HYDROTHERMAL SYNTHESIS AND CHARACTERISATION OF MOF-5 AND SYNTHESIS OF COPPER OXIDE NANOPARTICLE INCORPORATED MOF-5 AND THEIR ANTIBACTERIAL STUDY

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ABSTRACT

Metal organic frameworks (MOFs), especially MOF-5, are believed to be a promising class of new porous materials that has the ability of absorbing and holding particles within its pores which make them available for several applications such as gas adsorption, catalytic application, sensing applications etc. In this work, MOF-5 was synthesized by hydrothermal method and characterized using FT-IR, XRD and SEM analyses. Powder diffraction methods show that MOF-5 has crystallite size of about 38.17nm. The synthesized MOF-5 shows good crystallinity and porous structure hence can be used for many applications. Also, copper oxide nanoparticles are synthesized and incorporated into the MOF-5 to form CuO@MOF-5 and comparative antibacterial study between MOF-5 and copper oxide incorporated MOF-5 was conducted. CuO@MOF-5 showed better antibacterial property than MOF-5 against gram-positive bacteria and almost same antibacterial activity against gram-negative bacteria.

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LIST OF ABBREVATIONS

MOFs	Metal organic framework
MOF-5	Metal organic framework formed from Zn_4O nodes
IUPAC	International Union of Pure and Applied Chemistry
MIL	Materiaux de I'institut Lavoisier formed metal organic frameworks
IRMOF	Isoreticular metal organic framework
HKUST-1	Hong Kong University of Science and Technology formed from $Cu_2(CO_2)_4$
SBUs	Secondary building units
DMF	Dimethyl formamide
DEF	Diethyl formamide
DMP	Dess-Martin Periodinane
DMA	Dimethyl acetamide
DMSO	Dimethyl sulfoxide
TEA	Triethyl amine
H2BDC	Terephthalic acid
H3BTC	Benzene-1,3,5-tricarboxylic acid

MMOFs	Magnetic metal organic frameworks
XRD	X-ray diffraction spectroscopy
FT-IR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
HR-TEM	High resolution-transmission electron microscopy
Zn-MOF	Zinc based metal organic framework
DSM	Double solvent method
ZIFs	Zeolitic imidazolate frameworks

CHAPTER – 1

INTRODUCTION

Porous materials and their ability of absorbing and holding substances within the pores is often interesting. Porous materials that we encounter in our daily life such as sponges, wood, rubber and some rods have the potential to hold oil, natural gas or even underground water. The solid materials possessing high porosity especially nanoporous structures, often arouse great interest among chemists due to their broad application in the field of catalysis, separation and gas storage. There exist only few compounds of low density with nanopore structure that are mechanically stable enough to be used for the storage of gases without their surface being destroyed. More advanced materials of the kind are being invented, studied and modified for exploiting their potential for various applications. Metal-organic framework (MOF) is an important material among them which is most widely investigated. MOF was first synthesized by Prof. Omar Yaghi in the latter 1990s [1].

Porous solid materials are classified into two major categories (a) amorphous and (b) crystalline. Porous amorphous solids are solid porous materials which do not exhibit any ordered arrangement of repeated units in their structures, but they have importance that is to be researched. Main disadvantages of these materials are that they exhibit potentially wide range of molecular architectures with non-predictable channels or topologies and they lack long-range order that results in low mechanical stability. The porous crystalline solids are those materials having ordered structures with reproducible and predictable pores, channels and topologies which give them high thermal and mechanical stability. Nano porous silica and zeolites are characteristic examples of such ordered porous crystalline solids that have predicable structural features [2].

The porous solids are mainly subdivided into three categories on the basis of their pore size. According to the IUPAC, the porosity of crystalline solids is usually given by the diameter of the pore size and is categorized as microporous (5-20 Å) mesoporous (20-500 Å) and macro-porous (> 500 Å). The microporous materials are of great interest because of their wide range of applications such as catalysis and separation science [3]. They exhibit large physical surface areas and the pores have dimensions that are comparable to small molecules. There are several well-known classes of microporous material including zeolites, activated carbons, silica and metal organic frameworks. Nano porous materials that are based on zeolites and metal

phosphates have wide range of technological applications (for eg: acting as molecular sieves, desiccants, ion exchangers, and catalysts). Although they are chemically and thermally stable, these materials create challenges to the engineering of specific pore sizes [4] or to the formation of chiral channels [5] and allow comparatively limited variation of chemical formulation and functionality [6]. The relatively new field of microporous metallo-organic polymers [7-10], although offering great potential for chemical and structural diversity and also includes the direct incorporation of catalytic sites, suffers some general difficulties in the control of polymer dimensionality or framework stability [7].

Low dimensional coordination polymers can show selective absorption based on host-guest shape recognition [8], but lacks framework integrity. Even though the ligands can be designed in such a way that the resulting coordination polymer contains large voids but they are frequently suffered with lattice interpenetration [9] or breakdown of the framework during the removal of absorbates [10]. Crystalline aluminosilicate zeolites with tetrahedral frameworks are widely used in the areas of separation, ion exchange and shape selective catalysis [11-14]. However, the researchers were continuously trying to discover new nano porous materials in order to overcome the general drawbacks of conventional zeolites such as limited incorporation of metal element and limited pore sizes to induce diffusion problem [15]. As a result, there has been tremendous increase in the synthesis of non-aluminosilicate crystalline porous materials during past decade [16-23].

An advanced class of microporous material known as ***Metal organic framework (MOFs)*** have been developed and is one of the most fastest growing class of materials in chemistry today. These materials have highly ordered pores, ultrahigh porosity (up to 90% free volume) and enormous internal surface areas, extending beyond 6000 m^2/g and they have the ability to take up, hold and release molecules from their porous sites. MOFs are composed of metal ions or clusters (metal containing units or secondary building units (SBUs)) coordinated to organic ligands (known as linkers) to form one-, two- or three-dimensional structures showing distinctive feature of endless porosity, stable framework, very long surface area and pore volume [24-25]. The metals are known to offer flexible, coordination environment with different geometries, e.g. tetrahedral, trigonal bipyramidal, octahedral. Due to the usual liability of metal complexes, the formation of coordination bonds between the metal ions and organic linkers can be reversible. This property in fact enables the rearrangement of metal ions and organic linkers during the process of polymerisation to render the highly ordered framework structures. A typical approach of MOF synthesis is depicted in figure 1.
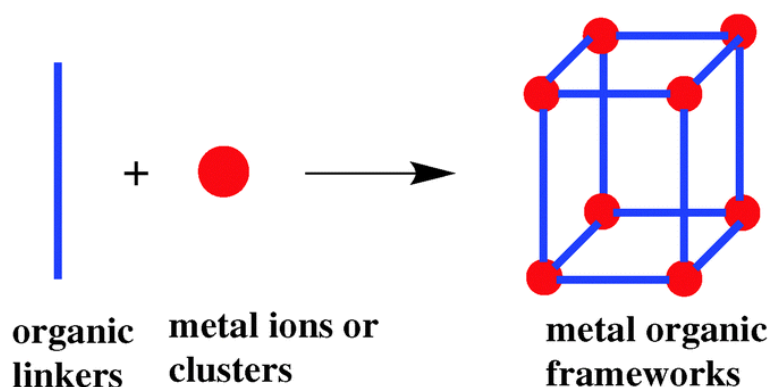
General representation of approach of MOF synthesis (figure 1)

The flexibleness with that the constituents, geometry, size and functionality could be varied has resulted to more than 20,000 different MOFs being reported and studied within the past decade. MOF based on zinc, MOF-5 ($Zn_4O(BDC)_3$, BDC–terephthalic acid) is an important compound in the class of MOF with high porosity. MOF-5 shows antibacterial activity [26].
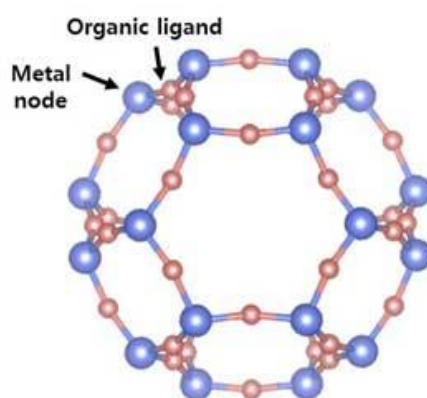
1.1 METAL ORGANIC FRAMEWORKS (MOFs)

MOFs are organic – inorganic hybrid crystalline nanoporous materials which consist of a periodic array of positively charged metal ions surrounded by the organic linker molecules. The metal ions act as nodes to which the arms of the linkers are bound together to form repeating cage-like structure. Because of this hollow structure, MOFs have an exceptionally large surface area. A schematic illustration of an MOF depicting metal ions and organic ligand is shown in figure (2)

Metal connectors are the ones which connect the organic linkers as main components resulting in the formation of MOFs having three-dimensional structure. Therefore, metal ions and organic compound used in the synthesis of metal organic frameworks are the primary building blocks of MOF [27]. Most commonly used metal ions of the transition series such as Cr^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+} as connectors for the generation of MOFs. Some alkali as well as alkaline earth metal ions are also used for this purpose. Sometimes, metal ion precursors such as Nitrate, Acetate, Sulphate, Chloride, Hydroxide and Oxide forms of metal ions are used for the synthesis of MOFs [28].

