FEASIBLE SYNTHESIS OF METAL ORGANIC FRAMEWORK AND ITS APPLICATION IN REMOVAL OF METAL IONS FROM WATER

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20PCH014

Dissertation work submitted to

Avinashilingam Institute for Home Science and Higher
Education for Women, Coimbatore – 641043,
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In Partial fulfilment of the Requirement for the Degree of
MASTER OF SCIENCE IN CHEMISTRY

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M. Amuthaselvi
Signature of the
Supervisor

26/5/2022
Signature of the
Head of the Department

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Preeethi S

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List of Abbreviation

MOF	**Metal Organic Frame work**
BDC	**Benzene Di Carboxylic acid**
TPA	**Terepthalic acid**
DMF	**Dimethyl Formamide**
Ni	**Nickel**
Cu	**Copper**
Zn	**Zinc**
Cd	**Cadmium**
Zr	**Zirconium**
Al	**Aluminium**
NaOH	**Sodium Hydroxide**
FTIR	**Fourier Transfer Infrared Spectroscopy**
TGA	**Thermo Gravimetric Analysis**
P-XRD	**Powder X-Ray Diffraction**
FESEM	**Field Emission Scanning Electron microscope**
$KMnO_4$	**Potassium Permanganate**
MLCT	**Metal Ligand Charge Transfer**
MB	**Methyl Blue**

1. INTRODUCTION

1.1 Environmental Status:

In this 21st century we are facing many social problems like infections and diseases. But the major problem in all century is pollution. Pollution affects all the resources of our life (land, water, air). To overcome this corona viral pandemic situation we follow lockdown, (i.e.) not using public transports, maintaining social distance, coming out of our residence only for essential purpose. Because of this practice, usage of vehicles and release of carbon di oxide, carbon monoxide were reduced in large scale, so the land and air pollution were considerably controlled.

But in this situation the water resources were polluted in the same level as in before pandemic, as the usage of medical field increases the level of producing biomedical waste also increases, the waste water from medicinal(pharmaceutical) industries also pollute water resources. In addition to this, waste water from fertilizer industries, paint industries, polymer processing industries, fabric industries, etc., also pollute water resources in considerable extent.

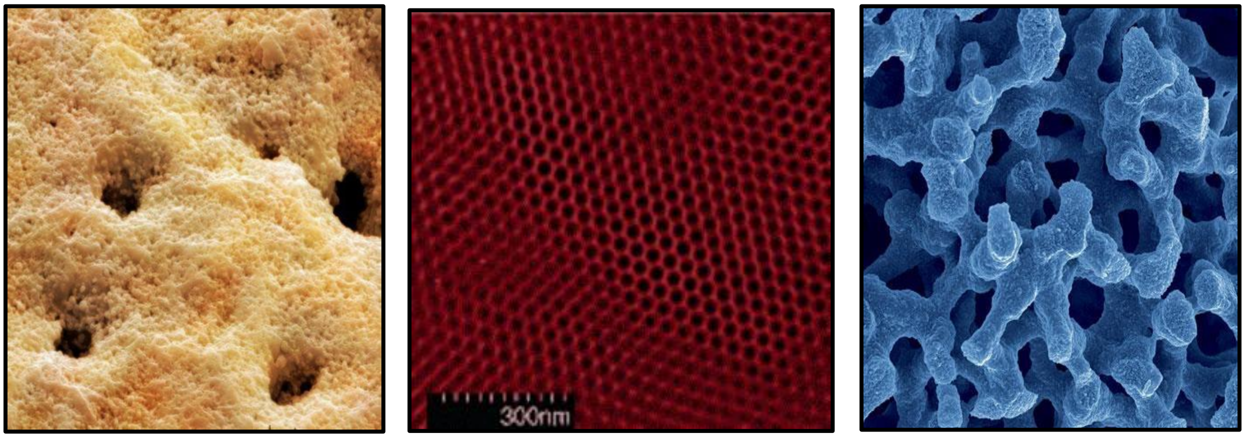
Figure 1.1 Contaminants IMAGE: THE HANS INDIA, 24 DEC, 2019

To overcome this pollution rate we have to choose a reusable and renewable method, here comes the boon for water pollution free environment, Metal Organic Frameworks (MOF) which is easy to use and recycle. By using Metal Organic Framework we can easily recover the pollutant particles. MOFs are sensitive and selective to particular pollutants. Metal Organic Frameworks follow adsorption technique to recover the pollutant particles. Adsorptions are of two categories, they are chemical adsorption and physical adsorption. Comparing to removing pollutants from land and air, water resources holds the complication in stability and pH of the liquid medium. The liquid may be polar or non-polar, organically or inorganically contaminated, which subsequently leads to the aquatic ecosystems damage by eutrophication. It is a Reliable and eco-friendly method, which can easily overcome these complications.

1.2 In Beginning Days:

Initially these pollutants are removed by advanced oxidation and biological oxidation method. As years passed, we utilized adsorbents for removing pollutants, some are Mesopores silica, Activated carbon, Cyclodextrins, Carbon nano particles (Nano tubes), Chitosan (Biopolymer - polysaccharide), Local clay, Silica beads, Egg shell.

Surface of Chicken egg shell **Carbon membrane** **Monolithic column**



Micropores(<2nm) **Mesopores (2-50nm)** **Macropores(<50nm)**

Figure 1.2 Adsorbents

Source: Google images

1.3 Reason to develop Metal Organic frame works

In the beginning we were used egg shells to remove heavy metals from water resources, it is also considered as an ecofriendly method. But the collection and processing made some complications, like difficulties in collecting and processing the raw materials to made adsorbents.

In case of egg shells their pores were uneven and roughness and pore size change by types and locality this may lead some difficulty in achieving desired adsorption and concentrations.

In case of charcoal adsorption technique, high molecular weight compounds could not be adsorbed and carried by them, at mean time highly pure substance cant suit for charcoal adsorption. Adsorption of readily flammable gas may lead to sudden combustions and chemical loss and fire accidents.

Till now studies were going on with carbon nano tubes and chitosan based materials in adsorption field. That's why we need advancement in this field, after that new adsorbent materials were designed and synthesized.

Newly Prepared Adsorbents:

- Covalent Organic Frame Works (COF)
- Porous Organic Polymers (POP)
- Covalent Triazine Frame Works(CTF)
- Metal Organic Frame Work(MOF)

1.4 Metal organic frameworks (MOF)

This innovative approach mixing and organic and inorganic field gives raise to the development of the field Reticular chemistry.

Origin of MOF:

In 1995, a unique class of crystalline porous materials, termed metal–organic frameworks (MOFs) by Yagh, emerged and has since distinguished itself with permanent porosity and high surface areas, due to the strong bonds between metal ions and charged organic ligands .

Metal organic frameworks (MOF) are irreplaceable field which connects both organic and inorganic fields. In this field, metal ions and organic linkers (ligands) are bound together to form 3- dimensional frameworks (Coordination bond links the metal ion and organic linkers). Organic linkers with hetero atoms undergo bonding in higher priority and holds beneficial usage in many areas. Normally the linkers were chosen as bidendate, tetradendate and polydendate to form desired frame woks. The linking between the metal ion and organic linkers build a cage like formation which aids the adsorption process. The linker may have ring structure like porphyrin, which creates a cavity within the MOF to facilitate it perform adsorption and storage feasibly.

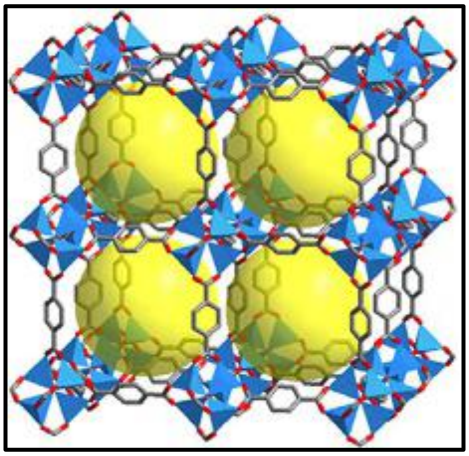


Figure 1.4 MOF Image [101]

The adsorptive tendency can be enhanced by functionalizing the MOF by post-synthetic modification, which involves incorporation of different groups and substituents into the synthesized MOF that improves the MOF performance in selectivity and sensitivity.

MOFs are crystalline particles, Mostly colored based on their central metal ion and ligands. Since these complex looks like cage structure, they can trap other materials and gases of desired condition.

Because of this tendency MOF mainly used in purification works in gas and water bodies through encapsulation and adsorption mechanism.

The adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface is known as adsorption. This procedure forms an adsorbate coating on the adsorbent's surface. This differs from absorption, which occur when a fluid (the absorbate) dissolves or permeates a liquid or solid (the absorbent)

1.5 Adsorption:

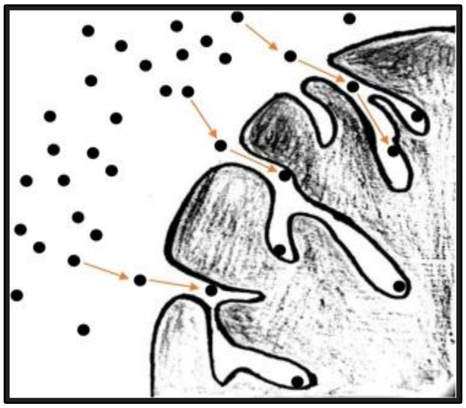


Figure 1.5 (a) Adsorption

Image Source: [113]

Adsorption is the main mark able character of Metal Organic Frame works, which is ruled by electrostatic attraction, Wander Waal’s force and Hydrogen

Adsorption holds two types,

- Physical Adsorption
- Chemical adsorption

Physical adsorption is a straightforward method that involves hydrogen bonding, van der Waals forces, electrostatic forces, and hydrophobic interactions to bind the target chemical on the adsorbent.

Chemical adsorption, also known as chemisorption, is performed by a significant sharing of electrons between the surfaces of the adsorbent and the adsorbate to form a covalent or ionic bond. As a result, chemical adsorption may not be completely reversible, and regeneration may need a huge amount of energy.

These two types of adsorption plays significant role in selective and efficient pollutants capture by Metal Organic Framework in aqueous medium.

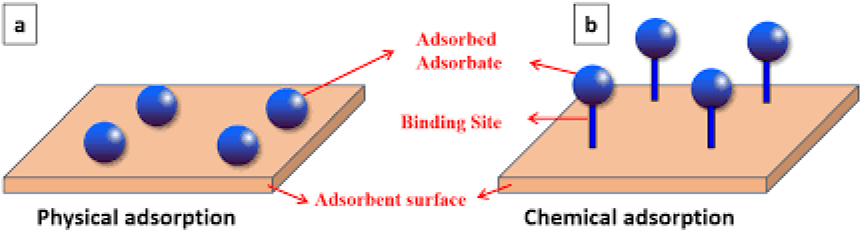


Figure 1.5 (b) Types of adsorption; **IMAGE:[81]**

Metal Organic Frameworks adsorption method is a conventional method which follows the mantra of triple-R (i.e.) Recover, Recycle and Reuse. Here both the adsorbate and adsorbent can be recovered, recycled and reused. Most of MOFs are water stable and hydrophobic, which do not cause any further pollution in the aqueous medium, so it can be easily recovered from water medium after water treatment by the means of filtration or evaporation.

The MOF adsorb the pollutants by just encapsulating them in-between their framework structures or the cavities in their network arrangement, because of this the adsorbed pollutants also not get affected and can be recovered easily by inducing desorption technology.

Recovery is the most important and necessary need in any inventions to move further in our lifestyle, here these Metal organic framework technologies can achieve it tremendously without any doubt, because they follow the property of adsorption, which doesn’t hold any strong boding with adsorbent and adsorbate.

1.6 MOF and its synthesis Techniques:

Now this field of reticular chemistry attracted many chemical researchers, because of its individuality, ability and stability. But its reproducibility makes more complication to researchers, MOFs were introduced in the fields like Drug scavenging, Gas adsorption, Gas storage, Heavy metal adsorption, Catalytic degradation, etc..

They were synthesized in many ways today like,

- Treditional method
    1. Solvothermal Synthesis
    2. Hydrothermal Synthesis
- Microwave Synthesis
- Sono-chemical Synthesis
- Electrochemical Synthesis
- Mechanical Synthesis

MOFs were prepared using the above mentioned methods and subjected to annealing and post synthetic modification if needed.

In solvothermal and hydrothermal methods MOFs were prepared by using Teflon lined Autoclave (Hydrothermal bomb) heated using furnaces to done the synthesize at high constant pressure for required time.

Annealing:

Annealing is a heat treatment process to increase ductility and reduce hardness to make more workable. It is done in post synthesis process, It may include, Recrystallization, diffusion.

1.7 Modern applications:

Metal organic frameworks have 1D, 2D and 3D structures made of metal clusters and organic linkers, they holds good cavity while interlocking between metal and ligands. Those ligands hold great affinity towards cationic and anionic species which fits to their MOFs cavity. By this way they can adsorb and remove pollutant particles from environment.

MIL (MIL stands for Materials Institute Lavoisier):

The MIL series (MIL stands for Materials Institute Lavoisier) focuses on carboxylate ligands (such as 1,3,5-benzene tricarboxylate, terephthalate, isophthalate, and others) and trivalent metal ions of V, Cr, Fe, Al, Ga, and In, as well as lanthanides, but also includes studies with metal ions in various oxidation states.

ZIF (zeolitic imidazolate frameworks):

The ZIF series is made up of zeolitic imidazolate frameworks made up of zinc and cobalt ions copolymerized with imidazole-type linkers. The ZIF structures are made up of nets of seven different alumino silicate zeolites with Zn or Co replacing the tetrahedral Si/Al clusters and bridging imidazolates replacing the bridging O (oxygen).

1.8 Functionalized Metal Organic Frame works:

MOFs have the potential to be effective drug delivery materials because their properties can be altered by finely tuning the pore size and altering the functional groups of the frameworks. The MIL family of MOFs, which may be made from trivalent metal centers and bridging carboxylates, is a promising class of drug delivery MOFs because of their high pore diameters (25- 24Å) and relevant surface areas (3100 -5900 m2/g).

Metal organic frame works always shows tremendous adsorption towards ions and molecules, we have to use it properly in correct situation and conditions.

Because of their cavity content due to the inter linking of linear ligand and porphyrin ligand in some Metal organic Frame works, they are used in gas storage and gas separation by selective adsorption.

The selectivity of Metal organic Frame works are achieved by the pore size and functionalized groups attached in ligands from the starting material or incorporated by post synthetic modification.

By Hydrogen bonding:

Using of multifunctional groups like –OH, -$NH_{2,}$ and carboxylate are used in hydrogen bonding formation which stabilize the interlocking structures of ligands with metal clusters, in addition to that they helps in controlling pressure during gas adsorption and gas storage.

By Electrostatic interaction:

[10] These extra functional groups produce a charged surface on the Metal Organic Frame works which makes electrostatic attraction towards the adsorbates (pollutants). This electrostatic attraction is the main key in selective and best adsorption in all conditions,.

This electrostatic attraction is the main reason in storing the adsorbates (pollutant) for long time within the Metal Organic Frameworks.

If the pollutant particles are neural this electrostatic attraction can’t hold them firmly, In these cases size of pores paly the major role, it may be mesoporous or macroporous according to the size of the pollutants MOFs can be used.

Dye adsorption:

In the field of dye adsorption, there are two types of dye cationic dyes anionic dyes whose adsorption can be achieved by electrostatic interaction property of MOFs, b.(63) aromatic dyes are readily degrade to carcinogenic toxic chemicals. They must be remove form the environment.

1.9 Scope of the work:

The growing accumulation of contaminants in the environment can cause direct and indirect water pollution. The fact that these contaminants are not or cannot be eliminated from the municipal water utilities, poses a significant concern. Researchers are currently pulling massive attention to improve existing technologies, develop new strategies for water contamination problems. Adsorption and photo degradation are two of the most sustainable technologies that are used in water purification. These technologies have many advantages because of the economic and simple. Within these applications, metal organic frameworks (MOFs) are playing a significant role as novel class of porous materials characterized by a crystalline structure. MOFs are considered good applicants to be employed in wastewater treatment technologies because of the tunability of their features.

With this interest we studied the interaction and stability of bonds between metal clusters and their stability in the Metal organic frame works and analyze the adsorption of metal ions in aqueous medium.

