUE

Fig. 3.7 gives the photograph of methylene blue and that of the mixture of methylene blue and Fe-Al MOF after 1 hour in the dark.

Fig 3.7Methylene blue solution before adsorption and after adsorption BMOF

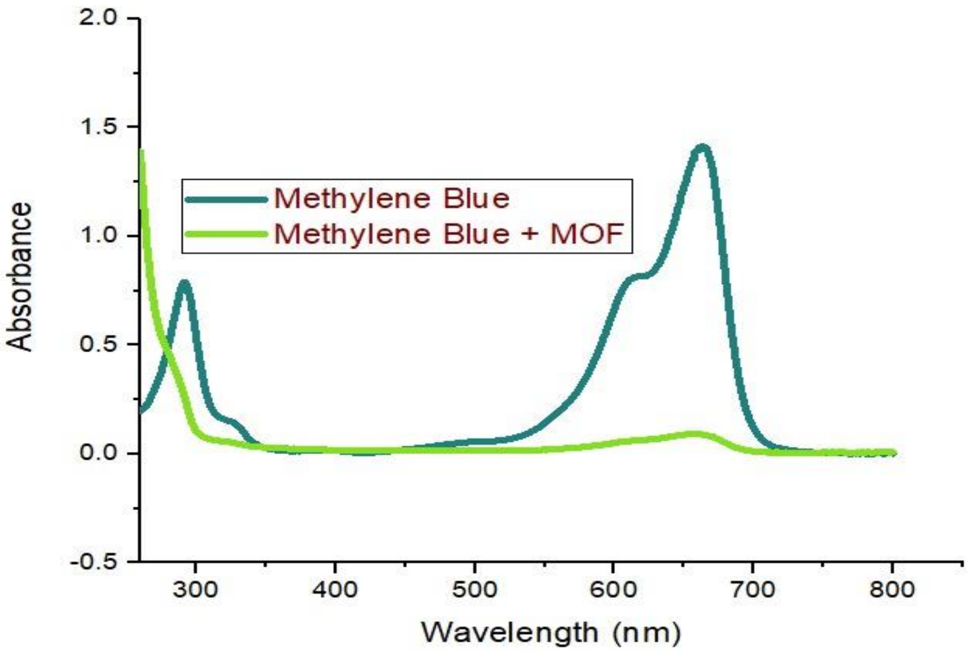

Fig 3.8 UV Visible spectrum showing dye adsorption by BMOF

- Methylene blue dye Adsorption spectrum has three main peaks. The maximum adsorption wavelength is around 665 nm, located in the visible light spectrum which attributes to the characteristic blue color of the dye.
- Smaller adsorption band located in the UV region at 300nm corresponds to π-π* the electronic transitions within the aromatic rings of the molecule.
- The peak around 600 nm corresponds to n-π* charge transfer (CT) transition.

Observations and conclusions after dye adsorption with Fe-Al Bimetallic MOF:

- The peaks found in UV visible spectrum of Methylene Blue dye are evidently absent in that of Methylene blue dye adsorption with Fe-Al MOF, indicating that the BMOF has adsorbed the Methylene blue dye.

Chapter 4

Conclusions

This study provides a distinctive approach for the synthesis of Metal Organic Framework (MOF) using Terephthalic acid (TPA) prepared from waste PET bottles. The synthesis method takes advantage of using waste PET bottles which is cost effective and promotes recycling of waste plastic bottles. Further, Fe-Al Bimetallic MOF was prepared using Ferrous Nitrate, Aluminum Nitrate and TPA. The prepared Bimetallic MOF were characterized using, Infrared Spectroscopy FTIR, XRD and SEM-EDX. XRD and FTIR results that validates the formation of MOF. The SEM images and EDX spectra provided an idea about the morphology and the elemental composition of the synthesized MOF respectively. The UV results shows that the synthesized Bimetallic MOF has ability to adsorb non-biodegradable dyes such as Methylene Blue.

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