MOFs contains both inorganic and organic linkers. Organic units (linker / bridging ligand) are carboxylates or anions such as phosphates, nitriles, sulfonates and heterocyclic compounds. Inorganic linkers are the metal ions or clusters which is termed as Secondary Binding Units (SBUs) [29]. Geometry of it may be determined by coordination number, coordination
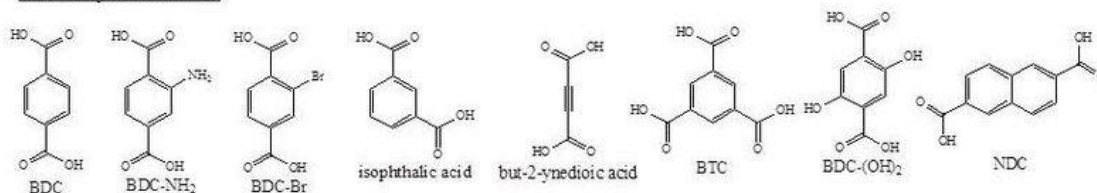
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geometry respective of the metal ions used and the nature of the functional groups. A wide variety of SBU geometries with different number of points of extension is available and they are octahedron (6 points), trigonal prisms (6 points), square paddle field (4 points) and triangle (3 points) have been observed in MOFs [30].

In principle, a closure bridge (ditopic, tritopic, tetratopic or multitopic linkers) responds to a metal ion with more than one vacant or labelled surface. The MOF structure is controlled by both SBU connectors and organic ligand connectors. Depending upon the SBUs used to the form the MOFs, a wide variety of them can be designed for various applications. So far, more than 90,000different MOF structures have been repoted and the number keeps on increasing on daily basis. MOFs with large gaps can lead to the formation of intrusive structures. Therefore, is very important to prevent intrusion by carefully selecting organic connectors [31]. Different types of SBUs shown in figure (3).
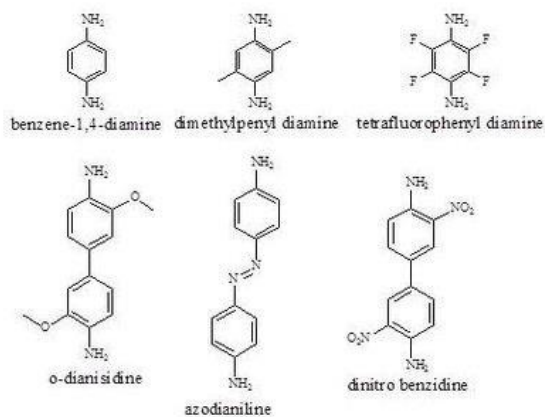

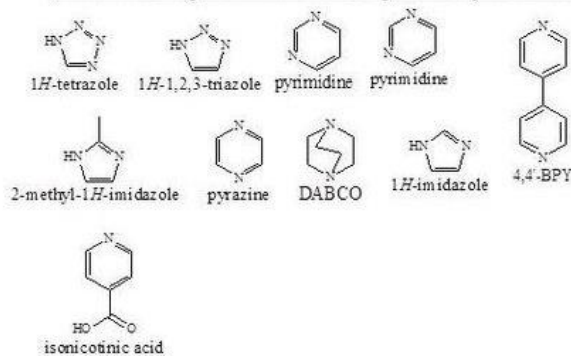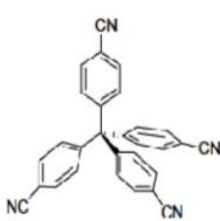*Schematic illustration of MOF (figure 2)*

Carboxylate linkers

BDC   BDC-NH₂   BDC-Br   isophthalic acid   but-2-ynedioic acid   BTC   BDC-(OH)₂   NDC

Nitrogen donor atom linkers

benzene-1,4-diamine   dimethylpenyl diamine   tetrafluorophenyl diamine

o-dianisidine   azodianiline   dinitro benzidine

Nuetral nitrogen atom containing heterocyclic linkers

1H-tetrazole   1H-1,2,3-triazole   pyrimidine   pyrimidine   4,4'-BPY

2-methyl-1H-imidazole   pyrazine   DABCO   1H-imidazole

isonicotinic acid

Nitrile   **Sulfonate**   **Phosphate**

BPCN   TCTPM   ADS   BPDS   EDP   ADTP
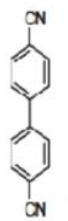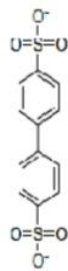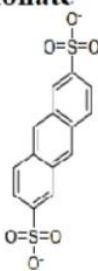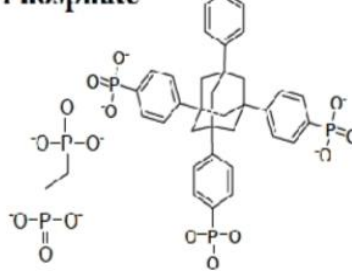
Different types of SBUs (figure 3)

1.11 CLASSIFICATION OF MOFs

MOFs can be classified based on different criteria. The classification of MOF is illustrated in figure (4) [32]. One important classification is based on their tailored and structural features, based on which MOFs classified into four [33].

1.111 Rigid frameworks : These are the MOF materials which retain its porous framework on adsorption or desorption of guest molecules. They possess stable and robust frameworks and can be used as molecular sieves [34]. MOF-5 is an example of this type.

1.112 Flexible / Dynamic frameworks : These are MOF materials which change their on introducing or withdrawing any guest particles. There exist some external factors which affect the shape of the particle and they are pressure, temperature and guest molecules [35]. Dynamic

MOFs tend to change their frame work on the removal of solvent molecules and their porous structure remain same on adsorption of gas molecules at high pressure [36]. MIL-5, MIL-8 are some of the examples of MOFs which have effects on adsorption and desorption [37-38]. In this case, there occurs a severe change on unit cell volume ie; the pore volume on adsorption or desorption of incoming molecules changes [39]. The breathing phenomena and large specific surface area of flexible MOF make them suitable for gas storage and separation [40].

1.113 Open metal site frameworks : MOFs become more active when it contains open metal site. A metal site endowed with labile ligands that can be eliminated to create a coordinatively unsaturated site is known to be open metal site MOF. For example, if it contains water in the open metal site there arises an increased CO_2 encapsulation ability. HKUST –1 ($Cu_3(btc)_2$), an example of this type of MOF, has an open metal site structure and contain paddle wheel units (Cu_2COO^-) which is connected through btc^{3-} ligands and they show definite increase in CO_2 adsorption when it consists of 4% weight water [41].

1.114 Surface functionalized framework : The adsorption capacity of MOF can be enhanced by inserting functional group on to their surface. They have high affinity towards CO_2 (Hydroxyl, Alkylamine, Arylamine) which leads to the increase of capacity and selectivity of MOFs. This can be achieved by two ways, either by ligand modification or by coordination to unsaturated metal centre [42-43].
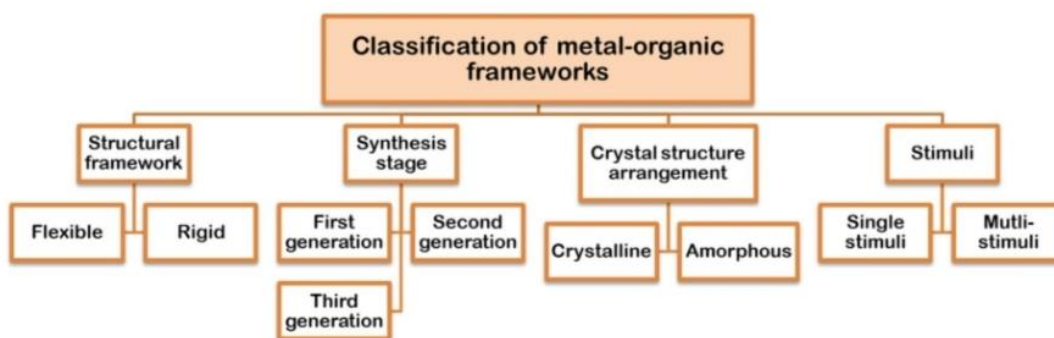
Classification of MOF (figure 4)

1.12 <u>SYNTHESIS OF MOFs</u>

A wide variety of methods have been proposed for the synthesis of MOFs. In most cases, MOF synthesis is done by mixing the SBU and metal in liquid solvent and the product is filtered, dried by evaporation to obtain a purified MOF. To get the purified MOF, various types of purification methods can be used. Purification refers to the elimination of impurities (metal oxides, recrystallized linker, dense hybrid compounds) that are occluded inside the pores to

ensure that the pores are free. It is done by sieving which is based upon the densities of the products formed [44-46].