2. Review of literature:

2.1. Inorganic pollutants review:

[1] Incorporating the sulfonyl and amide groups to the Dual functional Metal organic framework (TMU-81) enhance the removal of heavy metals cd(II), Cu(II), and CR(II) ions. The maximum adsorption capacity for Cd(II) was 526mg/g. It is achieved by the presence of high oxygen bearing functional groups on the surface of the pore cavity. The reusability can be achieved by pyrolysing the Metallic structures at 800°C in Ar atmosphere

[2] MOF-808 is synthesized with Zr metal cations and 1,3,5-benzenetricarboxylic acid ligands, The particle size of MOF-808 is improved from 40nm to approximately 1000nm with the help of a modulator formic acid, desired particle size can be achieved by varying the concentration of formic acid addition. It removes the oxometal ions. Mainly Chromium (VI) ion, It is prefored for potassium dichromate, the adsorption rate is 731.0mg/g.It is stable after four cycles,After that it may lose its crystallinity.

[3] MIL-100(Fe) is prepared hydrothermally with Fecl3.6H2O and trimesic acid. Fe-BTC Metal organic framework is also prepared by easy magnetic stirring method. These two MOF's individually shows good adsorption towards lead and cadmium ions. Their adsorption towards lead ion is 0.895mg/g.min . For this adsorption they follow pseudo second order reaction. Since, these two MOF's are reusable; the adsorbed heavy metal cations can be collected as whole. Recycle process of these MOF's were achieved by ethylene diamine tetra acetic acid di-sodium (EDTA-2Na). Here, MIL-100(Fe) is a highly crystalline micro porous and Fe-BTC is amarphous with macro porous. Adsorption rate is good at the pH of 7, which is alkaline

[4] Ag-Fe MOF is prepared with $Fe(NO_3)$, $AgNO_3$ metal clusters and Benzene 1,4-dicarboxylic acid in autoclave by using DMF as solvent. This Ag-Fe MOF has good adsorption capacity. It absorbs cadmium ions in the rate of 265 mg/g and copper ions in the rate of 213mg/g. Since this MOF is bimetallic the surface of the Ag-Fe MOF shows some acidity and can act as catalyst.

[5] La-MOF-900 was prepared by hydrothermal calcination method with La(NO3).6H2O and 1,4-dicarboxybenzene, using the solvent DMF. The synthesized MOF is pyrolysed at 900°C to

convert it into porous carbon and La_2O_3 composite. The pore size of composite shows $34m^2/g$ ~ 12.9nm.which shows efficient adsorption towards Butylparaben (BPB) by 98% in 240mins and Arsenic (III) by 80% in the wide pH range of 3 to 9 at single pollutant system.

[6] Here the Zr -MOF was prepared by reflexing the $ZrCl_4$ and pyromatallic acid mixtures in suitable solvent for 24 hrs. The synthesized MOF was a $Ni_{50}Co_{50}$-layered double hydroxide/UiO-66- (Zr)-$(COOH)_2$ nanocomposite (LDH/MOF NC). It is ultrathin and two dimensional in structure. It has high adsorbance tendency towards Hg (II) and Ni (II) cations. The metal cations were accumulated in between the two layers. The maximum adsorption of Hg(II) is 509.8 mg/g and Ni(II) is 441.0 mg/g. This much binding adsorption is achieved by the abandance binding sites like -COOH,-NH- and -OH groups.

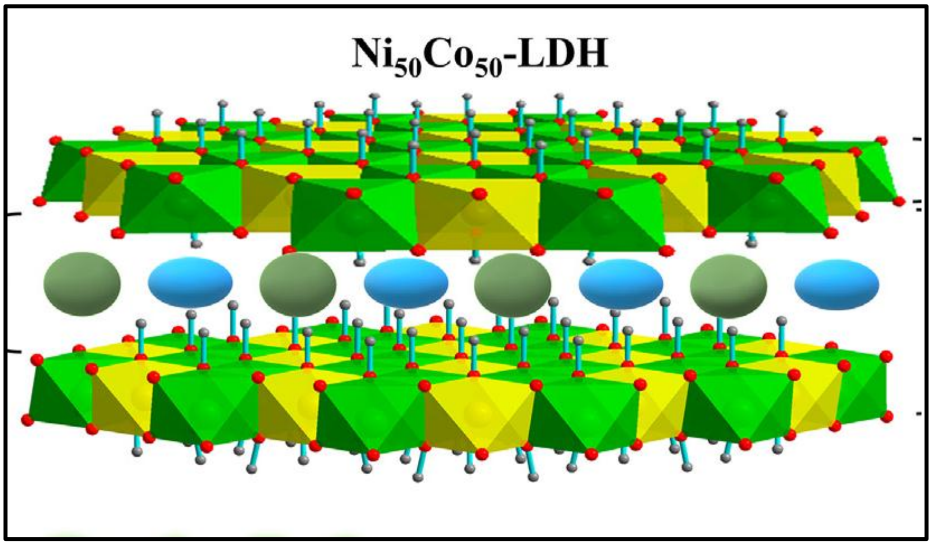


Figure 2.1 (a) NiCo-LDH/MOF nanocomposite Image [6]

[7] Zr(IV) based MOF with pyrene based ligands is functionalized with thio group. It shows cubic morphology and robust porous framework. The sulpher functionalized MOF shows hydrophobicity which is favorable for electrochemical sensing of Hg ion. The Pauling electronegativity of mercury ions shows higher affinity towards thio functionalized MOF. Ther is a strong affinity between Zr (lV) MOF. It adds to the high stability of the MOF.

[8] Three dimensional, water stable, microporous anionic metal-organic framework, is prepared with DMA, Eu $(NO_3)_3.6H_2O$ and 1,3-bis [(carboxy)-phenoxy] propane in a teflon lined stainless steel autoclave. It shows high poresity and adsorbance towards Nitrobenzene and Fe (II)

For good metal sensing [MeeNH2]+ cation is incorporated to the MOF. The amine group shows tremendous quenching towards the Fe(II) ion among other metal ions. Other metal ions like lead and copper also adsorbed at good rate lead (99.5%), copper (93.9%), Iron (99.2%). The time taken for complete adsorption is 24 hours.

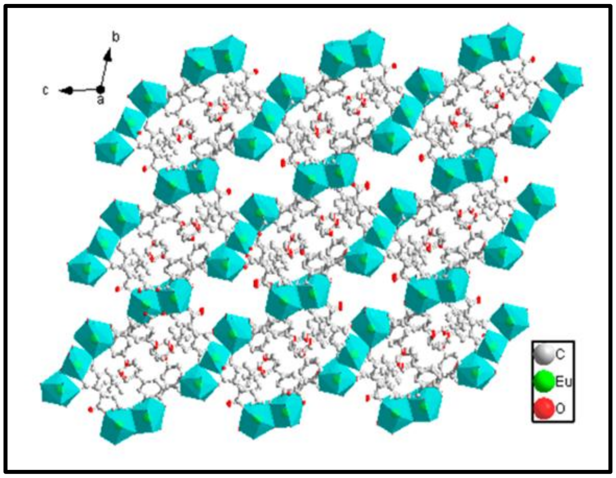


Figure 2.1 (b) 3D View of the Eu MOF along the a-axis [8]

[9] Fe-based MIL-(Fe) MOF is synthesized hydrothermally with graphene oxide to get a sandwich structure, with adsorbant active sites. Its capacity of adsorbance towards lead ions in aqueous medium is 128.6mg/g. It follows pseudo second order reaction. The reaction time is 15 minutes. This MOF is reusable and hydroxides by binding with oxygen or hydroxy groups of MIL-101(Fe)

[10] Mesophorous [PCN-221] a Zr -based MOF is prepared solvothermally with Zr cluster and meso-tetra (4-carboxyl) porphyrin, which holds the property of selective sensi5 ng of Hg^{2+} and fluorescent sensor for the same. This MOF shows fast fluorescent response under <1 min. It follows pseudo second order kinetics, and removes the 95% of suspended Hg2+ ions in 30 mins.

[11] A Highly luminescent Zn(II)-MOF, $[Zn_2(T_2T_2)(BDC)_2]$.2DMF, T_2T_2-2,5-di(4-pyridyl) thiozole(4,5-d) tioazole and BDC-1,4-Benzenedicarbixylic acid is solvothermally prepared. Products were obtained in crystal form. This MOF exhibit high and strong blue emission while sensing the choromate and MnO^{4-}.It is highly selective and recyclable. It follows energy transfer mechanism for its fluorescence. Its sensing property and adsorption tendency was high at the PH of 7.

[12] (Mn(TPA)-SWCNTs) MOF single walled carbon nano tubes was synthesized using manganese chloride, terephthalic acid and SWCNTs. Mn (TPA) MOF has stronger adsorption tendency towards lead ion (Pb^{2+}) than the other common heavy metal ions. This MOF also has high electrical conductivity; their practical adsorption experiment was done with industrial waste water, human serum. BET surface area for above synthesised Mn mof is 668.61 m^2/ g. the recovery of Pb2+ in industrial wastewater and serum samples are in the ranges of 99.5–103.0% and 98.1–106.8%, respectively.

[13] Fe-based metal-organic frameworks (MOFs), MIL-101 and NH2-MIL-101 were investigated to perform adsorption towards phosphate ions. The concentration of phosphates decrease sharply from the initial $0.60mg \cdot L^{-1}$ to 0.045 and $0.032mg \cdot L^{-1}$, respectively, within just 30min of exposure with the phosphate contaminated water. Iron based MOF shows high adsorbance towards phosphate ions than bromide, Chloride, nitrate and sulphate ions.

[14] Zn imidazolate framework (ZIF -8) was synthesized with high adsorbance capacity and pore size. ZIF-8 was tested for the adsorption of arsenate ions .ZIF-8 removes 38% percentage of suspended arsenate were ZnO functionalized ZIF-8 removes 70% of arsenate ions at the pH of 7. Here ZnO wurtzite crystals were used as a source for the Zn ions for ZIF-8 and as the nucleation site for the crystal growth of ZIF-8.

[15] In Hydrothermal method Terephthalic acid and pyrezene based MOFs were prepared with nickel and cobalt metal clusters. They show good adsorption tendency towards chromium ions is about 96% adsorption in 50ppm solution of chromium ion. FT-IR and XRD methods were applied to confirm the structure of the synthesized.

[16] High efficient sensing and removal of mercury from drinking water and agricultural products by copper based metal organic frame work (JUC-62). Which is made of copper and 3,3’, 5,5’-azobenzenetetracarboxylicacid, above prepared MOF is crystalline and porous and was characterized by scanning electron microscopy, thermo gravimetric analysis. It holds good adsorption capacity, maximum adsorption capacity of JUC-62 for Hg^{2+} was 836.7 mg/g, and the adsorption reached equilibrium in 15 min with the concentration of 0.1 mg/mL Hg^{2+}.

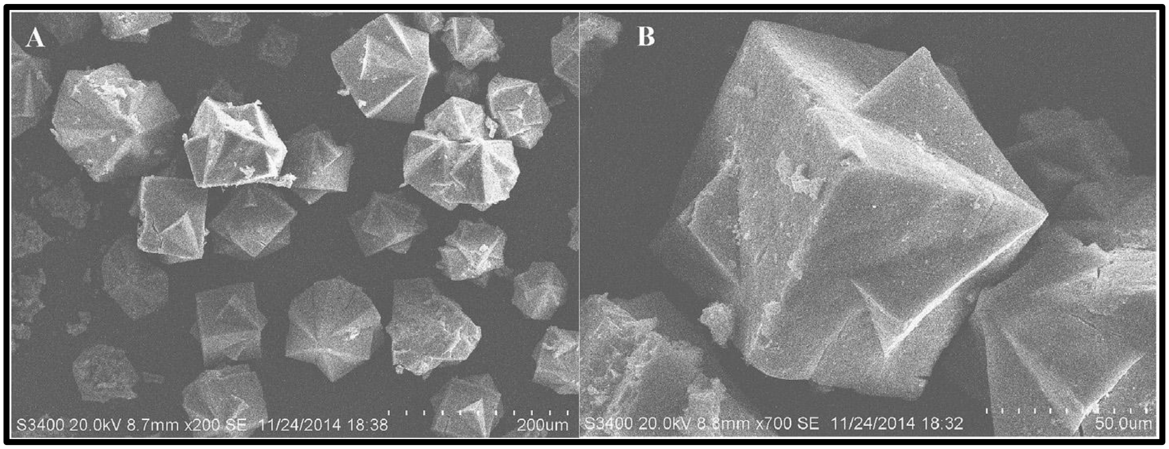


Figure 2.1 (c) FESEM image of JUC-62 [16]

[17] MOF-74-Zn a Zn based MOF $Zn_2(DHBDC)(DMF)_2 \cdot (H_2O)_2$ synthesized with the organic ligand DHBDC: 2,5-dihydroxy-1,4-benzenedicarboxylic acid, the calculated adsorption capacity for JUC-62 is 74.85mg/g, the maximum adsorption capacity of Hg(II) by MOF-74-Zn was reached to 63 mg/g . At ultra-low concentration of Hg(II) with the removal efficiency of 54.48%, 69.71%, 72.26% when the initial concentration of Hg(II) is 20ppb, 40ppb, 50ppb, indicating the potential application of it in the removal of ultralow levels of Hg(II) ions from the water.

[18] Nowadays the sensing and removal of Hg ion from drinking water is going worse and complicated UiO-66-SH showed high adsorption performance over a broad pH range (2.3–8.0) towards mercury ions. It displayed selective adsorption towards Hg(II) ions under the inteference of divalent metal ions (i.e., Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Ba^{2+} and Mn^{2+}). UiO-66-SH can reach the adsorption equilibrium with more than 99 % of the adsorption rate in less than 20 min; the adsorption capacity of UiO-66-SH calculated from the Langmuir isotherm model was 3.91 m mol/g (785 mg/g), which is considerably larger than those of many other thiol-functionalized adsorbents with adsorption capacities less than 300 mg/g.

[19] NH2-functionalized Zr-MOFs were prepared via a rapid microwave-promoted synthesis with $ZrCl_4$ and 2-NH_2-1, 4-benzenedicarboxylic acid dissolved in 40mL of N,N Dimethyl formamide. The adsorptive removal towards Pb (II) is 99.95% after 120 min at temperature of 30˚C and pH of 6 with an initial concentration of 10 mg·L-1, the adsorption capacity towards Cd (II) achieved 177.35 $mg \cdot g^{-1}$ at an initial concentration of 40 $mg \cdot L^{-1}$.The adsorption mechanism

followed is pseudo second order. The adsorption capacities of Pb (II) and Cd (II) decreased with pH, and this can be used to desorb the heavy metal ions. This may help in reusability of MOF.

[20] MOF holds huge surface area which promotes high adsorptive removal of contaminants from the environment; it can be a good conventional method in decontaminating the environment. MOFs contains open metal sites which can act as Lewis acid, these Lewis acid sites can remove Lewis base contaminants readily and efficiently from eater and air. For e.g., NU-110E holds (BET) surface area of 7140 m^2/g.

[21] ZIF-8 a Metal over organic frame work which is used to remove heavy metals from water bodies with the efficiency of 38% towards copper ions in water, when it is coated over polyacrylonitrile (PAN) nano fibers and performed adsorption, It shows higher efficiency of 96.5% towards copper ions in aqueous medium. This polyacrylonitrile (PAN) nanofiber facilitate good flexibility and heavy loading of MOF materials.

[22] the influence of heavy metals in water pollution are raising in higher concentration (ions of lead, arsenic, cadmium, mercury, chromium, zinc) the arsenic ions are in the form of arsenate AsO_4^{3-}, arsenite AsO_3^{3-} ,these ions can be removed by MOFs. MnO_2-MOF was synthesized by oxidation of $MnSO_4$ through $KMnO_4$. This MOF proved highly efficient for adsorption of lead (II) ions and adsorption capacity was found to be 917 mg/g and equilibrium has attained within 1 h. Initially, the pH of the solution was 6 and it dropped to 5 during the adsorption process.

[23] Zn based metal organic framework is prepared with zinc nitrate metal clusters and 5-amino isophthalic acid ligand, it shows wide range of sensing towards mercury ions compared to other metal ions in aqueous medium at the pH of 4 to 11. This MOF shows high water stability. Its selective mercury ion sensing ability helps in removing the highly toxic mercury ions from normal drinking water and sewage water In the presence of other metal ions.

[24] MIL-125 is functionalized with amine group to increase its efficiency of adsorption towards lead ions from aqueous medium, maximum adsorption capacity of this functionalized MOF towards lead ions is 561.7 mg/g at pH 5 and 298 K. It can be recycled over six cycles of adsorption and desorption of lead ions.