Different methods of synthesis of MOF (figure 5)

1.121 Hydrothermal / Solvothermal synthesis: In solvothermal synthesis, a mixture of metal ions and organic linkers in solvent is heated in glass vials (for low temperature) or in Teflon lined autoclaves or bomb reactor (for temperature higher than 400k). If water is used as solvent, the method is known as hydrothermal method. Parameters such as temperature, pressure, solvent composition, reagent concentration etc control the structure of synthesised MOF. When the temperature is higher than the boiling point of solvent, then the reaction is called solvothermal reaction and when the temperature is lower than the boiling point of the solvent called nonisothermal reaction. Some MOFs can be synthesised at ambient temperature and the method is known as direct precipitation reaction [47]. This method is more environmental-friendly than other methods [48]. The product formed is more uniform than those formed by other methods.

1.122 Microwave assisted synthesis: In microwave assisted synthesis, energy for reaction is given by microwave radiation. Fast crystallisation, phase selectivity, narrow particle size distribution and morphological controls are the main advantages of this method of synthesis [49]. Several MOFs containing metal ions such as Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+}, Ce^{3+} have been synthesised by this method. This method is carried out under Microwave radiation at a temperature over $100^{o}C$ with reaction time exceeding 1 hour. IRMOF-1 and HKUST-1 studied by this method [50].

1.123 Mechanochemical synthesis: A mixture metal salt and organic linker is grinded in a mortar pestle or in a ball mill without using solvent and then the mixture is heated gently to evaporate water or other volatile molecules which are formed as by products in the reaction

mixture [51] In this method, breaking of intermolecular bonds is by mechanical force followed by a chemical transformation. This method is known to be a green method because no solvent is used and can give high yield of product [52-53]. MOF particles are obtained in short reaction time of 10-60 minutes. Metal oxides are preferred over metal salt as the starting material as water is the only byproduct [54].

1.124 Sonochemical synthesis: It is a rapid and environmental-friendly method in which ultrasonic radiations (20kHz – 10MHz) is used for MOF synthesis. Homogeneous and accelerated nucleation results in a reduction of crystallisation time and significantly smaller particle size. Here occurs the both chemical and physical transformations by cavitation, which will produce small bubbles. Later, these bubbles collapsed leads to the generation of the hot spots with short life time having high temperature and pressure [54].

1.125 Electrochemical synthesis: This method is a new era for the preparation of MOF, which use Zn, Cu, Mg, Co as cathode materials and $1,3,5-H_3BTC$, H_2BDC, $1,2,3-H_3BTC$ as linkers. Instead of metal salts, metal ions are continuously supplied through anodic dissolution as a metal source, which reacts with the dissolved organic linker molecules and a conducting salt in the reaction medium [55]. Protic solvents are used inorder to avoid deposition of metal on cathode, but H_2 is produced in this process. $(Zn(MIm)_2)$ can be prepared by this process [56].

1.126 Ionothermal synthesis: This method uses ionic liquids as structural template, charge balance or reaction times. So that it provides pure ionic environment. The physical and chemical properties of the MOFs can be controlled by the change in the composition of the ionic liquid. The advantages of using this method are good thermal stability, lower melting point and wider liquid range [57].

1.127 Slow evaporation synthesis: Slow evaporation synthesis doesn't need any external energy supply. The advantage of using room temperature results in significantly longer synthesis times than the other methods. Here, the concentrated initial solution by slow evaporation of the solvent. In some case, mixture of solvents can be used to increase the solubility of the faster evaporation of low boiling solvents [58].

1.128 Spray drying method: Using a two –fluid nozzle MOF precursors are added to the atomizer and convert it in to small microdroplets. At a controlled temperature the droplets are surrounded by the gas. Increase in the solvent evaporation leads to increase in precursor concentration. This will happen until the critical concentration is reached and finally crystallization begins [59].

1.129 Diffusion method: Diffusion method is broadly classified in to liquid phase, gas phase, gel diffusion. Here diffusion of the one of the regents controls the reaction rate. Most preferring solvents in gas and liquid phase diffusion are volatile organic ligand solution, metal ions and organic ligand dissolved in immiscible solvents respectively. Diffusion methods held at mild reaction conditions and requires long reaction time [60].

There are several factors which affect the synthesis of MOF. Some important factors among them are discussed:

- Effect of Solvents: Solvent system plays a major role in MOF synthesis and also in deciding the morphology of MOFs. Solvents used in the synthesis of MOFs should have high boiling point and polar nature, such as dimethyl formamide (DMF), diethyl formamide (DEF), dimethyl sulphoxide (DMSO), dimethyl acetamine (DMA), alcohols, acetone, acetonitrile, etc. This is due to the difference in degree of deprotonation of organic linker in different solvent system. The coordination ability of solvent with the metal determines the dimension of MOFs [61]. And it also affects the pore size, there will be a difference in the pore size of the MOF with same reaction condition having different solvent, which indicates that the size of the solvent molecule is different. Size variation of solvents increases in the order like this DMP > DMA > DMF [62].

- Effect of p^H: Different types of coordination methods have chosen by linkers at different pH ranges. The degree of deprotonation of linker increases with increases in pH values [63]. By altering the pH value colour along with change in adsorption capability. At high pH the dimension of MOF will be greater [64]. Alteration pf pH values done by addition of various concentration of catalyst such as TEA (triethylamine), NaOH, Na_2CO_3 etc and that will change the complete network pore size of the MOF being synthesized [65].

- Effect of Temperature: High temperature favours high degree of crystallisation because of high solubility of reactants which result in high quality large crystals. ie; high temperature favours high crystallization because of the high solubility of the reactants [66]. Morphology can be varied by altering the temperature of the reaction medium. The MOFs prepared by Hydrothermal method that will be more stable than the other synthesized at room temperature. Because hydrothermal method provides high denser, less hydrated and higher dimensional solids [67-68].

1.13 APPLICATIONS OF MOFs

Due to the nanoporous structure and the properties, MOFs have several applications.

1.131 Gas storage and separation: There are few strategies for storage gas efficiently but these require tall weight tank and multistage compressor. These strategies are highly expensive for viable employments and there is a requirement of simpler and cheaper arrangement. To overcome these issues and to discover more secure capacity strategies, a few materials like Zeolite or actuated permeable carbons, have been studied for gas capacity. In this setting, MOFs have provided edge over other materials. Usually due to simple perspective methods, tall surface range, wide 18 openings for functionalization and tuneable pore structure which makes MOFs best compared to other porous material.

More than 300 MOFs have been tested for H_2 storage. Gases like CO, NO can moreover be separated from gas blends by utilizing MOFs. Though separation of CO in MOF might not be achieved. It is accepted that interaction between CO dipole and open metal locales in MOFs are the dominating calculate for the sorption execution. Other than gas molecules water molecules can also be captured by MOFs. Recent studies reveal that adsorption of NO gas can also done by MOF. MOFs show excellent methane storing properties when compared to zeolites or porous carbon structures. MOFs are found to be the most effective porous structure for CO_2 storage both under ambient conditions and high pressures [69-71].

1.132 Energy storage: MOF shows great potential for energy storage applications such as rechargeable batteries and supercapacitors. Lithium ion, sodium ion and lithium-sulphur batteries can be enhanced through the incorporation of MOFs as promising electrode materials. The high surface area and permanent pores of MOF structures allow efficient Li^+ ion storage and migration during charge and discharge cycles. For lithium- sulphur batteries, MOFs can also be used as a sulphur host in the battery [72-74].

1.133 Waste water treatment: MOF structures can be utilised in membrane separation as membrane fillers or as complete membrane system. Their porous tuneable structure assists the selective separation of organic and inorganic substances from water. MOFs used in water treatment are water-stable MOF structures. Either, hard acids combine with hard base (e.g. water-stable MOFs including MIL series and UiO series) or soft acids combines with soft base (e.g. ZIFs) to form strong bonds in the MOF structure. Water-stable MOFs show great performance in waste water cleaning because of their excellent selectivity and permeability, tuneable structure, better compatibility and potential recycle after their lifetime [75].

1.134 Catalytic application: MOFs show potential catalytic activity. The catalytic property of MOFs can be either directly due to their hybrid structure or induced by the incorporation of catalytically active but unstable nanoparticles. The periodic structure of MOFs provides active

sites for the transport of substrates and products. Moreover, the specific pore size and shape of MOFs can act as shape-selective catalysts.

MOFs can be utilised as heterogeneous catalysts in well-known organic reactions. E.g. HKUST-1 containing lewis acid sites, can be used as an acid catalyst in isomerisation and cyanosilylation reactions. MOFs can be utilised as potential photocatalysts by exploiting their semiconductor-like behaviour; used in organic pollutant degradation, various organic reactions, hydrogen / oxygen production from water splitting and reduction of CO_2. MOFs incorporated with nanomaterials improve their conductivity, show excellent electrocatalytic properties and is utilised in reactions like the oxygen reduction reaction, oxygen evolution reaction, hydrogen evolution reaction and carbon dioxide reduction [73-74].

1.135 Biomedicine: The unique structural diversity makes them an excellent material for biomedicine applications. In contrast to conventional nanomedicines, MOFs show biodegradability and high loading capacity. The high surface area, large pores and chemical properties of MOFs are best suited for novel drug delivery systems and controlled release of compounds. Promising applications have been researched on different drugs such as ibuprofen, procainamide and anticancer treatments [73-74].

1.136 Sensors: The porous and tuneable structure of MOFs and their composites have been exploited in chemical sensors. MOFs shows a luminescent property upon the incorporation of a guest molecule and this property is used for sensor applications. Furthermore, the physical and chemical structure of MOFs can be designed to selectively respond to desired molecules and their active sites on a high surface area leads to a highly sensitive sensor application. ZIF and UiO MOF groups have the sensor applications. MOFs are used for sensing of biomolecules, metal ions, environmental toxins and humidity [73-74].

1.137 Magnetism and applications: MOFs materials show magnetism when paramagnetic 3d transition metal nodes are utilized together with reasonable diamagnetic organic linkers and MOFs having magnetic metal organic systems. The MOFs comprise of first row transition metals (V, Cr, Mn, Fe, Co, Ni, Cu) have contributed altogether to develop permeable atomic magnets. Close – shell ligands such as oxo, cyano, azido bridges and polycarboxylic ligands which grant frail magnetic interaction are great candidature for this purpose.

Another reason for attraction of MOFs is the system structure, which may include layered geometry with a shorter conjugated separation between metal clusters. Organic linkers have more over been utilized for synthesis of MMOFs, where radicals show in organic linker are

good for attractive properties. This metal – radical combination approach has more over been utilized for synthesizing assortment of MMOFs [76-77].

1.138 Electrical property and application: MOFs are used for the energy storage purpose. Co doped MOFs can be used for energy storage. But it has lower capacitance. Zr based MOFs have high capacitance. Recently Mn based MOFs are employed as coating materials to enhance the storage capacity. Some of the MOFs' surface were modified with oxide materials that leads to show high discharge capacity, good thermal stability, high initial coulombic efficiency and high-rate capability [78-79].

1.14 IRMOF-1 (MOF-5)

MOF-5 also known as IRMOF-1 is one of the most typical representatives of the MOFs family having the formula $Zn_4O(BDC)_3$, where BDC^{2-} = 1,4-benzodicarboxylate. It is one of the first synthesised and widely studied MOFs.

The secondary building units is composed of M_4O with central oxygen surrounded by 4 divalent cations (M^{2+}) forming a tetrahedron and 1,4-benzenedicarboxylate as linkers. Each edge of the tetrahedron faces of a carboxylate group from a linker, with each oxygen coordinating with one of the two edge's cations (figure 6a). Linkers connecting the neighbouring tetrahedra, are oriented along either of 3 axes orthogonal to each other, so that the MOF-5 structure has cubic symmetry (figure 6b). It is a three-dimensional framework structure made up of terephthalic acid and metal cluster Zn_4O. MOF-5 possessing an open skeleton structure, controlled pore structure, pore surface area and high stability [80].
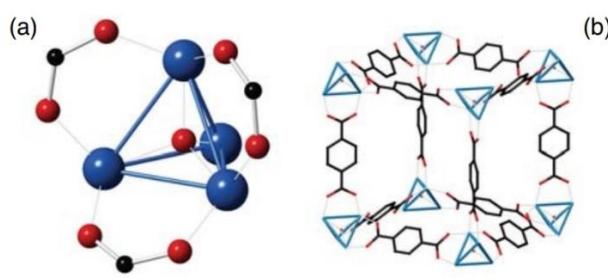
MOF-5 structure. Red, black and blue represents O, C and Zn respectively (figure 6)

Commonly used techniques for the synthesis of MOF-5 are hydrothermal, solvothermal, microwave assisted and sonochemical methods. Among all of these methods solvothermal method is simple and efficient, in which the amount of the product formed is massive.

The type of synthesis methods may affect the crystal growth, crystal structure, crystallite size, crystal morphology of MOF-5. 20 Subsequently, customary cubic – shaped and micro–crystallite of MOF -5 may well be gotten beneath certain mechanical conditions by

solvothermal methods. In the synthesis process of MOF – 5, the bond vitality of the coordination bond formed between metal and organic ligands are less than that of covalent bond and metal bond. On the other hand, the framework with a high penetrability structure isn't sufficient to back its quality. After expulsion of an expansive number of free solvents in the framework, these highly open structures will be obviously distortion and the loss of crystallinity.

The precious structure of the crystal MOF-5 will be seriously harmed due to the collapse, pulverizing the crystal structure of the MOF-5 material and cause misfortune of the topological structure into an amorphous powder.
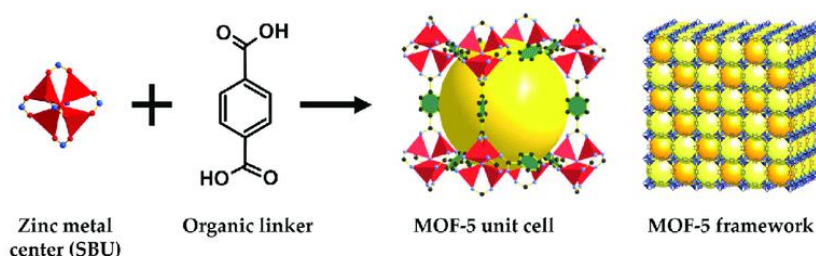
Schematic representation of formation of MOF-5 (figure 7).

There exist a number of applications for MOF-5 as that of all other MOFs. MOF-5 can be used as a photocatalyst, for gas storage i.e adsorption and desorption. It was established that MOF-5 is a very good semiconductor. Currently, it is used for drug delivery systems, adsorption of textile dyes, metal doping, nano particle doping etc.
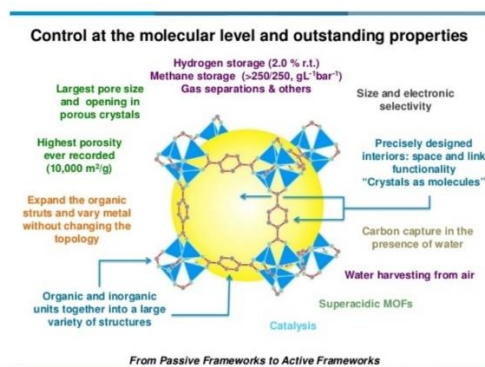
Representation of MOF-5 with its properties (figure 8).

1.2 COPPER OXIDE NANOPARTICLES

Research in nanomaterials has increased exponentially due to their unique chemical and physical properties, which are different from those of bulk materials, which includes increased electrical conductivity and resistivity, toughness and ductility, increased hardness and strength of metals and alloys, increased chemical reactivity, and diverse and versatile biological activity.

A nanoparticle refers to a particle of matter whose particle size ranges between 1 to 100nanometers in diameter. Nanoparticles includes carbon-based nanoparticles (e.g. carbon nanotubes, fullerenes, graphene, carbon dots), ceramic nanoparticles (oxides, carbides, carbonates, phosphates in nano range), metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles.

Among the various nanoparticles, metal oxide nanoparticles have been investigated with great interest because these particles are widely used as industrial catalysts, chemical sensing devices, in medical applications, disinfections, as antimicrobials, fillers, opacifiers, catalysts, semiconductors and versatile biological activity [81-85].

Metal oxide nanoparticles like Copper Oxide (CuO), have got great attention mostly because of their antimicrobial and biocide properties and used in biomedical applications. CuO is a semiconductor nanoparticle with unique optical, electrical and magnetic properties. They are relatively cheap, photocatalytic, and stable in regard to their physical and chemical properties.

Copper Oxide nanoparticle (figure 9).

1.21 SYNTHESIS OF CuO NANOPARTICLES

The synthesis of CuO Nanoparticles can be done by different methods which results in different sizes.

1.211 Electrochemical method: This method is included in the group of soft chemical techniques that produce CuO nanoparticles. One of the advantages of this method is that this method is able to control the morphology and size of the resulting CuO nanoparticles by changing temperature, time, current density, composition or voltage. In this method, Cu is taken as the sacrificial anode.

1.212 PEG-Dependent synthesis: Polyethylene glycol (PEG) is used for the synthesis of CuO nanoparticles and is used in biomedical applications as it has good biocompatibility. PEG 400 is the most commonly used due to its lower toxicity.

1.213 Sonochemical method: This is a simple method using ultrasonic sound, which follows three steps: formation, development and the implosive collapse of the obtained ones.

1.214 Sol-gel method: It is a simple and relatively fast method and is therefore mostly used in the synthesis of CuO nanoparticles. Control of particle size between 10 to 40nm can be synthesised by this method.

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1.215 Other synthetic methods: Other synthetic methods such as hydrothermal approach, thermal oxidation method, alcohol thermal synthesis, liquid ammonia and microwave assisted synthesis can also be used for the synthesis of CuO nanoparticles.

1.22 PROPERTIES OF CuO NANOPARTICLES

The properties of CuO nanoparticles depend on the method of synthesis and is very important for their various applications, especially in biomedical research. The size, morphology and surface properties of CuO nanoparticles, temperature etc are very important aspect in determining their optical, catalytic, electrical and biological properties, which make them useful for many applications such as the development of cosmetics, pharmacological alternatives, paints, coatings etc. Antibacterial activity is one of the most important aspects of CuO nanoparticles.