[25] Zn based MOF is made with zinc metal clusters and 1, 4- benzene di carboxylic acid. It has notable adsorption property, so it is used to scavenge heavy and toxic metal ions like

mercury and arsenic ions from water resources. It achieves its efficiency of adsorption nearly 100 percentages towards the heavy metal ions from water. The functionalized MOF is coater over grapheme sheets to perfume adsorption, the graphene sheet increases its elasticity but reduce its stability.

[26] Zr Based metal organic frame works prepared to adsorb the arsenite ions from water media, in the meantime modulator like acetic acid or trifluro acetic acid was added to the synthesis mixture to enhance the capacity of the mof to be prepared. After the modulator have introduced, the mof shows adsorption of 200mg/g towards arsenite in aqueous medium.

[27] Metal organic frameworks were designed to remove the oxyanion/cation (PO_4^{3-}, AsO_4^{3-}, SeO_3^{2-}, SeO_4^{2-}, $UO_2{}^{2+}$) from aqueous medium. The Zr based MOF NU 1000 can adsorb 102mg/g selenite ion impurities from water. UIO-66 shows good adsorption towards phosphates as 237mg/g.

[28] Zr based metal organic frame work was synthesized with the ligand biphenyl 4,4-dicarboxylic acid. Thus synthesized MOF was functionalized with amine and thio functional groups incorporation. The functionalized MOF UIO-66 shows good adsorption towards Eu(II) in the rate of 253.8 mg/g than non-functionalized UIO-66, which shows 147.1 mg/g, in aqueous medium. This shows greater stability in basic medium.

[29] Iron MOF was synthesized solvothermally with 1,3,5-benzenetricarboxylic as ligand. The synthesized Fe-BDC metal organic framework shoes gel like behavior and stable in common organic solvents. This polymer was tested for arsenic removal from water at different PH ranges. It shows spontaneous adsorption towards arsenic and shows 36 times more adsorption than commercial Iron nano composite.

[30] Polymer of Metal organic framework $[Cu_3(BTC)_2(H_2O)_3]_n$ (HKUST-1, BTC = benzene-1,3,5-tricarboxylate),a facile coordination based material was synthesized and functionalized with thiol group. It is used to adsorb heavy metal ions from aqueous medium. Its high adsorption capacity is (714.29 mg /g) for Hg^{2+} adsorption from water.

2.2 Organic pollutants adsorption review:

[31] MIL-53 a MOF of chromium and benzene di carboxylic acid shows tendency towards the adsorption of organic molecules. This particular MOF adsorb Bisphenol molecules in good rate which is a hazardous endocrine disturbing chemical. Within one hour MIL-53 show very fast adsorption of Bisphenol of 421m^2/g and micro pore volume is 0.49 cm^3/ g. Comparing to activated carbon MIL-53 shows quite high rate of adsorption towards Bisphenol.

[32] Zr based Metal organic frame works shows extraordinary effectiveness towards detoxification of phosphorous based chemical warfare agents (CWAs) especially sarin. Here they incorporated the organo phosphorous chemicals like sarin and its stimulant dimethyl methyl phosphate as secondary building block for Zr-MOF to enhance the MOF property. By this way the hazardous chemicals were used in safe conventional methods.

[33] Sn-MOF was synthesized hydrothermally at 170˚C using autoclave. This is used to remove Acid Red 3R. The adsorption capacity of Sn-MOF is 141.88mg/g and the adsorption mechanism followed is chemisorption. The capacity of this MOF in AR3R adsorption doesn't show any alteration after six cycles. Here the adsorptive rate is greatly influenced by inter particle diffusion and flim diffusion.

[34] Fe and Mn based MOF show promising development in removal of pharmaceuticals by adsorption method. Which is eco-friendly and conventional. Since Fe and Mn are in affordable cost compared to other d block metals, it is very easy to manufacture and use. These MOFs can also remove antibiotic resistant bacteria. Supportive materials such as polyethylene glycol (PEG) and zeolite are used to improve the performance of the adsorbents (Fe and Mn based MOF). Results show 10% more amoxicilline removal and 30% more ampicilline removal by PEG, while nearly 30% more ampicilline removal is found by zeolite.

[35] Nano composite arranged in carbon sheets of C@Ni and C@Cu, are synthesized through annealing of Ni-BDC and Cu-BDC metal-organic frameworks (MOFs) under an argon atmosphere at 600 °C. Their catalytic performance was tested for the catalytic reduction of environmental pollutants such as 4-nitrophenol, methyl orange and methylene blue. TGA showed successful carbonization of the MOFs and enhanced resistance to thermal decomposition

of the magnetic C@Ni and C@Cu nano catalysts compared to the parental MOFs. The above synthesized mof retain its stability after 5 cycles.

[36] Cu-BDC@GrO and Cu-BDC@CNT, are synthesized via a facile and one-pot green solvothermal method. GrO- Graphene oxide, CNT-carbon nanotube, they show good adsorption character towards chemical compounds, it is tested by adsorbing the bisphenol molecules which is a chemical present in many industrial waste water. The adsorption processes were exothermic and spontaneous at which the adsorption capacity decreased with raising temperature.

[37] [CoNi (μ_3- tp)$_2$ (μ_2-pyz)$_2$] MOF was prepared with the utilization hydrothermal procedure. The above synthesized MOF is mixed vigorously with $Na_2WO_4.2H_2O$ to prepare MOF/$CuWO_4$ composite. MOF/$CuWO_4$ composite system possesses 801m2/g specific surface area with a 2.3 nm average pore diameter and 0.47 cm^3/g pore volume. With the help of this composite MB and 4-NP contaminants were removed about 98 and 81%, respectively.

[38] A cationic MOF (SCNU-Z1-Cl) possessing tubular channels with diameter of 1.5 nm, was prepared with Ni(II) and a nitrogen-containing ligand. It holds high BET surface area of 1636 m2/g, and shows high hydrolytically stability in pH range from 4 to 10. The anionic dyes with different sizes including methyl orange, acid orange. The adsorption capacities for them are 285, 180, 585, and 262 mg/g, respectively. The adsorption capacities of CrO_4^{2-}, $Cr_2O_7^{2-}$, $MnO4^-$, and ReO_4^- are 126, 241, 292, and 318 mg/g, respectively. It can differentiate dyes by adsorbing them in three ways as size-dependent, charge-dependent, and kinetics dependent selective adsorption.

[39] Zr based MOFs are designed to remove per and poly alkylated substances from water bodies which are emerging contaminants, with bio accumulative tendency and persistence nature. (MOF) NU-1000 was designed for the adsorption of three perfluorosulfonic acids (PFSAs, C4−C8) and six perfluorinated carboxylic acids (PFCAs, C1−C9) from aqueous solutions. It exhibit outstanding adsorption capacities of 400−620 mg/g for PFSAs and 201− 604 mg/g for PFCAs. The recovery and removal of pollutants by NU-1000 for PFAS after five cycles was excellent and effective.

[40] Removal of Persistent Organic Pollutants (POPs) POPs can be categorized into persistent toxic substances (PTS), pesticides and herbicides, phenols, antibiotic drugs. Cr-based MOFs (MIL-101(Cr) and MIL-53(Cr) were used to remove methyl orange, methyl blue, ethylene

di amine. UiO-66, MIL-101(Cr), MIL-53(Cr), and MIL-100(Cr, Fe), shows the remarkable adsorption capacity of H2-PA (Q_m of 654 mg/g). By this method POPs can be recovered and MOFs can be recycled.

[41] (Fe_3O_4@MIL-53(Al)) was prepared by solvothermal method. It holds excellent adsorbing tendency, bisphenol A (BPA), tetracycline (TC), congo red (CR), and methylene blue (MB). Its adsorption capacities were found to be 160.9 mg/g for BPA, 47.8 mg/g for TC, 234.4 mg/g for CR, 70.8 mg/g for MB. A UV/Vis spectrophotometer was used to measure the dye concentrations in the solution. MIL-53(Al) {$Al(OH)[O_2CC_6H_4$- $CO_2]$}, which has a high thermal stability, structural flexibility and less toxicity.

[42] MIL-101(Cr) was prepared solvothermally. To induce the magnetic property Fe_3O_4 molecules were incorporated into MIL-101(Cr) metal organic framework .this modified MOF is used to adsorb ciprofloxacin an antibiotic from aqueous medium, the maximum adsorption value for ciprofloxacin was 63.28 $mg.g^{-1}$ at 298 K and 22.93 $mg.g^{-1}$ at 313 K, indicating the exothermic nature of the adsorption. Its desorption is done with the phosphate buffered solution.

[43] A double layered MOF (M-ZIF-8@ZIF-67) is synthesized with Fe_3O_4-ZIF-8 as magnetic core and a layer of ZIF-67 is wrapped outer. It is used to adsorb and desorb the fipronil and its metabolites from aqueous media. Its surface area is 219 m^2/g and show high adsorption capacity for fipronil, fipronil desulfinyl, fipronil sulfide and fipronil sulfone. Removal rate of fipronil in water and cucumber by above mentionesd MOF were 70.9–99.7%.

[44] MOF-74 (Zn) a Zn based MOF is modified to (ZnO-C) composites. To enrich them with high adsorption tendency, it shows surface area of 782.971 m^2/g and pore volume of 0.698m3/g, when the above composite pyrolyzed at 1000^o C (ZnO-C1000) exhibit the best performance for organic pollutant uptake by adsorption. 50 mg of ZnO-C1000 can remove all the suspended dye of Rhodamine B from aqueous medium at the high concentration of 40 mg/L. it also exhibit super capacitance property, which is retained ~97.8% capacitance after 1000 cycles of usage. It is really high and stable.

[45] They synthesized a Fe3O4/MOF@GO hybrid composite, which is a nanoadsorbant with magnetic property, it is used to adsorb methyl blue dye and some common metal ions (Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, SiO_3^{2-}). In the above composite framework can be altered varying the metal

clusters of MOF. Here they have compared the Ni and Co MOF composites. The adsorption towards Methyl blue is an average of 30.52 and 13.75 mg/g for the Co and Ni composite. For sulfate ions, adsorption increases by 92.1 mg/g for Co composite and 112.1 mg/g for Ni composite. After adsorption, each of the adsorbents was rinsed with acetone and heated to 100 ºC for 12 h in order to fully degrade the adsorbed dye.

[46] Ni-MOFs was synthesized solvothermally and carbonized in nitrogen atmosphere, with this self assembled hydrogels were made by adjusting the water and ethanol ratios, since those two were used for self align the composite particles. With this nano fibers low density aerogels with high hydrophobicity and flexibility was prepared, its low density and hydro phobic character facilitate us to treat oily water pollutants by adsorption technology. And also used in hydrogenation reactions, its adsorption tendency towards nonpolar molecules are high than adsorption towards polar molecules in aqueous medium by Ni Metal Organic Frame works.

[47] $Zn_6(IDC)_4(OH)_2(Hprz)_2]$ MOF is made by solvothermal methods as nano flowers and nanosheets with particle size average of 95 and 116 nm, respectively. Nano flowers are thermally stable up to 365 ℃. They are used to photo degrade antibiotic molecules which pollute water bodies. They can degrade 37% of the amoxicillin compounds within 180 min. they can eliminate 92.5%, 88% and 89% of the antibiotic molecules from the 60-ppm concentration of amoxicillin, ampicillin and cloxacillin solutions. Their adsorption process follows pseudo first order kinetics.

[48] Zr based MOF is functionalized with (UiO-66-H, $–NH_2$, $–NO_2$, -Cl) amino, nitro and chloro groups. Its highest adsorption capacity (2.3 to 0.4 mg/g), its adsorption capacity towards ampoxillin (AMX) molecules varies accordingly with the substituents added for modification. Ampoxillin a largely produced drug, In addition to this electrostatic interaction and molecular interaction also accounts to the AMX adsorption. there were at least 13 kinds of hydrogen and π-hydrogen bonding interactions for AMX adsorption, which also helps in its adsorption.

[49] Porous starch-chitosan-UiO-66-COOH composite was designed to remove pharmaceutical waste from sewage; its Zr and carboxylic acid group presence merely attract the sulphanamide group from sewage. Adsorption isothermic studies were done at 25°C. The concentration of sulfanilamideis 160 mg/l. 20 mg of adsorbent was added into 50 mL of

sulfanilamide solution and then shaken at 200 rpm for 8 h. then UV was taken before and after adsorption to study the adsorption.

[50] Water stable Metal Organic Frame works were designed to recover the highly toxic water pollutants from water bodies, by eco-friendly adsorption pathway. To increase its ability of adsorption secondary building units were incorporated into MOF, they also possess large surface area of about 1000 to 10000 m2/g, which helps in adsorbing the large size pollutant molecules from water bodies. A Zr base mof, MOF(DUT-67) has octahedral-type, cage size and cuboctahedra-type cage size of 11.7 Å and 14.2 Å and window sizes of about 6.5 Å and 8.5 Å respectively. Its Sorption capacities are 11.2 mg/g and 110.2 mg/g for nicotinamide and niacin respectively, at 1:1 ratio solution.

[51] MIL (101) and amine functionalized NH_2- MIL (101) are prepared solvothermally, Amine functionalize MIL (101)Fe was designed to remove imidacloprid in aqueous solution. The maximum IMC removal values were determined as 100%, it is also used to photo degrade pesticides pollutants, this MOF shows good thermal and water stability. The adsorption tendency of the NH2- MIL-101(Fe) was notably higher than that of MIL-101(Fe) found to be much more effective because of electrostatic interaction at acidic pH levels.

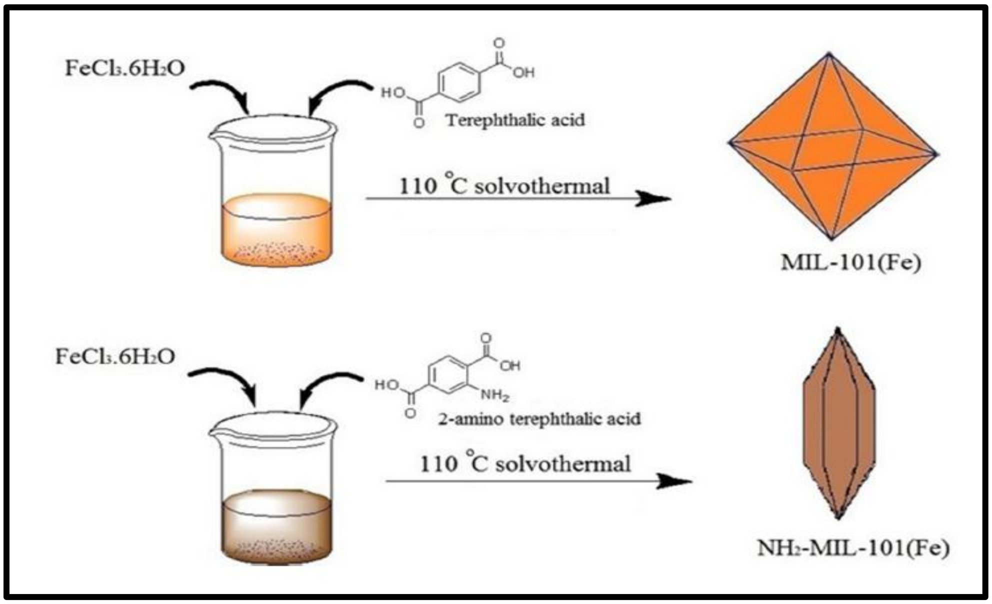


Figure 2.2 (a) Solvothermal synthesis [51]

[52] NU-1000 a Zr based MOF shows extremely high water stability, $[Zr_6(\mu_3O)_4(\mu_3OH)_4(OH)_4(OH_2)_4]^{8+}$ an yellow solid, was synthesized with $ZrOCl_2{\bullet}8H_2O$ clusters and H4TBApy ligand in solvothermal way with DMF as solvent. It holds many OH groups and protons. Its protons characters also influence in its performance of adsorption. This mof also functionalized with OH and some functional group incorporation. Each functional is group specific in its action, and helps in adsorbing specific pollutant molecules.

[53] $[Co(3\text{-bptzp})(1,4\text{-BDC})(1,4\text{-H2BDC})_{0.5}]$ and [Cu(3-bptzp)(1,4-BDC)] are copper and cobalt based MOFs synthesized with flexible bis(pyridyl-tetrazole) ligand (3-bptzp = 1,4-bis(5-(3 pyridyl)tetrazolyl)propane) and an aromatic dicarboxylic acid
(1,4-H2BDC = 1,4-benzenedicarboxylic acid) as mixed ligands. Adsorption Studies were done with methylene blue (MB) and rhodamine B (RhB). This showed that it has good tendency of removing organic ligands through adsorption.