2.221 Antibacterial activity of CuO Nanoparticles

Any specific mechanism of antibacterial effect of CuO nanoparticles is not known, but several mechanisms of action of CuO nanoparticles on bacterial cells have been put forward. The antibacterial activity of CuO nanoparticles vary depending on the particularities of bacterial cells. The cellular walls have great impact on antibacterial effect of CuO nanoparticles. For eg *E. coli* cells, which are gram negative, were killed to 100%, when CuO nanoparticles higher than 9.5% was used. But for *Staphylococcus aureus* which are gram positive, the killing ability was lower [86]. It was also reported that CuO nanoparticles inhibit the growth of *E. coli and S. aureus* depending on time and utilized dose [87]. It was reported that small particle with a large surface area have better antibacterial activity than larger ones. CuO nanoparticles also show antimicrobial activity against *Bacillus subtilis* [88].

1.23 APPLICATIONS OF CuO NANOPARTICLES

CuO nanoparticles are utilised mainly as antimicrobial agents. They are used in hospitals because of their antimicrobial ability to kill more than 99.9% of Gram-positive and negative bacteria within 2 h of exposure of a suitable dose. Research studies reported that utilization of CuO nanoparticles reduces the hospital-acquired infections the costs associated with healthcare. One of the most interesting inovation in this field is the development of bedsheets containing CuO nanoparticles which reduce microbial attachment and hence prevent microbial infections in hospitals [89].

Studies were conducted on women who used pillowcases and beddings containing CuO nanoparticles found an improved aspect of the facial skin and use of socks impregnated with

CuO nanoparticles showed an increased foot skin elasticity [90]. The major advantages of using CuO nanoparticles in textile materials are:

- It is potentially active against susceptible and antibiotic resistant microorganisms causing nosocomial infections.
- It has wide range antifungal spectrum and antibacterial properties.
- It inhibits biofilms or the development of microorganisms on the surface of materials.
- It does not cause skin irritation.
- It is safe to use externally and in low amounts.

CuO nanoparticles shows wound healing activity due to their capacity to limit microbial colonization to avoid infections and to promote the regeneration of damaged tissues. Wound dressings and have been developed to treat burns and skin injuries [91].

Thus, the main applications of CuO nanoparticles are due to their potent antimicrobial property that can be utilised in the development of several products. Studies are being continuing to reduce its toxicity and also to find different ways to utilize their antibacterial property [92].

1.3 NANOPARTICLES@MOF COMPOSITES

Nanoparticles@ MOF composites are recently attracting significant attention in various researches. Such composites possess the unique features of MOFs (crystal structure, high surface area, single site catalyst, special confined nanopore, tunable and uniform pore structure), but avoid some intrinsic weaknesses (limited electrical conductivity). The synergistic effects of both MOFs and the nanoparticles cause the composites to possess new properties and unprecedented performance, which are not attainable by individual parts. Nanomaterials such as metal or metal oxide nanoparticles, carbon materials and quantum dots can be incorporated in MOFs.

There are three main established approaches for the incorporation of nanoscale objects in MOFs, namely, "ship in bottle" approach, "bottle around ship" and one-step synthesis approach.

The "ship in bottle" approach involves the encapsulation of nanoparticles precursors in the cavities of MOFs, followed by further treatment leading to the desired functional structure. Various techniques, such as solution infiltration, vapor deposition, and solid grinding have been used for introducing nanoparticles precursors into MOFs. A double-solvent method (DSM) combined with reduction with reducing agents such as H_2 and $NaBH_4$, is successful in immobilising metallic nanoparticles including Pt, Pd, Rh, Ni nanoparticles and AuNi, RuNi,

AuCo and CuCo bimetallic nanoparticles inside the pores of MOFs without aggregation on the external surface of the framework.

The "bottle around ship" approach also known as the template synthesis approach involves two steps – the nanoparticles are synthesised individually stabilised by capping agents or surfactants and then adding it into synthetic solution containing MOF precursors to assemble the MOF. The nanoparticles do not occupy the pore size of the MOF but are surrounded by grown MOF material. This method controls the problems of the aggregation of nanoparticles on the external surface of MOFs, the size, morphology and structure of entrapped nanoparticles can be easily controlled because they are performed prior to the assembly of MOF framework. However, the introduction of nanoparticles sometimes results in difficulties with the subsequent growth of the MOF and also the presence of the capping agents might be unfavourable for the complete exposure of active sites and alter or degrade the performance of the nanoparticles.

The one-step synthesis approach involves directly mixing the precursors solution of nanoparticles and MOFs together, followed by the simultaneous growth of nanoparticles and MOF, assembling both of them into a nanostructure. When compared to the above strategies, this one is straightforward and simple, but it needs to balance the rate of the self-nucleation and growth of the nanoparticles and MOFs.

The applications of nanoparticle@MOF composites for CO oxidation, CO_2 conversion, hydrogen production, organic transformations, degradation of pollutants and enhancement of antimicrobial properties [93].

Microbial variations caused due to the abuse of antibiotics, disinfectants and other chemical drugs, is a very serious problem. The development of multidrug resistant (MDR) infectious microbes is a major challenge faced by healthcare system today. Moreover, most of the microbial infections in humans are caused by biofilm-forming pathogenic microorganisms. New, advanced and effective antimicrobial agents have to be developed to overcome the problems of conventional antimicrobial agents. The antibacterial agents are substances which can effectively kill pathogenic bacteria, which have become an important area of research nowadays. The application ranges of these compounds include various fields such as biomedical equipment, food packaging, reduced food corruption and improved water purification equipment. Nanomaterials especially, metal and metal oxide nanoparticles are a promising class of antibacterial agents that can overcome the problems related to conventional antibacterial agents. The aggregation of nano particles and to disperse them uniformly in substrate are the major concerns while working with nanoparticles, which can be overcome by

incorporating them into porous materials. Advanced porous materials having pore size in nano range (nanoporous material) can be used for the purpose.

Nanoporous zinc-based metal organic framework (Zn-MOF) was found to have antibacterial property [94]. Also, copper oxide (CuO) nanoparticle-based antibacterial agents have high antibacterial activity, broad antibacterial spectrum and low tendency to induce bacterial resistance [95]. CuO nanoparticles have higher antibacterial property, but they have the tendency to spontaneously aggregate into larger particles and cannot be dispersed uniformly in substrate. CuO nanoparticles are loaded on a suitable carrier to prevent them from aggregation and to promote antibacterial property. Nanoporous zinc-based metal organic framework (e.g. MOF-5) can be used as a carrier for CuO nanoparticles. A combination of CuO nanoparticles and MOF-5 can give enhanced antibacterial activity. The synthesis and characterisation of MOF-5 is an important aspect for the purpose which is to be studied in detail.

➢ **FUTURE SCOPE OF THE STUDY**

The research studies on metal organic framework have been gaining importance during recent years due to versatility in their applications. Some confusions regarding the structure, stability and properties of MOFs still prevails. Hence, further studies on MOF should be carried out, finding its importance in utilizing them for much more applications. Due to the high nanoporous structure of MOFs, they can be studied for the loading and delivery applications of several materials especially those of nanoparticles. Nanoparticles possessing many unique properties compared to that of bulk, may be loaded into MOFs and delivered to suitable sites; and detailed investigations should be carried out on this. One of the most important property of nanoparticles being their high antimicrobial activity, can be incorporated into MOFs and further studies including toxicological investigations can be employed in this field for utilising them for much more applications salutary for the world

CHAPTER 2

REVIEW OF LITERATURE

Metal organic frameworks, MOFs are a new class of hybrid organic-inorganic supramolecular materials comprising of ordered networks formed from organic electron donor linkers and metal cations. They can exhibit extremely high surface areas, as well as tunable pore size and functionality, and can act as hosts for a variety of guest molecules. Such properties enable them to be used in various fields. The review made by Mark D Allendorf group covers advances in the MOF field from the past three years, mainly focusing on applications, including gas separation, catalysis, drug delivery, optical and electronic applications, and sensing. They also summarize the recent work on methods of MOF synthesis and computational modelling [96].

Yu-Ri Lee introduced rapidly expanding MOF research works which presents a brief introduction to the currently available MOFs synthesis works including solvothermal or hydrothermal synthesis, microwave-assisted, sonochemical, electrochemical, mechanochemical, ionothermal, dry-gel conversion and microfluidic synthesis methods [97].

Rosi N L et al studied the hydrogen adsorption ability of metal organic frame work (MOF-5) composed of Zn4O(BDC)3 (BDC=1,4 benzene dicarboxylate) with a cubic three-dimensional porous structure. They found an uptake of 4.5 wt% (17.2 hydrogen molecules per unit formula) at 78K and 1 wt% at room temperature and 20 bar pressure. Inelastic neutron scattering spectroscopy of the rotational transitions of the adsorbed hydrogen molecules indicates the presence of two well-defined binding sites (termed I and II), which associated with hydrogen binding to zinc and the BDC linker, respectively. Preliminary studies on topologically similar isoreticular metal organic frameworks, IRMOF-6 and IRMOF-8, having cyclobutylbenzene and naphthalene linkers gave approximately double and quadruple (2.0 wt%) uptake of H_2 than found for MOF-5 at room temperature and 10 bars [98].

Among MOFs, MOF-5 being a promising new porous material for hydrogen absorption. Dipendu Saha and his co-workers made a comparative study of MOF-5 synthesis, characterisation and hydrogen adsorption was performed to examine the effects of different synthesis conditions on crystal structure, pore textural properties and hydrogen adsorption performance of MOF-5 materials. Three MOF-5 samples, MOF-5(α), MOF-5(β) and MOF-5(γ), synthesised with dimethyl formamide (DMF) as solvent and slightly different procedures

have shown similar phase structure and chemical composition, diverse crystal structures, varying pore textural properties and different hydrogen adsorption performance [99].

Iswarya N and his co-workers synthesized MOF-5 using zinc nitrate and terephthalic acid in dimethyl formamide. The synthesized MOF-5 is characterized using Fourier Transform IR Spectroscopy, X-Ray Diffractometry, Thermal analysis, Scanning Electron Microscopy and Transmission Electron Microscopy. The sample was found to be stable at high temperatures up to 3500 ^{0}C and can be used for high temperature applications. Adsorption studies showed that they are suitable for CO_2 and H_2 adsorption [100].

Among the several methods employed for the synthesis of MOF-5 powder, solvothermal synthesis or hydrothermal synthesis has been a prominent method. Colin McKinstry and his co-workers showed that crystals of MOF-5 powder can be formed in a solvothermal continuous process and are viable and can produce high quality, high yield of MOF-5 with a space time yield of nearly 1000kg m^{-3}day^{-1} [101].

Tri Ana Mulyati and co-workers synthesised MOF-5 using solvothermal method in which reaction mixtures of zinc nitrate hexahydrate and 1,4-benzenedicarboxylic acid (BDC) in dimethylformamide (DMF) were heated at various heating temperatures and times in order to observe the influence of heating temperature and time on crystallinity and morphology of the obtained MOF-5. The heating temperatures used were 105, 120 and 140 ^{0}C, respectively with heating times of 12-144 h. Phase purity and crystal morphology of the MOF-5s synthesised were studied using XRD and SEM. MOF-5 crystals with a higher crystallinity were obtained when the reaction mixtures were heated at 105 ^{0}C for 144 h, 120 ^{0}C for 24 h or 140 ^{0}C for 12 h. The maximum weight of MOF-5 crystal was generated from the reaction mixture heated at 120 ^{0}C for 72 h [102].

Aghajanloo M et al synthesized MOF-5 by hydrothermal method. Three-step activation treatment including preservation in initial solvent, solvent exchange and drying under evacuated condition was performed and it was found that activation is efficient by increasing the methane adsorption capacity of samples. The final product was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and pore size distribution (PSD). The corresponding pore size of MOF-5/DEF (sample A) and MOF-5/DMF (sample B) which was determined by nitrogen adsorption at 77 K, were equal to 31.27 Å and 42.65 Å and also BET surface area of samples 25 were 2157 and 1532 m2/g, respectively. Methane adsorption equilibrium for both samples was measured in a volumetric adsorption unit and it was found

that the adsorbent (A) and (B) in this work have methane adsorption capacity of 18.15 and 11.36 mmol/g at temperature of 298 K and pressure of 36 bar, respectively. Four different models (Langmuir, Unilan, Toth and Sips) were used to correlate the experimental equilibrium data. The root means square error values demonstrated that the Toth and Sips equation provide better models for correlating adsorption isotherms [103].

MOF-5 has nanoporous structure and hence can accommodate nanoparticles within them. As most of the metal and metal oxide nanoparticles possess several distinct features and an important one among them being their good antibaterial property, when incorporated in MOF can avoid their problem of aggregation and dispersion in the medium. Yinchun Hu and co-workers fabricated Ag@MOF-5 nanoplates by the template of MOF-5 and studied its antibacterial activity. MOF-5 was prepared by hydrothermal method and Ag@MOF-5 nanoplates were obtained to improve the antibacterial activity and dispersion of Ag nanoparticles. Ag@MOF-5 were characterised SEM, HR-TEM, EDS, XRD, FTIR and TGA. MOF-5 was found to be cube-like crystalline flaky particles with the size of 20-50 micrometers and Ag@MOF-5 were nanoscale sheets and 3-5nm Ag nanoparticles were uniformly dispersed and loaded on MOF-5 nanoplates. The results of antibacterial study shown that antibacterial ability of MOF-5 was limited, while Ag@MOF-5 showed good antibacterial ability to *E. coli and Staphylococcus aureus* [104].

CuO nanoparticles have known to have good antibacterial properties. Sunita Jadhav and co-workers prepared CuO nanoparticles by electrochemical reduction method and the synthesised CuO nanoparticles were characterised by UV-Visible, FT-IR, XRD, SEM-EDS and TEM analysis techniques. The nanoparticles were tested for antibacterial activity against *E. coli* and *Staphylococcus* strains and which are proved to be excellent [105].

Alabur Manjunath and co-workers synthesised CuO nanoparticles by aqueous precipitation method and CuO doped PVA nanocomposites by solution casting method. XRD studies confirmed the crystalline nature of CuO nanoparticles and the average crystalline size is found to be around 8nm [106].

CuO nanoparticles behave similar to ZnO nanoparticles. Harisankar Asadevi and c-workers prepared fluorescent active ZnO@MOF-5 composite encapsulating ZnO Nanoparticles onto the zinc terephthalate MOF (MOF-5). The new composite material was characterised by FTIR spectroscopy, powder XRD, UV-Visible spectroscopy, TEM, x-Ray photoelectron spectroscopy, Brunauer-Emmett-Teller analysis, Dynamic light scattering (DLS), Differential thermal analysis (DTA) and Photoluminescence spectroscopy [107].

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CHAPTER – 3

OBJECTIVES OF THE STUDY

- Hydrothermal synthesis of Zn-based MOF (MOF-5) using Zinc nitrate $(Zn(NO_3)_2.6H_2O)$ and Terephthalic acid (H_2BDC) and Dimethyl formamide (DMF) as solvent.
- Chemical composition and morphological characterization of Zn- MOF using: XRD (X-ray diffraction), FT-IR (Fourier transform spectroscopy) and SEM (Scanning electron microscopy).
- Hydrothermal or solvothermal synthesis of copper oxide nanoparticles incorporated MOF-5 (CuO@MOF-5) using CuO nanoparticles and MOF-5 using DMF as solvent.
- Comparative antibacterial study of MOF-5 and CuO@MOF-5 using a gram-positive bacteria, *E. coli* and a gram-negative bacteria, *Staphylococcus aureus*.

CHAPTER – 4

MATERIALS AND METHODS

4.1 APPARATUS REQIRED

- Beaker (100 ml, 250 ml)
- Glass rod
- Dropper
- R B flask
- Watch glass
- Funnel
- Standard measuring jar
- Filter paper
- Conical flask
- Magnetic stirrer
- Hydrothermal tray hot air oven
- Vacuum oven

4.2 REAGENTS AND SOLVENTS

Zinc nitrate hexahydrate ($Zn(NO_3)_2 . 6H_2O$, 98%) and Terephthalic acid (H_2BDC)) from Nice chemicals Pvt. Ltd. Dimethyl formamide (DMF) was purchased from Merck. Copper (II) acetate ($Cu(CH_3COO)_2.H_2O$), Glacial acetic acid (CH_3COOH) and Sodium hydroxide (NaOH) from Nice chemicals Pvt. Ltd. Ethanol (CH_3CH_2OH), Distilled water. The above purchased chemicals were of an analytical grade and were used without further purification.
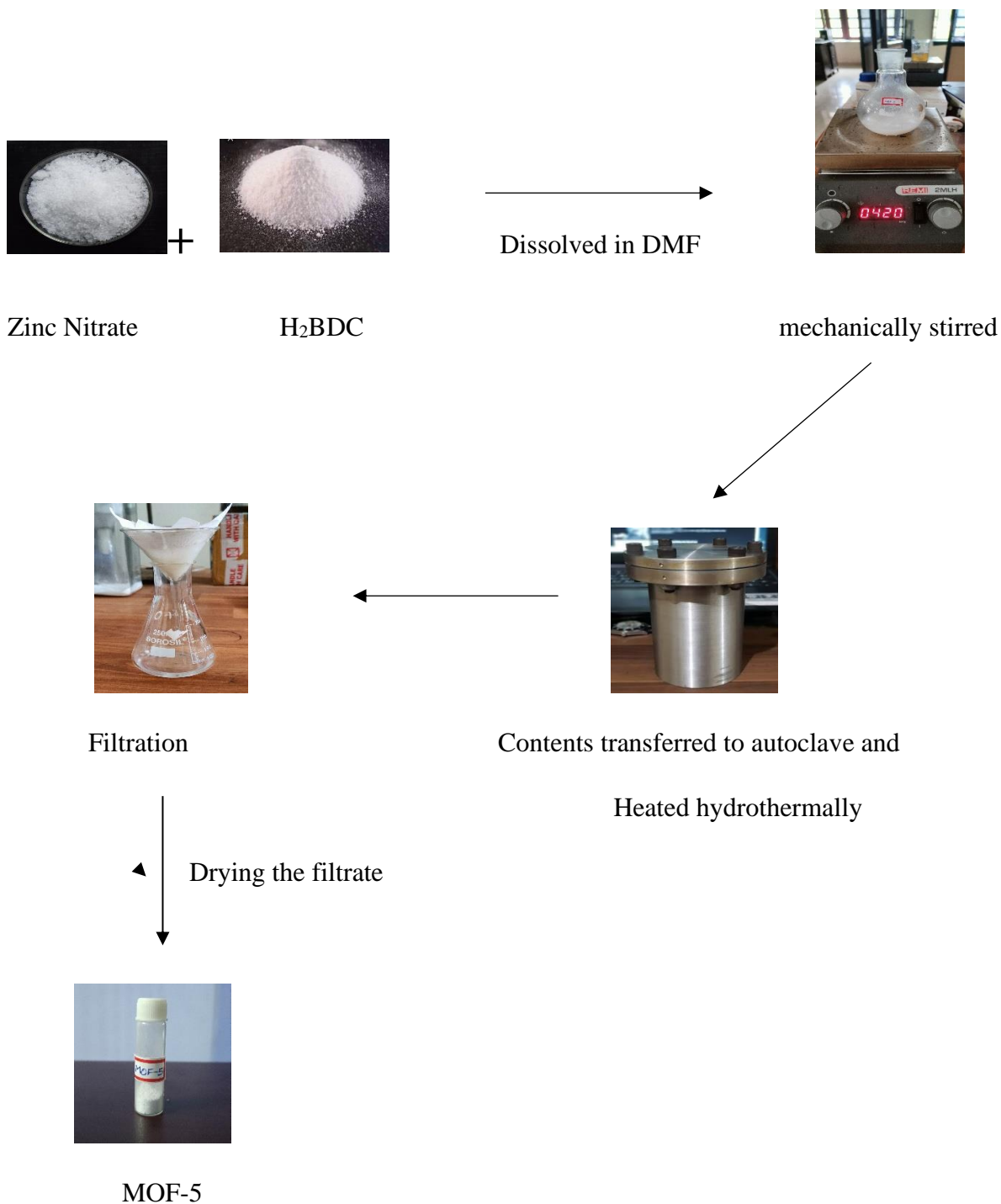
4.3 INSTRUMENTS REQUIRED