[54] $Zr_6(m_3\text{-}OH)_8(\text{–}OH)_8(TBAPy)_2$ Metal Organic Framework NU-1000 was synthesized hydrothermally with ligands of phorpyrin ring structure which facilitate pore cavity to adsorb the pollutant molecule. (BET) surface area values ranged from 600–1700 m/ g. It is widely used in Co_2 adsorption.

[55] $\{[Co_4(FcDCA)_4(bpy)_4(H_2O)_6]\ 11H_2O\}n$ [FcDCA ¼ 1,10-ferrocene dicarboxylic acid and bpy ¼ 4,40-bipyridyl] a ferrocene based crystslline MOF, its crystal structure was studied using single crystal XRD technique, it holds notable adsorption and desorption properties, it specifically adsorb Chicago Sky Blue (CSB) and Congo Red (CR) dyes in maximum rate. Their adsorption of the dyes reaches 76% and 56% for CSB and 72% and 46% for CR at pH 5.0 and 2.0, respectively.

[56] Mesoporous copper–gallic acid Metal Organic Frame work (CuGA MOF) is synthesized using green route of synthesis, here solvent used is DMF. Its surface area of 198.22 m^2/g, a pore diameter of 8.6 nm, and a thermal stability of 219 C. it exhibit excellent adsorption capacity, it adsorbs methylene blue (124.64 mg/g) and Congo red (344.54 mg/g). Its high adsorption efficiency (> 90%) after 5 adsorption and desorption cycles.

[57] Metal Organic Frame works are constructed using the terephthalic acid derived from waste harmful PET bottles. This is a conventional and safe method to recycle the non-degradable PET bottles. Using metal clusters nano composites were produced with the recovered terephthalic acid. Since MOF holds excellent adsorption tendency it is used to collect

Antibiotic contaminated from water bodies. Iron composite made from above TPA holds the adsorption capacity towards antibiotics 671.14 mg/g.

[58] Cu5-cluster based MOF,$[Cu_{4.5}((H_4TZPP)(TZPP)C_{l2})(H_2O)_{0.5}]$ $CH_3NH_2CH_{3.}$ $7EtOH.8H_2O$ (LIFM-WZ-3) was synthesized from the tetrapodal ligand 5, 10, 15, 20-tetrakis [4-(2, 3, 4, 5-tetrazolyl) phenyl] porphyrin (H_6TZPP) and copper chloride. It holds high adsorption tendency with that it can separate CO_2/CH_4, CO_2/N_2, C_3H_6/CH_4, C_2H_6/CH_4, and C_2H_4/CH_4, it can also adsorb dyes its high adsorption capacity for methylene blue (MB^+, 983 mg /g) and crystal violet (CV^+, 713.5 mg/ g)

[59] Terephthalate derived from waste TPA bottles were used as organic linkers in production of metal organic frame works with lanthanide series metal for sensing nitro aromatics like picric acid, tri nitro toluene and di nitro toluene. They are highly explosive and toxic. This method of utilization waste plastics improves eco-friendly recovery of wastes.

[60] Metal organic framework were fabricated to remove the pollutant particles from environment, they can easily adsorb dye molecules, so they are majorly used to remove dye particles from industrial waste water. These MOFs holds nearly large surface areas (79.52 m^2 g^{-1}), which facilitate the encapsulation of pollutant molecules, the pi-pi interaction between the dye molecules adds to the higher adsorbance of dye molecules. It is widely used to remove Methyl blue dye from waste water. They are more effective in its adsorption even after five cycles.

[61] MOF MIL-100(Fe) is functionalized with thio glycolic acid and ethylene di amine to enhance its function of adsorption towards dyes. Their adsorption capacity was increased in the order of ED-MIL-100 < MIL-100 < TH-MIL-100. Their adsorption studies were done with eosin B dye. Here Acid-base interaction between the acidic thiol group (–SH) and the alkaline medium of eosin B dye solution. Their adsorption follows pseudo second order kinetics.

[62] Zeolite imidazole framework-8 (ZIF-8) is doped with Fe to form Fe-ZIF-8, were synthesized by hydrothermal. This frame work is used to remove Deep Black (RDB) RGB dye from aqueous medium. The electrostatic interaction and π-π interaction between the aromatic rings of the RDB dye and the aromatic imidazolate rings of the adsorbent is responsible for the adsorption of RDB dye. The specific surface areas are 1380 and 1243m^2/g for ZIF-8 and Fe-ZIF-8, respectively. The monolayer adsorption capacity for Fe-ZIF-8 (193.56$mg^{-1}\cdot g^{-1}$) was approximately 1.4 times higher than that of ZIF-8 (133.76$mg^{-1}\cdot g^{-1}$) towards.

[63] Metal-organic frameworks MIL-53(Fe) (MIL -Materials of Institute Lavoisier) was made to adsorb ibuprofen a chemical waste which highly pollute water medium. This MOF can adsorb 80% of ibuprofen from the tested water medium. Its maximum adsorption capacity towards ibuprofen is 10.67 mg/g. the adsorption process reaches its equilibrium position within 90 minutes. It follows chemisorption mechanism and monolayer behavior.

[64] {[Tb $(L_1)(L_2)$0.5(NO_3)(DMF)].DMF}n is a bi ligand MOF of 1,10-phenanthroline (phen) and 3,30,5,50-azobenzene-tetracarboxylic acid. This MOF is used in sensing and quenching of acetone and 2, 4, 6- tri nitro phenol. Delocalized p-electrons of organic chromophores increase electrostatic interactions between the MOF and electron deficient NAC (Nitroaromatics) analytes. Energy transfer from the ligands to Tb^{3+} gives eminent fluorescence in acetone sensing and shows notable NAC selective quenching.

[65] Copper (II) based metal organic frame works were fabricated with 1, 3, 5- benzene tri carcobylic acid. This MOF employed in dye adsorption process, mainly cango red (CR) from aqueous medium. Electrostatic and pi–pi stacking interactions between the dye and MOF increases the tendency of adsorption towards dyes. Since here the synthesis process follows the microwave method, mostly crystalline products were obtained. It is stable up to 800˚C. The highest adsorption of CR was 85.45% at 300 min.

[66] A zirconium-based metal organic framework (MOF-801) adsorbent was prepared using a solvothermal method and it holds the adsorption efficiency for removal of fluoride ions from water. Adsorption tests were conducted to determine the efficiency of defluorination by altering contact time (30–150 minutes), adsorbent dose (0.3–1.5 g /L), adsorbate concentration (5–25 mg). At equilibrium, the greatest removal efficiency for fluoride using MOF-801 was found to be 92.3 percent. MOF-801 was reusable and could be used up to four times for fluoride removal, with a removal effectiveness of roughly 79 percent after the fourth cycle.

[67] The MOF was produced by combining MIL- 101(Cr) with an organosiloxane polymer based on N-methyl-d-glucamine. Because of the extraordinarily high loading of functional groups responsible for boron adsorption, the resultant MOF composite has a high efficiency for removing boric acid from water. This material has the potential to be used in seawater desalination for boron removal. The original adsorption capacity of 0.46 mmol/g. Thus the anions had a negligible effect on the adsorption of boric acid and that the functionalized MOF composites show high selectivity towards boric acid.

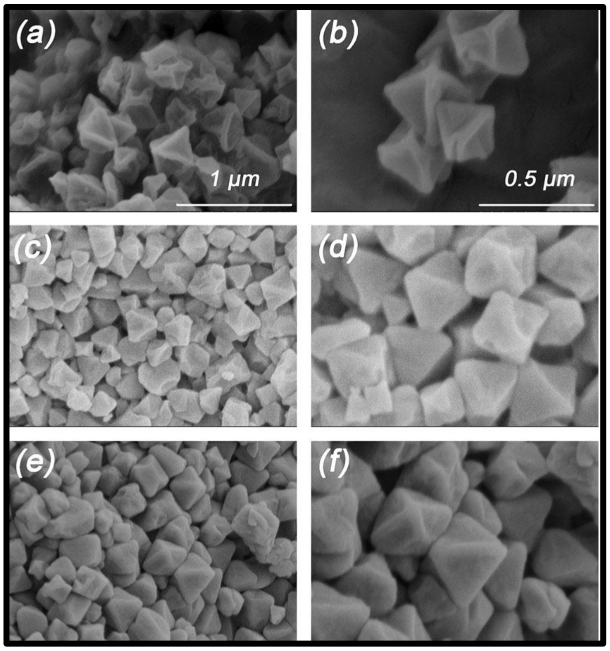


Figure 2.2(b) SEM images of the activated MIL-101(Cr) (a, b), and activated Poly (Si-NMDG)@MIL-101(Cr) (c, d), and poly(Si-NMDG)@MIL-101(Cr) after adsorption(e, f).

[68] Using metal-organic framework (MOF) as an adsorbent to remove specific Pharmaceutical products PhACs (carbamazepine (CBM) and ibuprofen (IBP)). This research was done to characterise the MOF and then confirm its suitability for eliminating the PhACs of interest. Because of its electrostatic affinity with the negative charges of methyl orange, MIL-101-Cr grafted with ethylenediamine (with positive charge) has a higher adsorption capacity than pure adsorbent (with neutral charge). When it comes to explaining the removal of PhACs, naproxen adsorption, and clofibric acid adsorption, acidbase interactions are rarely mentioned. The main explanation for functionalized MIL-101-Cr has been in terms of interactions between acids and bases.

[69] Zr-MOFs have been suggested as possible adsorbents for cationic and anionic pollutants in water. MIL-140, MIL-53, MIL-88B (Iron), and MIL-101 (Chromium) derivatives are stable in lactic acid solution, removing 15–42 percent of the lactic acid. These excellent results demonstrated that this class of MOF (MIL) would be exploited as emerging candidates for the commercial removal of lactic acid. These MOFs have showed hydrogen bonding as well as accepting groups for lactic acid attachment. With MOF, uranium anions (UO_2 $^{2+}$) show affinity for hydrogen bonding, – interaction, and electrostatic interaction.

[70] MIL-53(Cr), MIL-96(Al), MIL-101(Cr), MIL-100(Cr, Fe), ZIF-8(Zn), and UiO-66 were used to remove and isotope separate boric acid from aqueous solutions. ZIF-8(Zn) absorbed the most boric acid, 191 mg /g, MIL-101(Cr), on the other hand, was shown to be a more robust MOF with a lower maximum adsorption uptake of 60 mg /g. MIL-53(Al) has also been evaluated for its ability to remove As from water. When employing 10 ppb solutions, this MOF showed a remarkable maximum adsorption uptake of 105.6 mg g/l at pH = 8, and it was able to adsorb up to 15.4 mg g/1. When competing anions are Cl^-, F^-, NO^{3-}, and $SO_2{}^{4-}$, this adsorption behavior is maintained, but it decreases when PO4- is present.

[71] The MOFs ZIF-8 and ZIF-67 were prepared solvothermally. Its Brunauer–Emmett–Teller (BET) surface area of the ZIF-8 and ZIF-67 is 1229 and 1279 $m^2\ g^{-1}$, in the aerogel form; both ZIF-67 and ZIF-8 preserve their adsorption capacity. More than 90% of (Rhodamine-B) RhB is adsorbed onto the surface of the cell. Within 2 hours, ZIF-8/AG aerogel is formed, and ZIF-8/AG has a high recyclability. The dye that has been adsorbed can be easily removed within a short amount of time by an ethanol solution. Furthermore, the adsorption efficiency of ZIF-8/AG remains stable over time and several cycles.

[72] An organic-metal structure (PCN-222). Its maximal adsorption capacity of 333.33 mg /g is remarkable. The pi-pi interaction and electrostatic interaction are found to be important in the adsorption process, making PCN-222 a promising adsorbent of the beta-lactam antibiotic family from water. In a 1 L flask, dissolve $ZrOCl_2.8H_2O$ (2.0 g) and TCPP (0.4 g) in a combination of DMF (500 mL) and formicion acid (300 mL). The solution was then agitated and refluxed for 80 hours at 135 degrees Celsius. Kermesinus crystals were isolated as-synthesised. Cefradine is a typical β-lactam antibiotic and its molecular structure (the size is about 1.3×0.6×0.6 nm) contains a β-lactam heterocycle with aromaticity, this is readily adsorbed by PCN-222.

[73] well-known chemically stable metal-organic framework (MOF), zeolitic imidazolate framework (ZIF-8) was prepare and studied their application in encapsulation, Leaching of Pb atoms was also confirmed by quantitative method. Methyl ammonium (MA^+), ethyl ammonium (EA^+) cations or both MA^+ and EA^+ were incorporated inside the ZIF-8 in a large scale at room temperature. MOF walls served as a protective layer for the HBP-NCs, preventing any form of deterioration and resulting in the materials' extraordinary resilience. Composite materials have

been investigated as potential heterogeneous photocatalysis for the degradation of deadly organic compounds, contaminants in aqueous media immediately

[74] Perfluorooctanesulfonate (PFOS) is a bioaccumulative and hazardous persistent organic pollutant. PFOS removal from concentrated aqueous solutions was investigated using UiO-66 metalorganic frameworks (MOFs) with various concentrations as sorbents. Its maximum Langmuir sorption capacity of 1.24 m mol/g, which is ~2× times greater than powdered activated carbon (PAC). It holds large pore size (~16 and ~20 Å). The PFOS head groups are bound by coordinatively unsaturated Zr sites. Chloride ions had no effect on PFOS sorption among the major co-contaminants in chrome plating wastewaters, but sulphate and hexavalent chromium anions fight for cationically charged adsorption sites. UiO-66's improved PFOS and PFBS adsorptive properties demonstrate the benefit of structurally deficient MOFs in water treatment.

[75] Uio-66-$(OH)_2$/graphene oxide (GO) composite nanomaterial was synthesized by hydrothermal method using a functionalized zirconium-based MOFs and GO.
Its adsorption properties of the Uio-66-$(OH)_2$/GO were confirmed by the adsorption of two characteristic pollutants, methylene blue (MB) and tetracycline hydrochloride (TC). the concentration of the solution was 20 mg/L, the adsorption efficiency of Uio-66-(OH)2/GO on these two pollutants reached 99.96% (MB) and 94.88% (TC), respectively. Samples were taken at given time intervals, centrifuged at 5000 rpm for 10 min, and the concentration of contaminant was measured by an ultraviolet–visible spectrophotometer.

[102] B.40 Metal Organic frame works are prepared for the adsorptive removal of inorganic – metal cations, inorganic acids, oxyanions/cations, nuclear wastes and other inorganic anions and organic pharmaceuticals and personal care products, artificial sweeteners and feed additives, agricultural products, organic dyes and industrial products – contaminants commonly found in wastewater. MOF derived from L-methionine amino acid, $\{Ca(II)Cu(II)\ 6[(S,S)\text{-}methox]_3(OH)_2(H_2O)\}\ 16H_2O$, has different conformations of the functional thio ether “arms” decorating the walls, thus emphasizing the tunable accessible void space. This helps in encapsulating the pollutant particles of various sizes from aqueous medium.