- X-ray diffraction spectroscopy (XRD)
- Scanning electron microscopy (SEM)
- Fourier transform infrared spectroscopy (FT-IR)
- UV-Visible spectroscopy

4.4 EXPERIMENTAL METHODS

4.41 Hydrothermal synthesis of MOF-5

Nanoporous MOF-5 was synthesised by following the procedures of Yinchun Hu and co-workers [104]. About 1.93 g zinc nitrate hexahydrate and 0.41 g of terephthalic acid (H_2BDC)
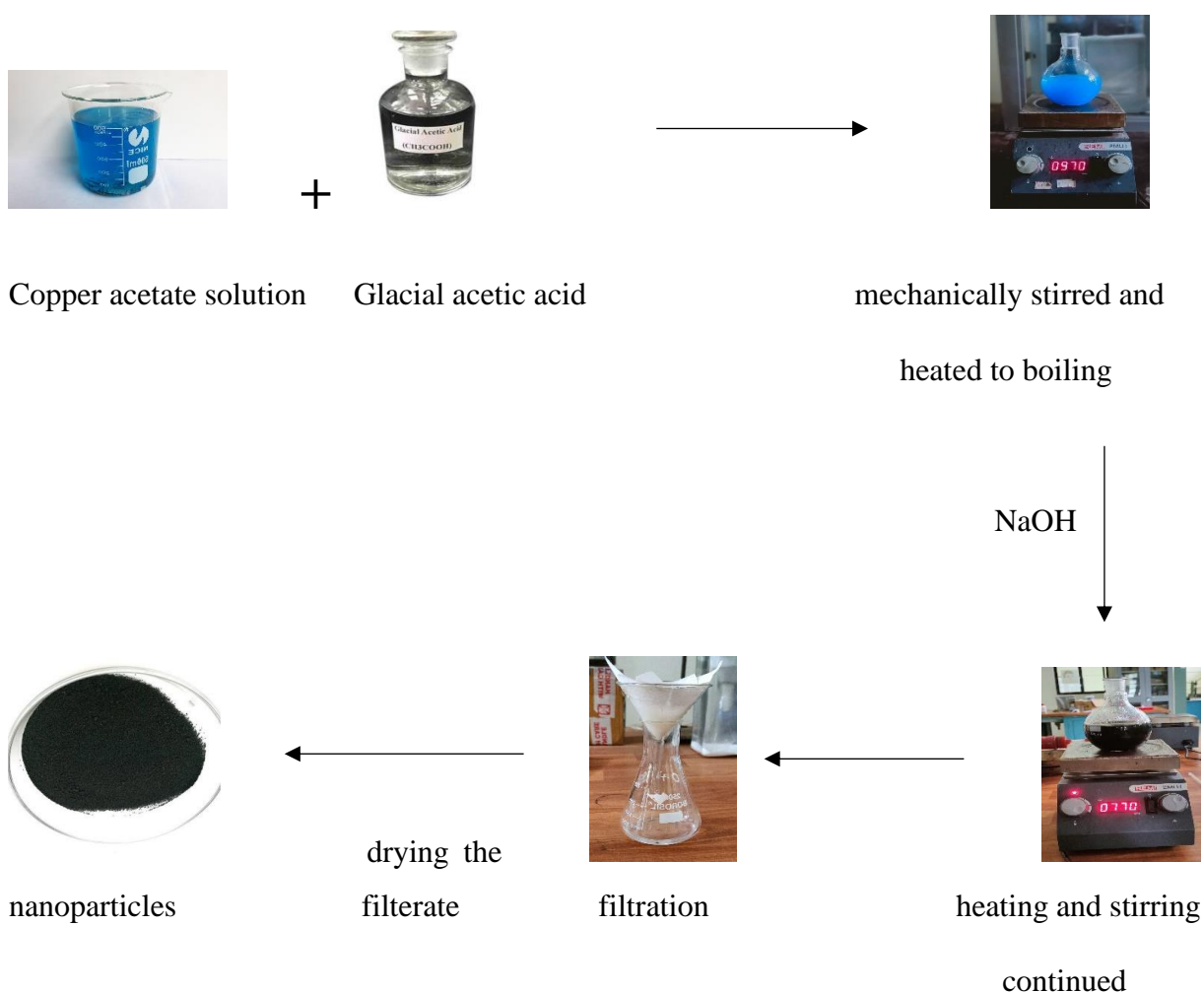
23

were dissolved in 56.4 ml of Dimethyl formamide (DMF) under constant agitation at atmospheric conditions. The resulting colourless solution was poured into a Teflon-lined hydrothermal autoclave, sealed and is heated in a hydrothermal tray hot air oven for 4 h at 130^0C. The white crystals of MOF emerged was separated by filtration and washed with DMF. The remaining solid was dried in vacuum oven at 60^0C for 3 h in vacuum oven.

Zinc Nitrate + H$_2$BDC   Dissolved in DMF   mechanically stirred

Filtration   Contents transferred to autoclave and

                                            Heated hydrothermally

Drying the filtrate

MOF-5

Schematic representation of hydrothermal synthesis of MOF-5 (figure 1)
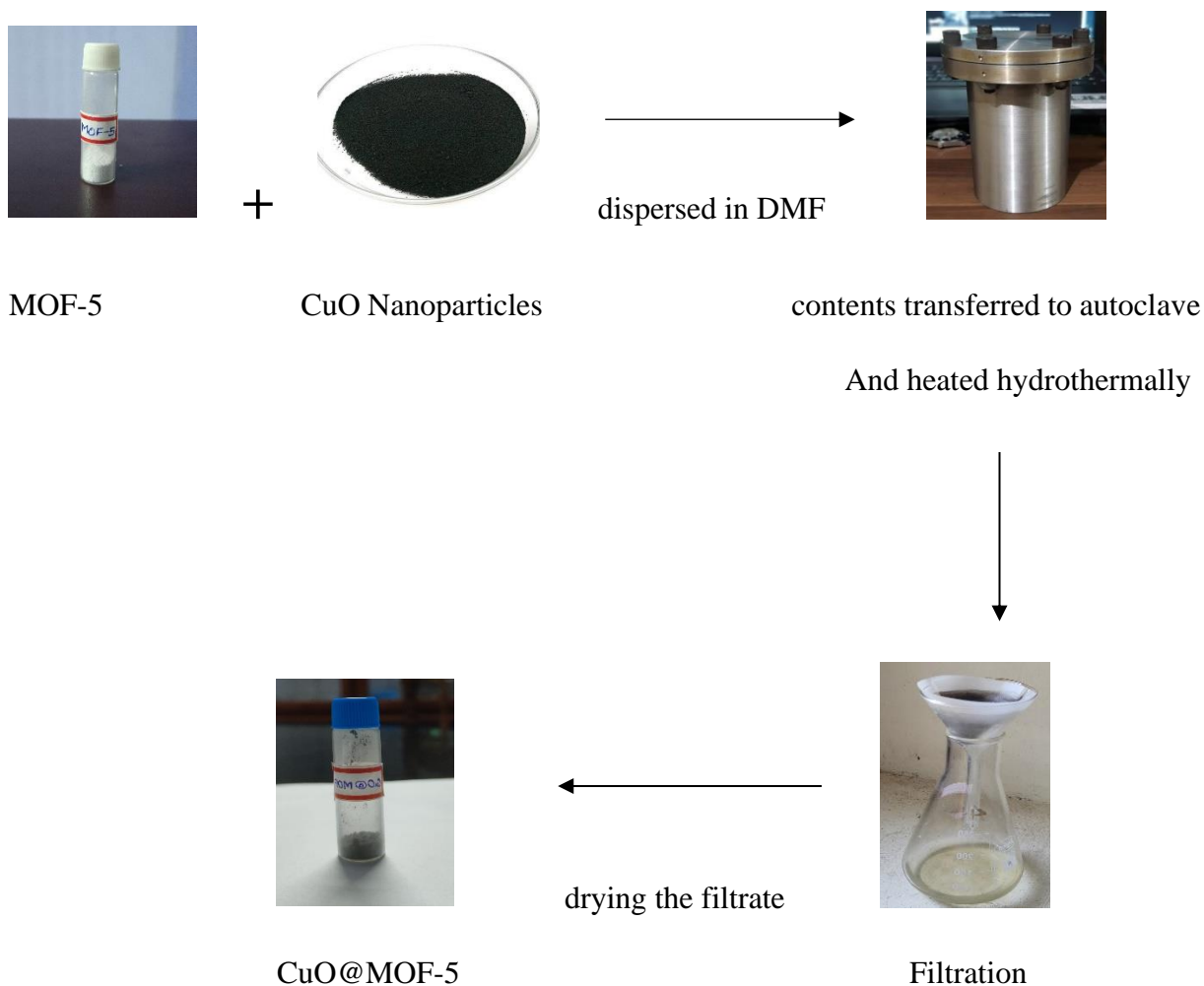
4.42 Synthesis of CuO Nanoparticles