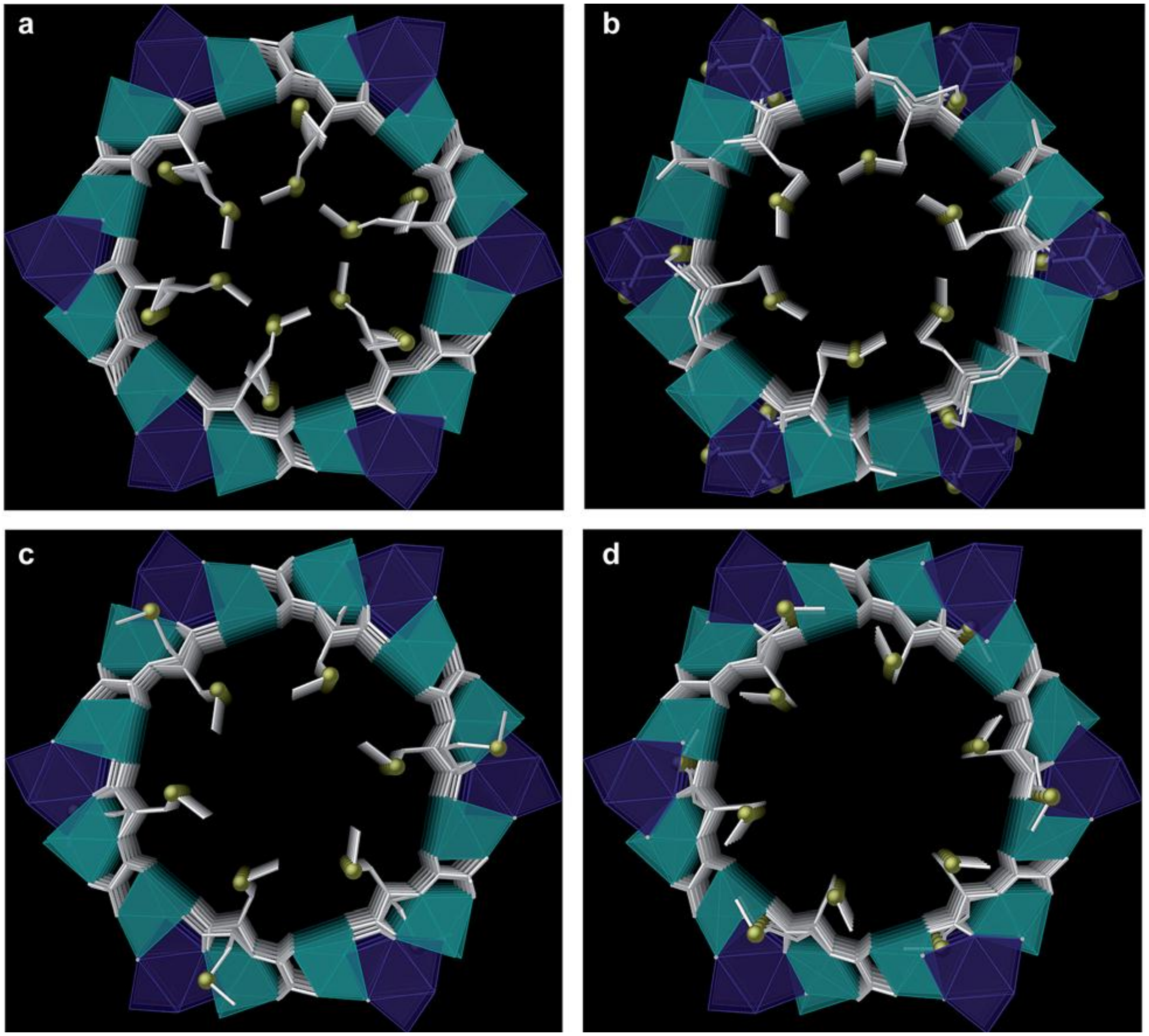


Figure 2.2 (c) MOF derived from L-methionine amino acid

3. Materials and methods

Different Metal Organic Frameworks were obtained using Terepthalic acid as linker and changing the metal ion clusters.

3.1. Chemicals and Solvents used:

1. Nickel(II) chloride hexahydrate [$NiCl_2$. $6H_2O$]
2. Copper (II) nitrate trihydrate [$Cu(NO_3)2{\cdot}3H_2O$]
3. Zinc nitrate hexahydrate [$Zn(NO_3)2.$ $6H_2O$]
4. Zirconium(IV) oxychloride octahydrate [$ZrOCl_2.8H_2O$]
5. Cadmium(II) nitrate tetrahydrate[$Cd(NO_3).6$ H_2O]
6. Aluminium nitrate monohydrate [Al $(NO_3)2.$ H_2O]
7. Benzenedicarboxylic(BDC) acid [Terephthalic acid](TPA)
8. Dimethyl Formamide (DMF)
9. Ethanol

The above mentioned chemical were used for the MOF synthesis, were bought in analytical grade, they are commercially available and affordable, these chemicals were used as such as purchased without any further purification.

3.2. Apparatus and Instruments required:

1. Iodine flasks
2. Beakers (100ml, 50ml, 25ml)
3. Measuring cylinder
4. Glass rod
5. Magnetic stirrer
6. Iron stand and clamps
7. G4 Sintered crucibles
8. Vacuum pump

Iron stand and clamps were used to hold the iodine flask containing reaction mixture with the magnetic stirrer to avoid bumping and damage due to fluctuations in magnetic stirrer in a long time reaction.

3.3. Synthesis of Metal Organic Frame Works:

3.3.1. Magnetic stirring method:

Metal organic frameworks were prepared by slightly modifying the procedure reported by ***(Nurettin Sahiner et al., 2017)***[54]

1. Ni-MOF (or) Ni-BDC Metal Organic Frame works

Figure .3.3.1 (a) Ni-BDC Metal Organic Frame work (Powder form)

Nickel chloride.6H_2O, 0.7 g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid was dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate was dissolved in 10ml of DMF, both were mixed and stirred. To maintain the alkalinity 7ml of NaOH (Sodium Hydroxide) of 5N concentration was added to the above mixture. The pH was maintained at 8, the whole content was stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate was collected and stored. The precipitate was washed with 30ml of ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container.

2. Cu-MOF (or) Cu-BDC Metal Organic Frame works

Figure .3.3.1 (b) Cu-BDC Metal Organic Frame work (Powder form)

Copper nitrate.3H_2O, 1.3 g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid was dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate was dissolved in 10ml of DMF, both were mixed and stirred. To maintain the alkalinity 6ml of NaOH (Sodium Hydroxide) of 5N concentration was added to the above mixture. The pH is maintained at 8, the whole content was stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate was collected and stored. The precipitate was washed with 30ml of ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container.

3. Zn-MOF(or)Zn-BDC Metal Organic Frame works

Figure .3.3.1 (c) Zn-BDC Metal Organic Frame work (Powder form)

Zinc nitrate.$6H_2O$, 1.5g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid is dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate is dissolved in 10ml of DMF, both were mixed and stirred. To maintain the alkalinity 6ml of NaOH (Sodium Hydroxide) of 5N concentration is added to the above mixture. The pH is maintained at 8, the whole content were stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate is collected and stored. The precipitate is washed with 30ml of ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it is stored in an air tight container.

4. Cd-MOF (or) Cd-BDC Metal Organic Frame works

Figure .3.3.1 (d) Cd-BDC Metal Organic Frame work (Powder form)

Cadmium nitrate.4H_2O, 1.5g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid was dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate was dissolved in 10ml of DMF, both were mixed and stirred. To maintain the alkalinity 6ml of NaOH (Sodium Hydroxide) of 5N concentration was added to the above mixture. The pH was maintained at 8, the whole content was stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate was collected and stored. The precipitate is washed with 30ml of ethanol and dried at 80°C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container.

5. Zr-MOF (or) Zr-BDC Metal Organic Frame works

Figure .3.3.1 (e) Zr-BDC Metal Organic Frame work (Powder form)

Zirconium oxychloride.8H_2O, 1.7 g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid was dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate was dissolved in 10ml of DMF, both were mixed and stirred. To maintain the alkility 8ml of NaOH (Sodium Hydroxide) of 5N concentration was added to the above mixture. The pH is maintained at 8, The whole content was stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate was collected and stored. The precipitate was washed with 30ml of ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container.

6. Al-MOF (or) Al-BDC Metal Organic Frame works

Figure .3.3.1 (f) Al-BDC Metal Organic Frame work (Powder form)

Aluminium nitrate.H_2O, 1.9g and linker terepthalic acid (1,4 Benzene di carboxylic acid), 1.7g. The above metal and linker were taken in 1: 2 ratios. The terepthalic acid was dissolved in 20ml of DMF (Dimethyl Formamide) and the metal nitrate was dissolved in 10ml of DMF, both was mixed and stirred. To maintain the alkility 6ml of NaOH (Sodium Hydroxide) of 5N concentration was added to the above mixture. The pH is maintained at 8, the whole content was stirred at the speed of 600 rpm overnight (12 hours) with the help of magnetic stirrer). Obtained precipitate was filtered and collected using G4 sintered crucible, with the help of vacuum pump. The filtrate was collected and stored. The precipitate was washed with 30ml of ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container.

3.4 Characterization of synthesized MOFs:

The Metal Organic Frame works prepared from above mentioned procedure were characterized using various techniques like Fourier Transfer Infrared Spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA), Powder X-Ray Diffraction Studied (Powder XRD), Flame Emission Scanning Electron Microscope (FESEM), their results give information about the bonding, structure and properties of the synthesized MOFs.

3.4.1 Fourier Transfer Infrared Spectroscopy (FTIR):

Fourier Transfer Infrared Spectroscopy (FTIR) studies were done for all the above synthesized powder form MOFs by magnetic stirring method to determine the bonding and functional groups present. FTIR spectra were obtained with **Shimadzu IR spectrometer** using Zinc Selenide sample cavity to place the sample for analysis in the instrument over the range of 400 – 4000 cm^{-1}.

3.4.2 Thermo Gravimetric Analysis (TGA):

Thermo Gravimetric Analysis (TGA) studies were done for Cu-BDC Metal Organic Frame work. This gives the information about the thermal decomposition and thermal stability of that MOF. Their stability was studied using **TG/DTA – EXSTAR/6300 (Thermo Gravimetric Analyzer).** The thermograms were obtained from continuous Nitrogen flow with the sample which is placed in a alumina pan. The plots were made for weight loss against temperature. Graphical image of thermogam was prepared using **Origin Pro.**

3.4.3 Powder X-Ray Diffraction Studied (Powder XRD):

Powder X-Ray Diffraction Studied (Powder XRD) studied were done for the powder MOF particles of Cu-BDC Metal Organic Frame work, this gives the information about the crystal size and nature of the sample under analysis.

3.4.4 Flame Emission Scanning Electron Microscope (FESEM):

FESEM is an advanced instrument to study the morphology of the analyte, in this a stream of high energy electrons were allowed to pass through slits to get a fine beam and allowed to fall on the sample and dissipated in different directions according to the morphology of the sample and electron sample interaction, they were recorded to get the FESEM image of the sample (MOF). FESEM image (2D image) of Cu-BDC MOF was taken using **Jeol JSM 6390 Scanning Electron Microscope.**

4. Result and discussion:

4.1 Fourier Transfer Infrared Spectroscopy (FTIR):

FTIR were taken for all the prepared Metal organic frame works: Ni-Terepthalic acid, Cu-Terepthalic acid, Zn-terepthalic acid, Zr-Terepthalic acid, Cd-Terepthalic acid and Al-Terepthalic acid.

The IR spectrums of Metal Organic Frame works, A peak at 1500 nm and 1400 nm confirms the carboxylate ion of terepthalic acid. A peak at 700 nm and 1100 nm shows the presence of C-H bond vibration in aromatic ring. Peak at the range of 850 nm to 900nm is due to asymmetric stretching vibration phenyl ring. A peak at 2800 nm to 3000 nm shows the presence of asymmetric vibration C-H bond in DMF (Di Methyl Formamide). A peak at 3600 nm and 3900 nm shows the presence of -OH group. A peak from the range 420nm to 498 nm confirms the formation of metal and oxygen bond in the MOF.[108][109]

Table4.1 Functional Group analysis of synthesized MOFs by FTIR spectroscopy

MOF	**-OH (cm^{-1})**	**CH of DMF (cm^{-1})**	**C=C (cm^{-1})**	**COO^- (cm^{-1})**	**CH of phenyl (cm^{-1})**	**Metal-O (cm^{-1})**
Ni-MOF	**3700**	**2800**	**1558.48**	**1411**	**825**	**455**
Cu-MOF	**3657.04**	**2978.64**	**1558.48**	**1396.46**	**825.53**	**462.92**
Zn-MOF	**3442.94**	**2850.00**	**1562.34**	**1409.96**	**829.39**	**450.00**
Cd-MOF	**3603**	**2978**	**1558**	**1411**	**825**	**470**
Zr-MOF	**3700.00**	**2800.00**	**1558.48**	**1411.89**	**825.53**	**578.64**
Al-MOF	**3471**	**2978**	**1558**	**1411**	**825**	**470**

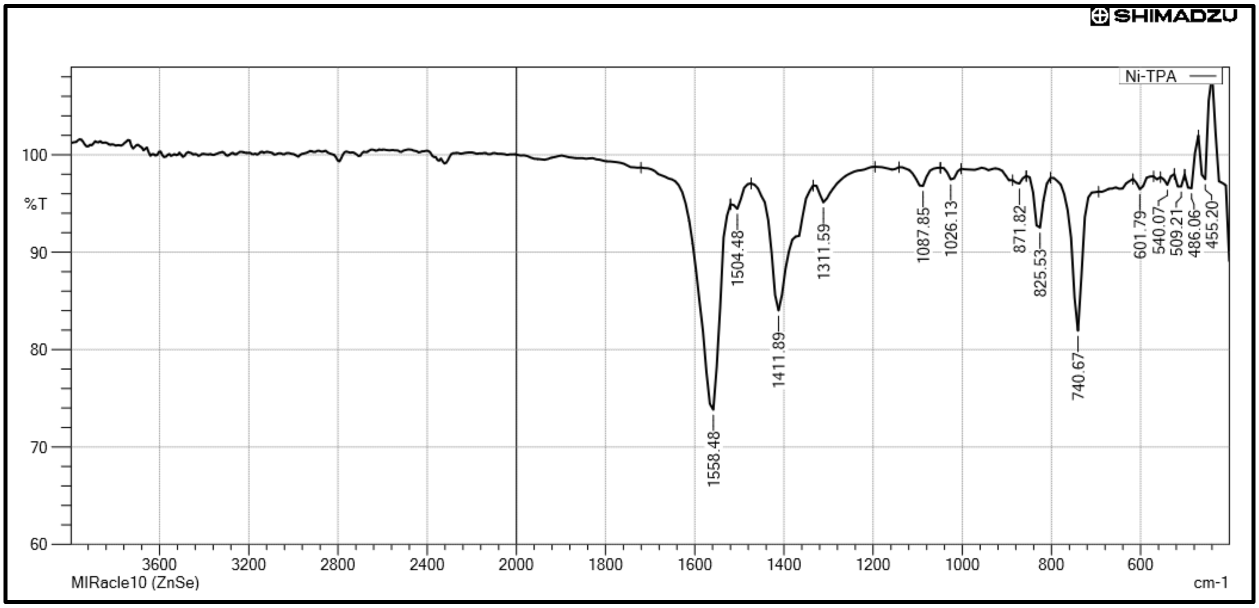


Figure 4.1 (a) FTIR spectra of Ni-Terepthalic acid Metal Organic Frame work

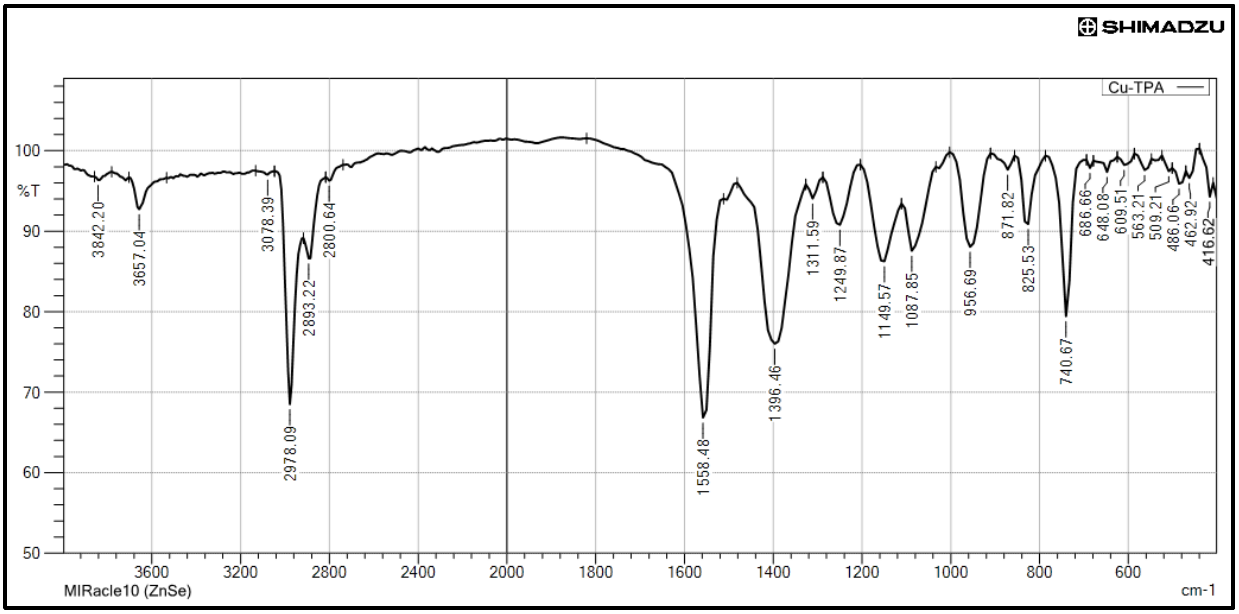


Figure 4.1 (b) FTIR spectra of Cu-Terepthalic acid Metal Organic Frame work

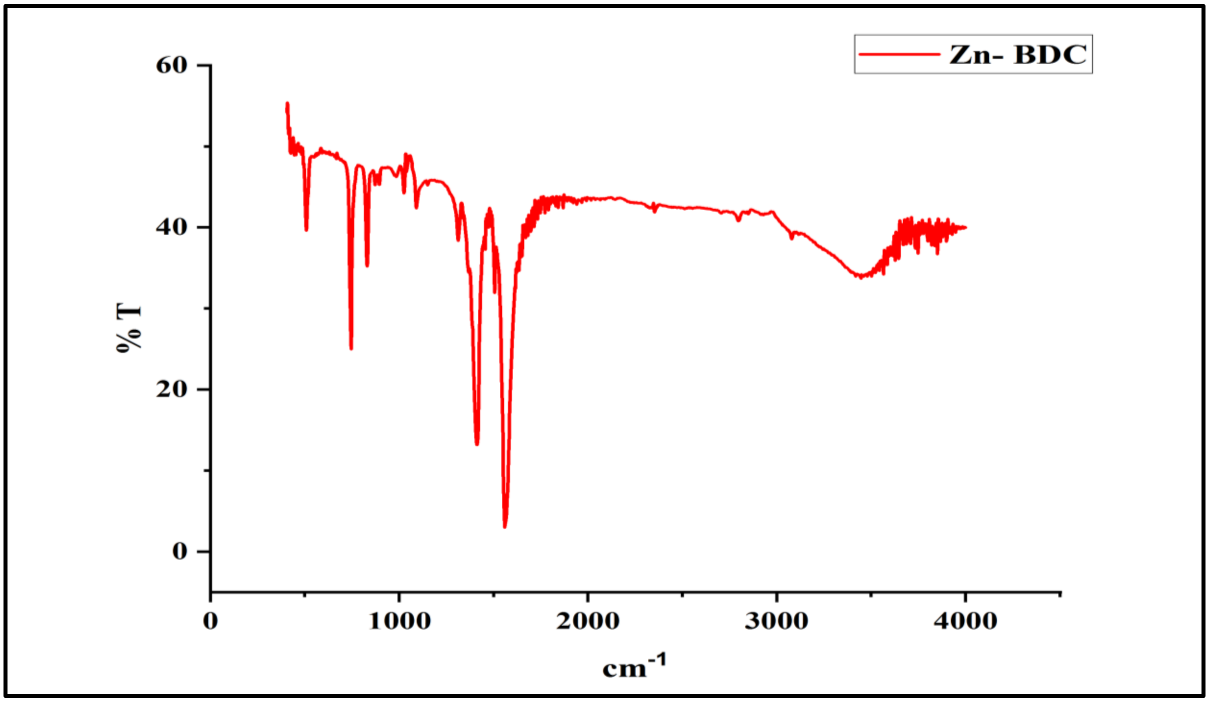


Figure 4.1 (c) FTIR spectra of Zn-Terepthalic acid Metal Organic Frame work

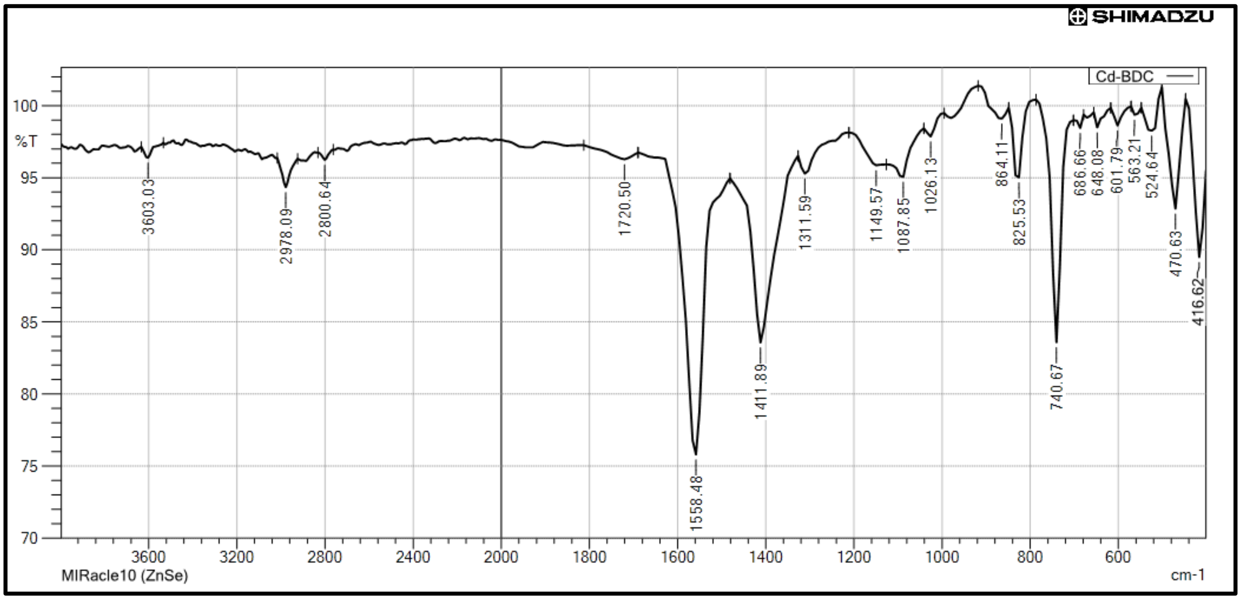


Figure 4.1 (d) FTIR of Cd-Terepthalic acid Metal Organic Frame work.

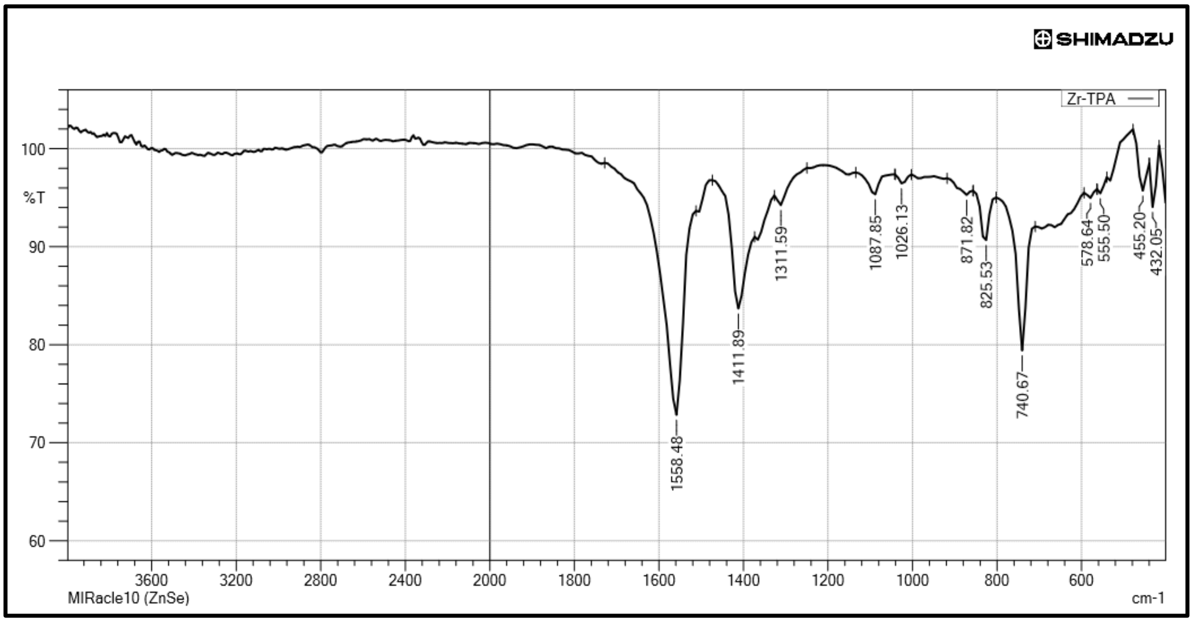


Figure 4.1 (e) **FTIR spectra of Zr-Terepthalic acid Metal Organic Frame work.**

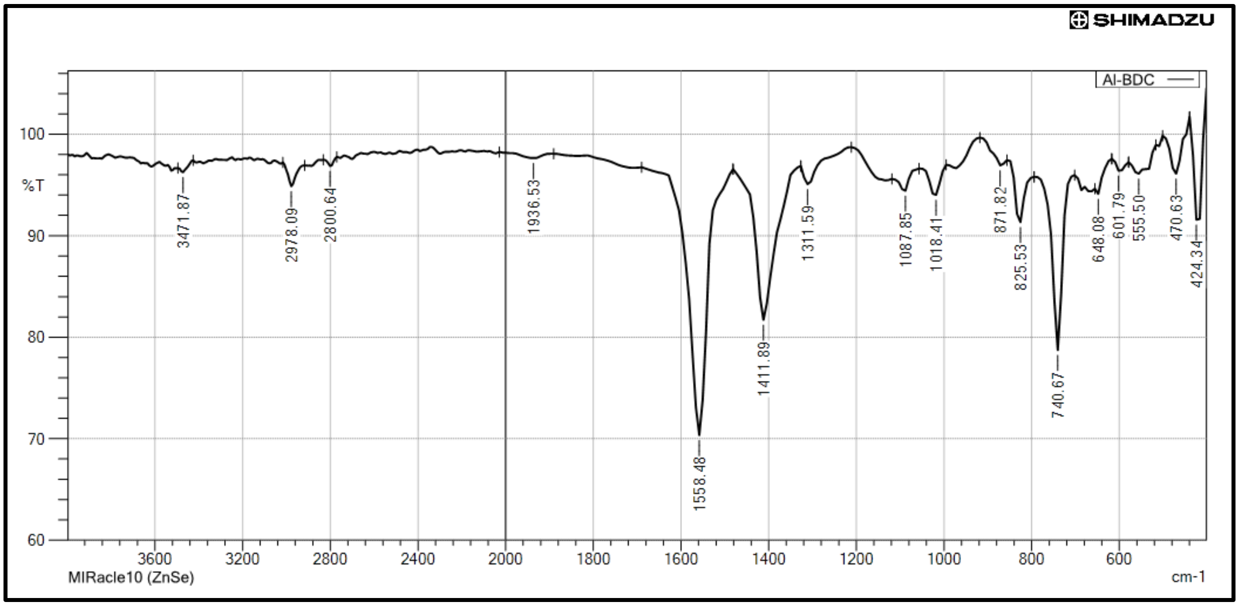


Figure 4.1 (f) **FTIR spectra of Al-Terepthalic acid Metal Organic Frame work.**

4.2 Thermo Gravimetric Analysis (TGA):

Thermo Gravimetric Analysis (TGA) provides detailed information about the decomposition temperature of analyte at various temperatures.

TGA was taken for Cu-terepthalic acid (Cu-BDC) Metal Organic frame work, At temperature 90˚C there is a slight weight loss due to loss of water molecules. And 380˚ there is a considerable weight loss due to elimination of solvent DMF (Dimethyl Formamaide), around 620˚C there is a constant loss due to the elimination of metal ions in the analyte MOF as metal oxides.[112]

Table 4.2 Range of decomposition

Temperature range(˚C)	**Compound eliminated**
50-150	H_2O
80-450	DMF(solvent)
480-800	Metals as oxides

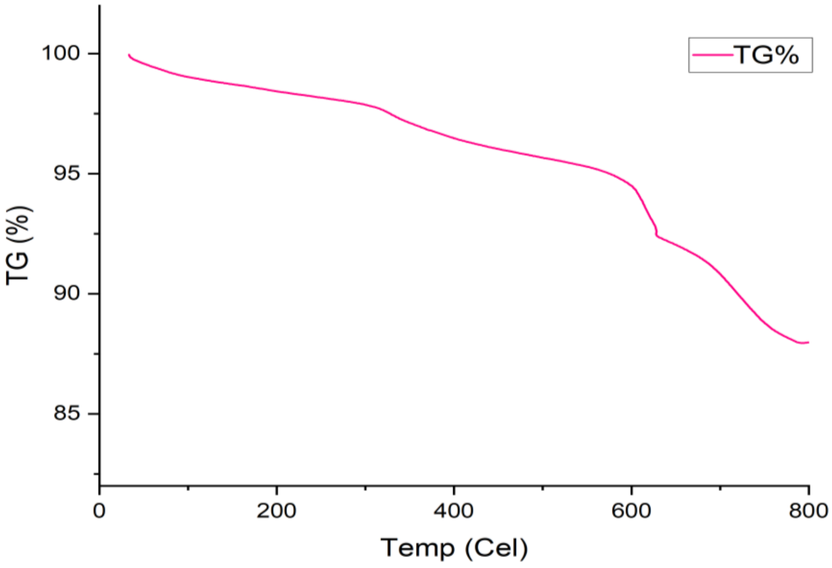


Figure 4.2 Graphical output of TGA for Cu-BDC

4.3 Powder X-Ray Diffraction Studies:

Powder XRD gives the information about the crystalline nature of the analyte. These details can be enumerated from the peaks and values of the graph with the help of scherrer equation.

The sharp peaks on the graph represent the crystalline nature of the analyte Cu-BDC.

Measurement Condition

X-ray tube

target = Cu
voltage = 40.0 (kV)
current = 30.0 (mA)

Slits

divergence slit = 1.00000 (deg)
scatter slit = 1.00000 (deg)
receiving slit = 0.30000 (mm)

Scanning

drive axis = Theta-2Theta
scan range = 5.000 - 80.000
scan mode = Continuous Scan
scan speed = 10.0000 (deg/min)
sampling pitch = 0.1000 (deg)
preset time = 0.60 (sec)

With the help of scherrer equation approximate crystalline size can be calculated using the data obtained from Powder XRD analysis,[111]

$$D = \frac{\mathrm{K} \cdot \lambda}{\beta \cdot \cos\theta}$$

Where,

D the crystallite size

K a size factor

β the full width at half maximum height of the peak (FWHM)

θ the Bragg angle for the peak identified in the diffraction pattern.

Table 4.3 crystal size calculation

S.no	d- Spacing (Å)	Peak position (2 theta) (degree)	FWHM (2 theta) (degree)	x-Ray wavelength (nm)	Size of crystal (nm)
1	2.90815	30.7153	1.06030	0.15418	8.12
2	9.59748	9.2057	0.86950	0.15418	9.58
3	5.16431	17.1563	0.79260	0.15418	10.59

From the table 4.3, we can find the approximate crystalline size of the Cu-BDC Metal Organic Frame work (MOF)

The graph obtained from Powder XRD analysis holds few sharp peaks and many dwarf peaks represent that the analyte is a semi crystalline in nature.[110]

This data shows that the prepared Cu based MOF is a mesoporous semi crystalline in nature. [103][104]

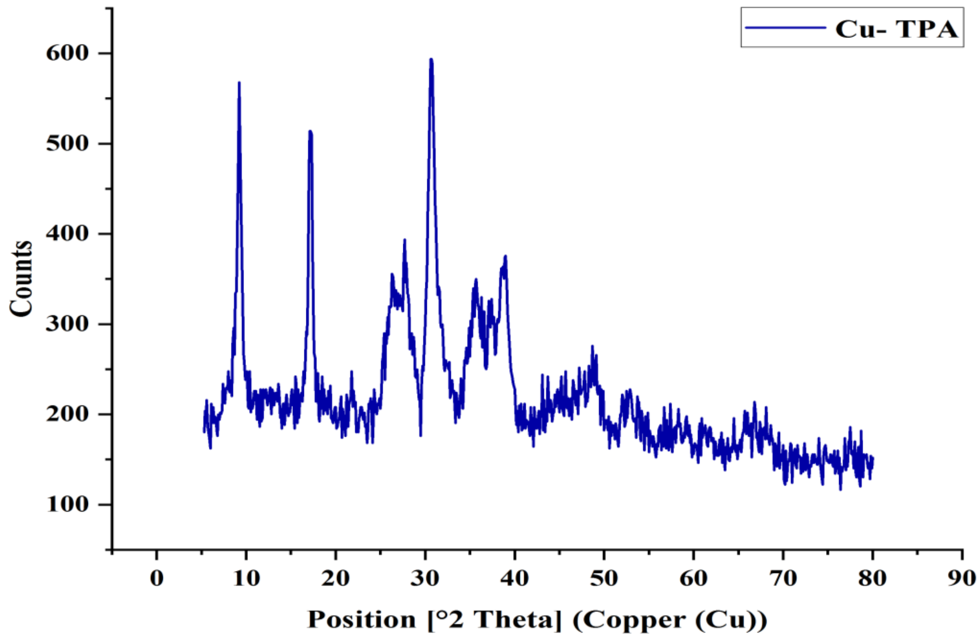


Figure 4.3 Powder X ray diffraction study result for Cu-Terepthalic acid MOF.

4.4 Field Emission Scanning Electron microscope (FESEM):

FESM analysis gives the information about the physical appearance and shape of the analyte. In the form of images, The FESEM result of Cu-BDC MOF the MOF particles were in rod and granules like structure.

The size of the grain can be calculated by,

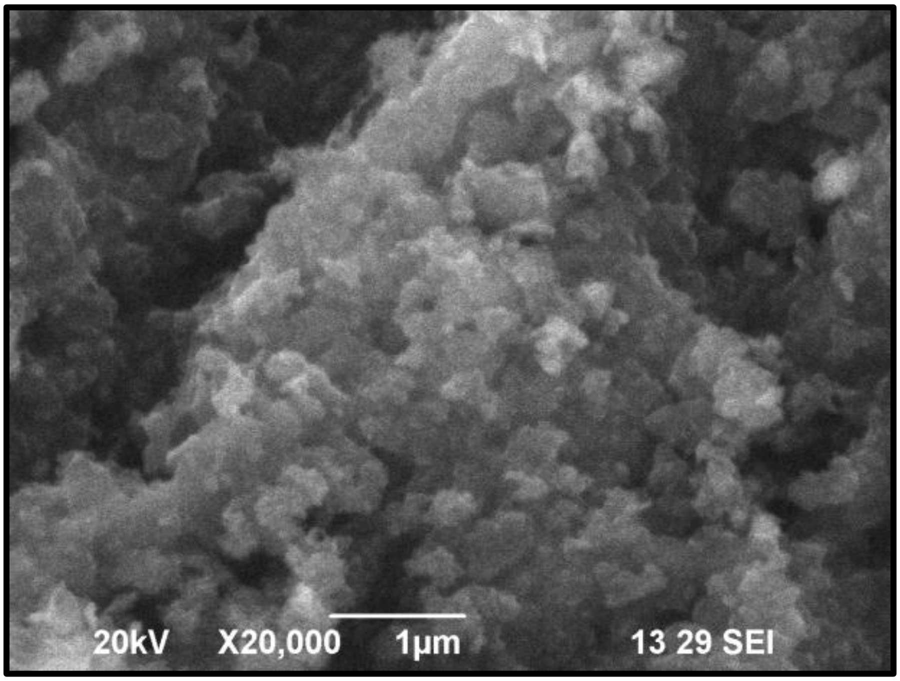
$$= \frac{\text{particle size in SEM image (cm)}}{\text{line measurement in SEM image (cm)}} \times \text{Magnification range } (\mu\text{m})$$

For Cu-BDC a particle size was calculated,

$$= 0.6\, cm/2.2\, cm \ \times 10\ \mu\text{m}$$

= 2.7273 µm.

The particle size was calculated as 2.7273 µm



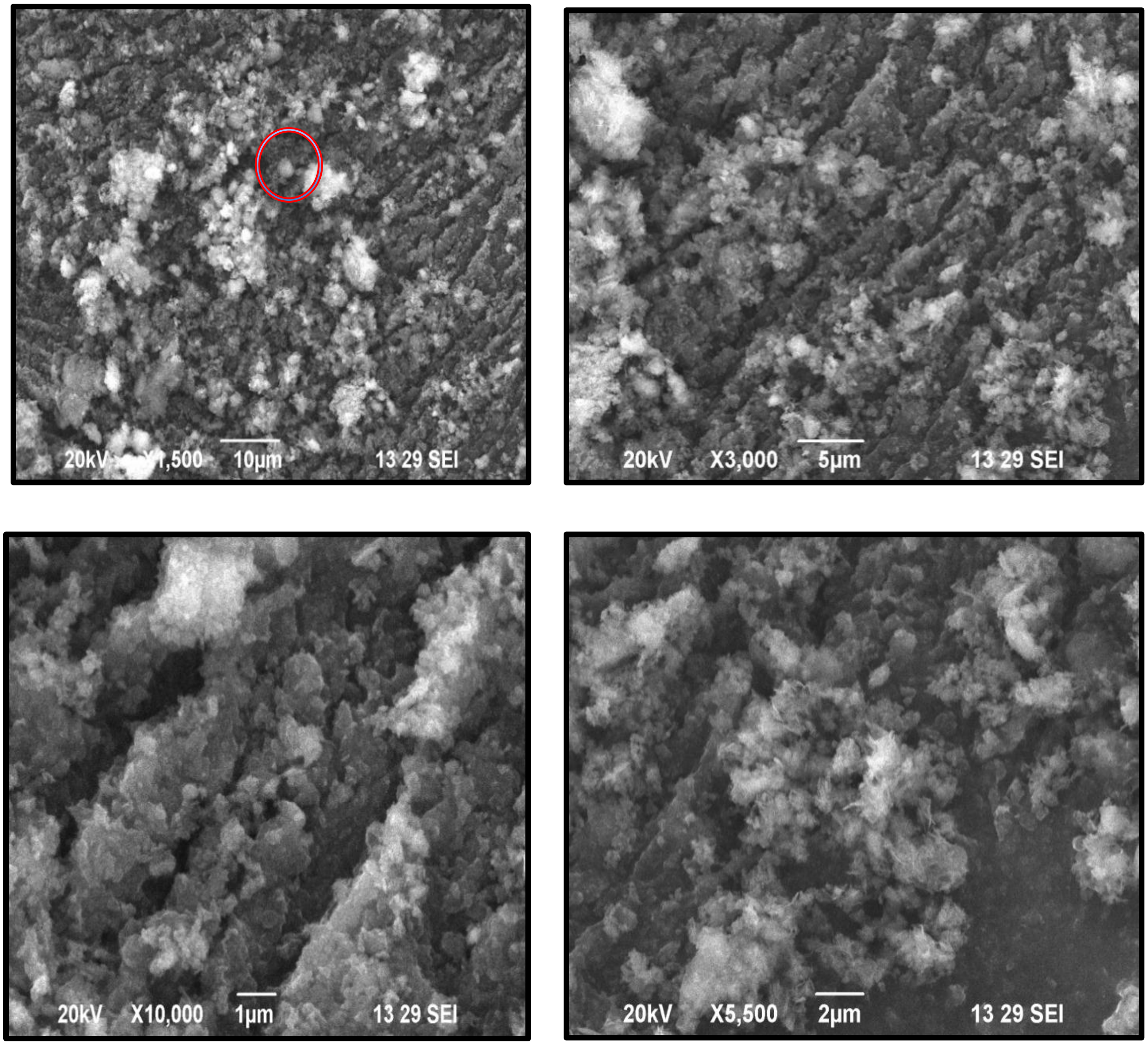


Figure 4.4 FESEM images of Cu-BDC Metal Organic Frame work

4.5 Adsorption of Potassium Permanganate Solution ($KMnO_4$) solution

Application studies were done by doing adsorption studies with Potassium Permanganate Solution ($KMnO_4$) solution. Their adsorption study was characterized by Ultra Violet Spectroscopy and Infrared Spectroscopy.

4.5.1 Ultraviolet spectroscopy:

The sample taken for adsorption study was Potassium Permanganate ($KMnO_4$) a violet colour solution. The deep violet colour of Potassium Permanganate Solution ($KMnO_4$) was not due result of d-d transition in manganese ion in manganite ion of Potassium Permanganate ($KMnO_4$), because Mn ion is in +7 oxidation state, d^0 so there wsa no d-d transition, the colour is due to MLCT (Metal Ligand Charge Transfer) effect, $KMnO_4$ absorb green- yellow colour between 500-550nm,[105] to emit violet colour. At first UV was taken for Potassium Permanganate ($KMnO_4$) without adding the MOF material using a spectrophotometer. Since it is a coloured solution absorbance were obtained in visible region.[105]

Adsorption of $KMn0_4$ by MOF:

Then adsorption was performed with the Potassium Permanganate ($KMnO_4$) solution, by adding the MOF material of 0.5 g in 20 ml of 0.1N concentrated Potassium Permanganate ($KMnO_4$) solution then introduced to shake for 30mins using an electronic shaker and the solution was allowed to settle down for 1 hour. The MOF materials were completely settled down, violet colour Potassium Permanganate ($KMnO_4$) solution become colourless and transparent. From this 6 ml of transparent liquid is taken in a centrifuge tube and centrifuged using an electronic centrifuging machine to get a clear solution for UV analysis, with the clear solution UV was taken, which shows high absorbance at UV region of 200nm-400nm not at visible region 400nm-800nm, because all the metal ions of Potassium Permanganate ($KMnO_4$) were adsorbed by the subjected MOF material. Adsorption was performed separately for each synthesized MOF in separate containers in the same time.

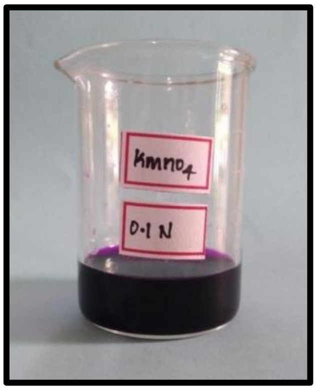


Figure4.5.1 (a) **Potassium Permanganate(KMnO$_4$) solution before addition of MOF.**

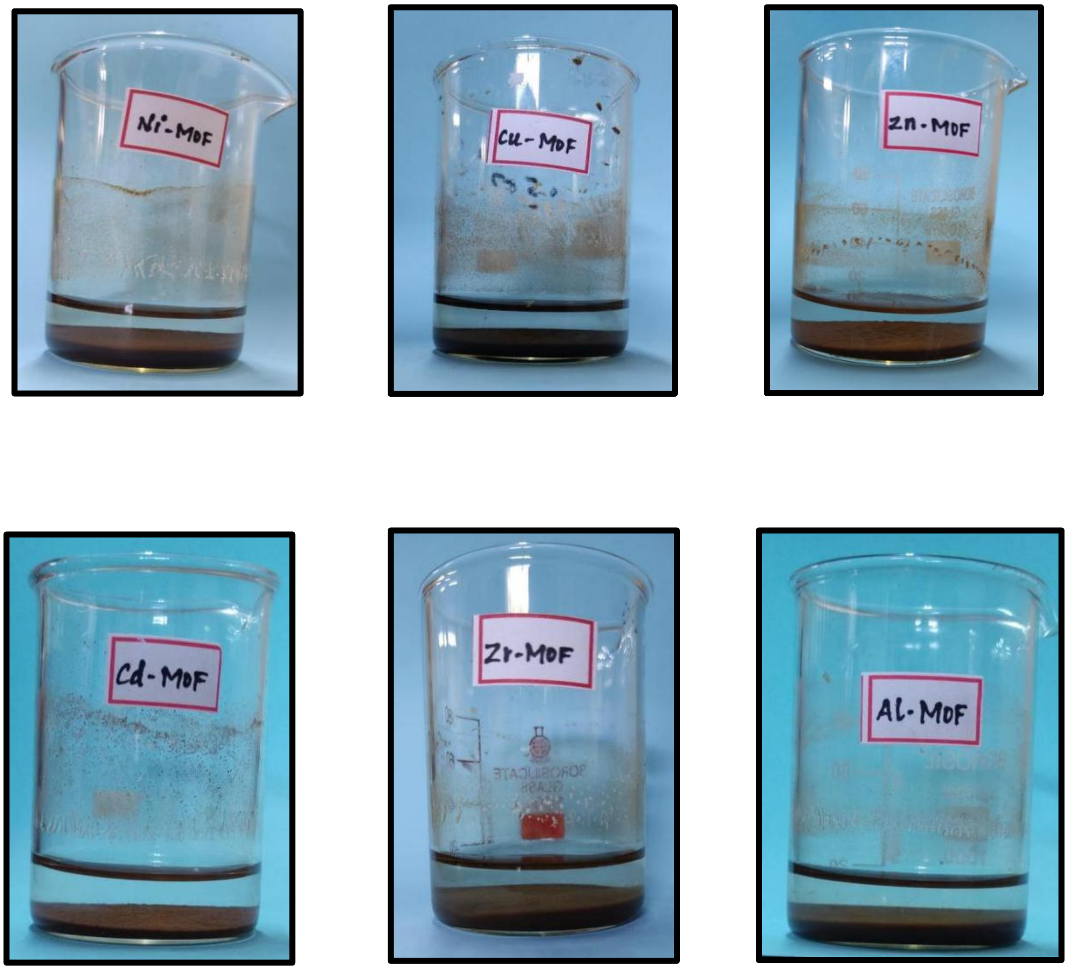


Figure 4.5.1 (b) **KMnO$_4$ solutions after adsorption.**

4.5.2 UV spectrum of $KMnO_4$ solution.

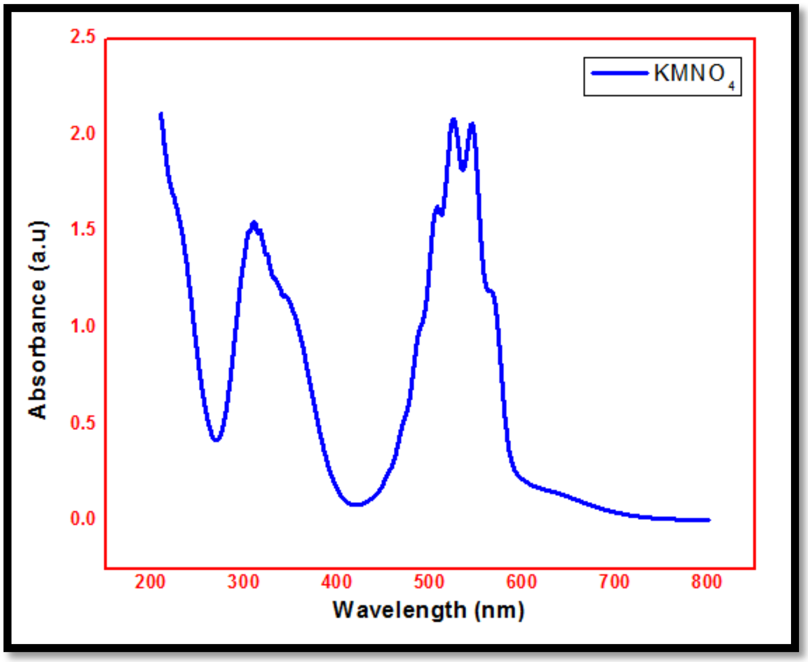


Figure 4.5.2 (a) **UV spectrum of $KMnO_4$ solution**

UV Peaks for Potassium Permanganate ($KMnO_4$) solution after adsorption by addition of Ni-MOF, Cu-MOF, Zn-MOF, Cd-MOF, Zr-MOF and Al-MOF materials individually.

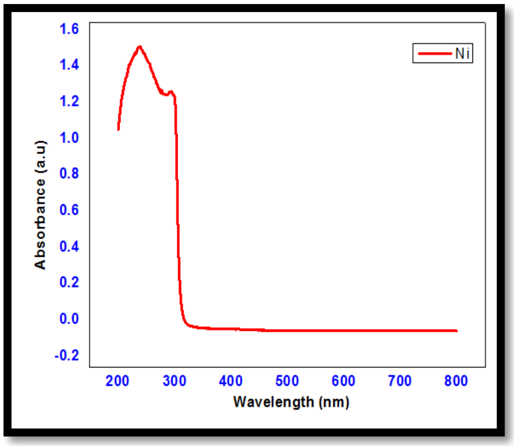


Figure 4.5.2 (b) Adsorption peak for Ni-BDC

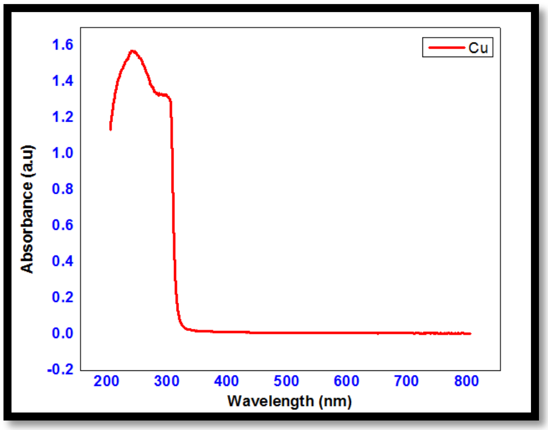
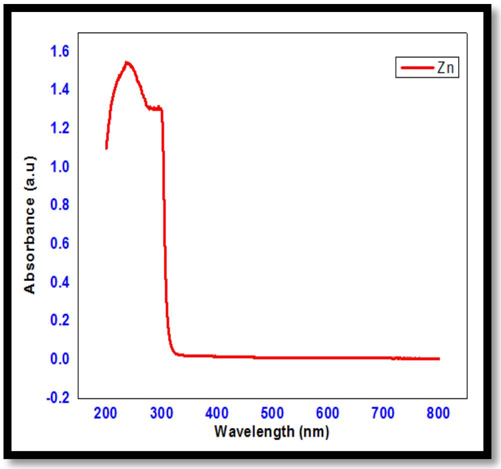


Figure4.5.3(c) Adsorption peak for Cu-BDC



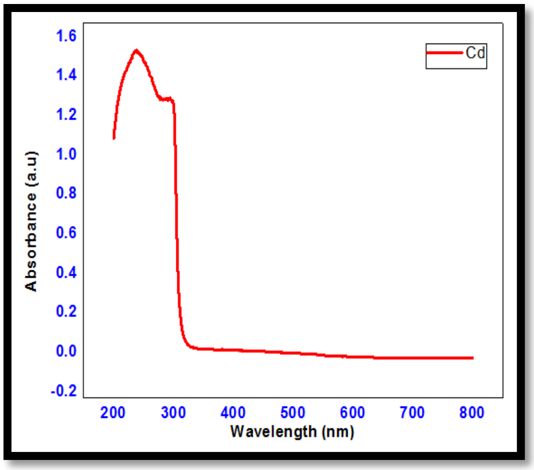
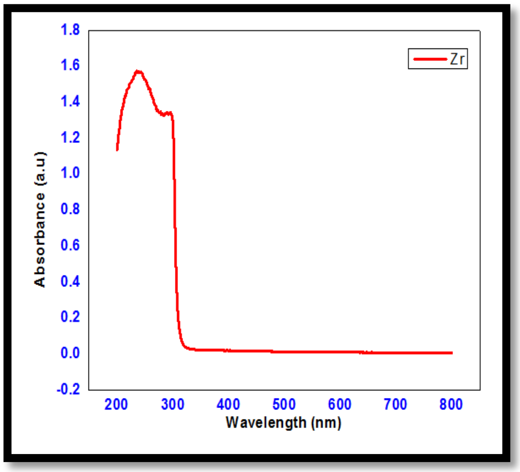


Figure 4.5.2(d) Adsorption peak of Zn-BDC

Figure 4.5.2(e) Adsorption peak of Cd-BDC



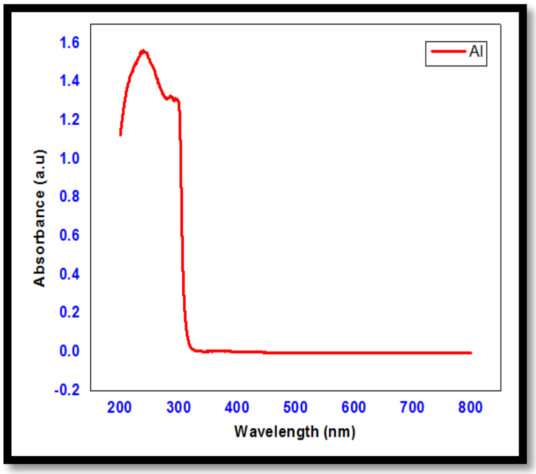


Figure 4.5.2(f) Adsorption peak of Zr-BDC

Figure 4.5.2(g) Adsorption peak of Al-BDC

Comparison for UV spectra of adsorption of $KMnO_4$:

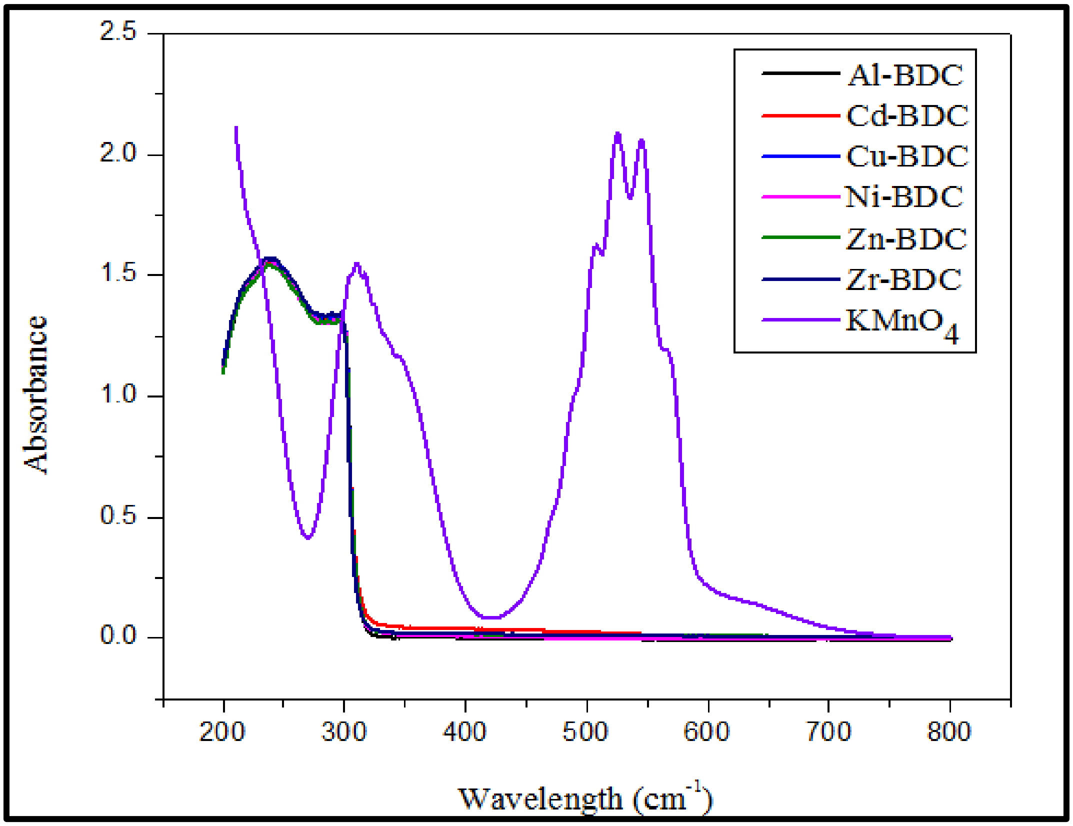


Figure 4.5.2(h) Comparison of UV spectra of adsorption of $KMnO_4$ by Metal organic frameworks Ni-MOF, Cu-MOF, Zn-MOF, Cd-MOF, Zr-MOF and Al-MOF.

According to Beer-Lamberts law in UV analysis the absorbance is directly proportional to the concentration of the analyte taken[91][92].

According to Beer lambert's law,

$$\mathbf{A = \in [C]\, l}$$

Here, A is the absorbance,

$\in = [L^2/M]$ is the mass absorptivity,

C = [M/L3] is the concentration,

l = L is the path length of the sample.

UV graph for Potassium Permanganate ($KMnO_4$) without MOF contains higher absorbance at 400nm-800nm range for potassium ions and manganite ions (contains Manganese metal). But in the UV graph of Potassium Permanganate ($KMnO_4$) solution after mixing the MOF material has no absorbance at visible region, which confirms the adsorption of potassium and manganite ions by the MOF particles added to the Potassium Permanganate ($KMnO_4$) solution.

4.5.3 Absorption studies by Infrared Spectroscopy (FTIR):

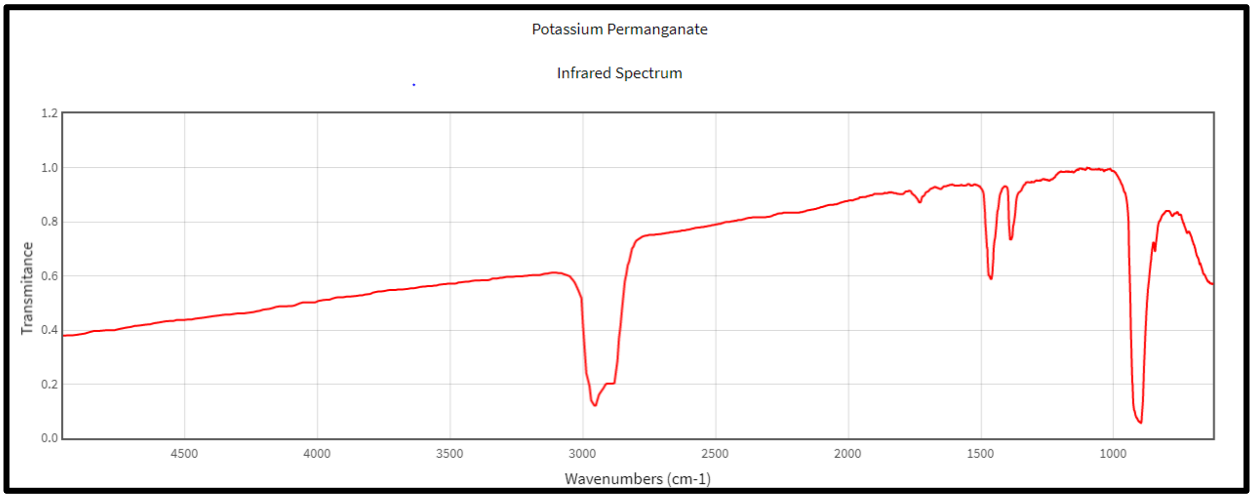


Figure 4.5.3 (a) **FTIR spectroscopy result for pure Potassium Permanganate ($KMnO_4$) solution. 2021 by the U.S. Secretary of Commerce on behalf of the United States of America**

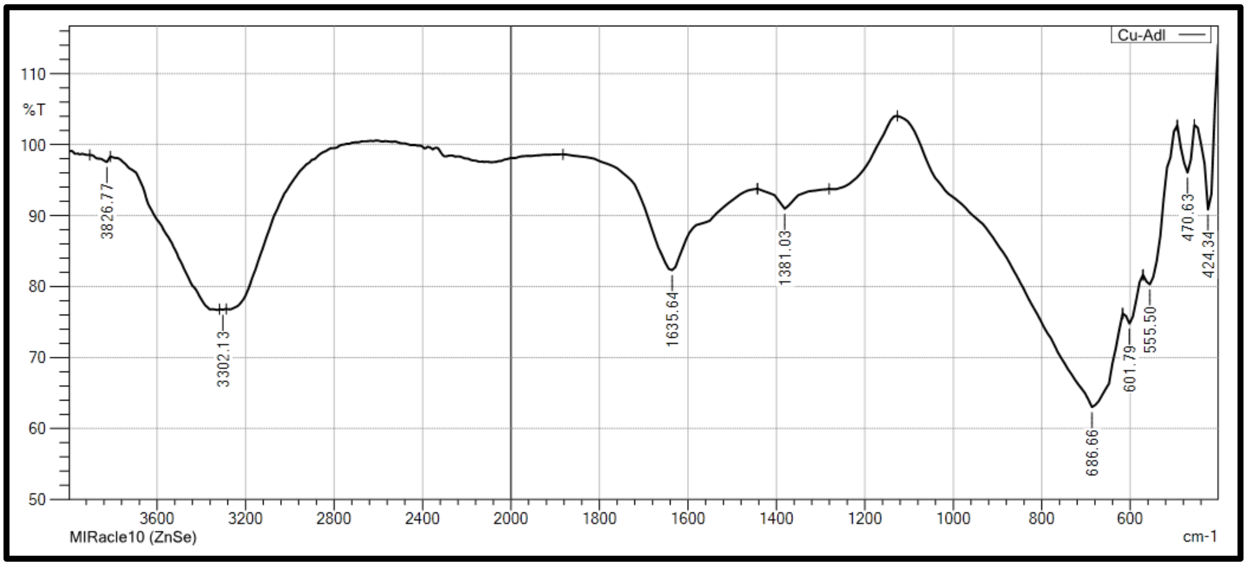


Figure 4.5.3 **(b) FTIR spectroscopic result of Potassium Permanganate ($KMnO_4$) solution after the adsorption study done with the Metal Organic Frame work, Cu-BDC.**

In FTIR spectroscopic result of pure Potassium Permanganate ($KMnO_4$) solution shows transmittance peaks at 2800 cm^{-1}, 1450 cm^{-1} and 500- 600 cm^{-1}.

Intense transmittance peak at 500-600 cm^{-1} indicates the Mn-O (metal- oxygen) strong bonding on $KMnO_4$.

Transmittance peak at 1450 cm^{-1} is due to water molecules of the solvent [107].

Transmittance peak at 2800 cm^{-1} is because of hydrogen bonding within the $KMnO_4$ solution [107].

The FTIR result of MOF solution after adsorption of $KMnO_4$ does not show the peaks of manganite ions and potassium ions.

This absence of FTIR peaks at exact position as in the result of pure Potassium Permanganate ($KMnO_4$) solution shows that there is no Potassium (K^+) and Manganate (MnO_4^-) ions remain in the Potassium Permanganate ($KMnO_4$) solution after the adsorption by synthesized Metal Organic Frame works.

Thus we are confirming that, there is adsorption take place by the MOF materials.

5. Summary and conclusion:

Metal Organic Frame works (MOF) were prepared using different metals (Nickel Nitrate, copper Nitrate, Zinc Nitrate, Cadmium Nitrate, Zirconium Nitrate and Aluminum Nitrate) and Terepthalic acid as ligand, using feasible magnetic stirring method.

Each Metal Organic Frame works were prepared separately by keeping basic condition as pH of 8 using 10N sodium hydroxide sufficiently during the reaction.

MOF products were collected by filtration using G4 sintered crucible, dried in oven for few hours then kept in desiccators for few days, and then stored in an air tight container.

Prepared MOFs were highly water stable, and insoluble in all commonly used solvents, which adds to the confirmation of MOF formation.

Products obtained were confirmed as MOF by characterizing the precipitate using Fourier Transfer Infrared spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA), Powder X-Ray Diffraction (P-XRD) and Field Emission Scanning Electron Microscopy (FESEM).

From FTIR analysis a peak at the range 400 cm^{-1} - 550 cm^{-1} indicates the formation of Metal and Oxygen bond between Metal and ligand. This confirms the formation of MOF.

From P-XRD data it is clear that, the precipitate of MOF is a semi crystalline particle, and approximate grain size of the MOF particle is calculated using scherrer equation.

Basically MOFs holds adsorptive tendency, it is tested using Potassium Permanganate Solution ($KMnO^4$) solution of 0.01N concentration.

The adsorption tendency all the prepared MOFs were tested separately in the same time.

Ultra violet spectroscopy technique is used to compare the adsorptive capacity of MOFs.

Adsorption is done by taking 20 ml of Potassium Permanganate Solution ($KMnO^4$) solution in 6 separate 50 ml beakers, then 0.5 grams all the six prepared MOFs are added to Potassium Permanganate Solution ($KMnO_4$) solution beakers separately at the same time then shanked for 20 minutes, allowed to settle down.

Clear supernatant liquid of $KMnO_4$ was taken for Ultra Violet Spectroscopy studies to find the $KMnO_4$ concentration.

The result of UV shows that there are no potassium and manganate ions in $KMnO_4$ solution after adsorption by MOFs.

Absorbance peak at 530 nm in pure $KMnO_4$ solution UV result, absence of absorbance peak at 530 nm in the UV result of $KMnO_4$ solution after adsorption by MOFs, confirms that potassium and manganate ions were adsorbed by MOFs.

To the FTIR result of the same clear supernatant $KMnO_4$ solution also does not contain the intense characterization peaks of KMnO4 solution at 500-600 cm^{-1} due to Mn-O bond and at 2800 cm^{-1} for hydrogen bonding.

From the above results and information, it is evident that the potassium and manganite ions of potassium permanganate solution ($KMnO_4$) solution are adsorbed by the MOF particles.

Future Work

Using this easy conventional synthesis method, MOFs with mixed ligands can be produced.

Determine a convenient and reliable method to quantify the amount of metal ions adsorbed by the MOF material.

Further studies have to be done to find the mode of binding between the adsorbate and the MOF materials.

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