CuO nanoparticles were synthesised by aqueous precipitation method by Alabur Manjunath and co-workers. 300 ml of 0.2 M copper (II) acetate solution and 1 ml glacial acetic acid were added to a round-bottom flask and heated to boil under magnetic stirrer. About 15 ml of 3 M NaOH solution were poured and the colour of the solution turned from blue to black immediately and a black suspension was formed simultaneously. The reaction was carried out under stirring and boiling for 3 h. The mixture was cooled to room temperature and centrifuged by which a wet CuO precipitate was obtained. The precipitate was filtered and washed with distilled water and absolute ethanol for several times. The resulting product was dried at 80^0C for 8 h to obtain the dry powder of CuO nanoparticles.

Copper acetate solution   Glacial acetic acid   mechanically stirred and

heated to boiling

NaOH

drying the
nanoparticles   filterate   filtration   heating and stirring

continued

Schematic representation of synthesis of Copper Oxide Nanoparticles (figure 11)

4.43 <u>Synthesis of CuO@MOF-5</u>

CuO@MOF-5 was synthesised following the procedure of Harisanker Asadevi and co-workers. Pure CuO nanoparticles and MOF-5 were mixed in a 1:4 ratio and were dispersed and mixed in 40 ml of dimethyl formamide. The reaction mixture was stirred continuously for 30 minutes. The mixture was poured into a teflon-lined autoclave, sealed and heated at 150^0C for 3 h. The remaining mixture after cooling was filtered, washed with DMF and dried under room temperature.

MOF-5   CuO Nanoparticles   contents transferred to autoclave

And heated hydrothermally

drying the filtrate

CuO@MOF-5   Filtration

Schematic representation of hydrothermal synthesis of CuO@MOF-5 (figure 12)

4.5 <u>CHARACTERISATION TECHNIQUES</u>

4.51 <u>X-Ray Diffraction (XRD)</u>

Analysing the crystal size by X-ray diffraction using a Rigaku Miniflex-II X-ray diffractometer with CuKα emission in assynthesized conditions of the materials. Power X-ray diffraction (PXRD) is widely used to determine the structural parameters and crystallinity of the MOFs.

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Once the diffraction peaks are identified, the crystallite size is calculated using the Scherrer's equation, usually with the most intense no-overlapped peak.

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

D the crystallite size, K a size factor (values among 0.84–0.98 depending on the equipment), β the full width at half maximum height of the peak (FWHM), and θ the Bragg angle for the peak identified in the diffraction pattern.

Powder XRD analytical service is most widely used for the identification of unknown crystalline materials. The scattered intensities are angle dependent in the Bragg-Brentano geometry the X-ray beam falls at an angle 2Θ. In this geometry atomic spacing between planes "d" can be calculated using Braggs relation [108].

➤ 2d sin Θ =n λ, where Θ is the angle of incidence and λ is the wave length. The MOF -5 sample analysed over a range of about 5˚< 2θ < 80˚.

4.52 Scanning Electron Microscopy

The SEM technique is routinely used for MOFs characterization. It generates high-resolution two-dimensional (2D) images that display the shape of the material and its spatial variations, revealing information about the external morphology, dispersion, and mixture of phases. The porous structure that characterizes MOFs gives rise to particles of curious shapes, such as cubes, bars, rhombohedra, and so on, yielding a varied morphology. Depending on the SEM equipment used and the insulating nature of some MOFs, the SEM characterization can require a previous pre-treatment by coating the surface with a conductive material, usually gold. To examine the sample crystal structure and size, each sample was analysed with 33 scanning electron microscopy in a Hitachi TM-1000 table-top device without any prior gold deposition. All the MOF-5 samples were also investigated for their crystal phase structure.

4.53 Fourier Transform Infrared-Spectroscopy (FT-IR)

FT – IR analysis helps clients understand materials and products. FT- IR offers quantitative and qualitative analysis for organic and inorganic samples. Fourier Transform Infrared Spectroscopy identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FT- IR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.

Fourier transform infrared (FTIR) spectra were obtained by using a Nicolet FT-IR Impact 400 system and KBr pellet samples. The sample was scanned over the spectral range of 400 to 4000 cm^{-1}.

4.54 <u>UV-Visible spectroscopy for nanoparticle analysis</u>

UV-Visible spectroscopy is often used for identifying, characterising and studying nanoparticles as nanoparticles possess optical properties that are sensitive to size, shape, concentration and refractive index near its surface. The relative percentage of scatter or absorption from the measured extinction spectrum depends on the size, shape, composition aggregation state of the sample. The sample absorb light or scatter light or both and the smaller particles will have a high percentage of their extinction due to absorption. CuO nanoparticles are identified using uv-visible absorption spectrum between 200-800nm wavelength.

4.6 <u>ANTIBACTERIAL STUDY</u>

Agar well diffusion method was used to evaluate the antibacterial activity of MOF-5 and CuO@MOF-5. Petri plates containing 15-20 ml Muller Hinton Agar medium was seeded with bacterial culture of *E. coli* and *Staphylococcus aureus.* Four wells with a diameter of 8 mm (20 mm apart from one another) were punched aseptically with a sterile cork borer in each plate. The test samples (50 and 100μL) were added into the wells T1 and T2 from 10 mg/ml stock. Gentamycin and the solvent used for sample dilution were added as positive and negative control respectively. The plates were incubated for 24 h at 37^{0}C, under aerobic condition. After incubation, the plates were observed and the zone of bacterial growth inhibition around the wells was measured in mm.

CHAPTER-5

RESULT AND DISCUSSION

MOF-5 metal organic framework was prepared by hydrothermal synthesis method by the reaction of zinc nitrate hexahydrate and H_2BDC. DMF was used as the solvent because it can dissolve both the solvents. After heating in hydrothermal tray hot air oven, the crystals of MOF-5 formed and was washed with DMF. Sample obtained after drying in vacuum oven is shown in figure (13).

MOF-5 (figure 13)

After the synthesis a white powder of MOF-5 was obtained, which was further confirmed by using Fourier transfer infrared spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM) and High-resolution transmission electron spectroscopy (HR-TEM).

The prepared MOF-5 was mixed with CuO nanoparticles in DMF solvent and heated hydrothermally in hydrothermal tray hot air oven. The CuO@MOF-5 was formed which was washed with DMF. Sample obtained after drying in vacuum oven is shown in figure (14).
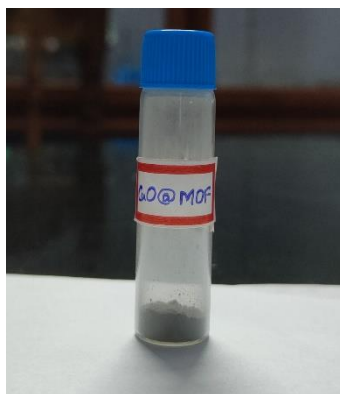

CuO@MOF-5 (figure 14)

Comparative antibacterial study of synthesised MOF-5 and CuO@MOF-5 were conducted.

5.1 Scanning electron microscopy (SEM)

Figure (15), (16) and (17) shows the SEM images of synthesised MOF-5 material. These images indicate cubic morphology for the prepared crystals of MOF-5. MOF-5 is a powdery material with a good level of crystallinity. The crystalline nature of MOF-5 leads to higher specific surface area and probably better adsorbent. The images also show the porous nature of the prepared MOF-5. It is evident from the SEM images that the powder morphology is ordered for this particular sample.
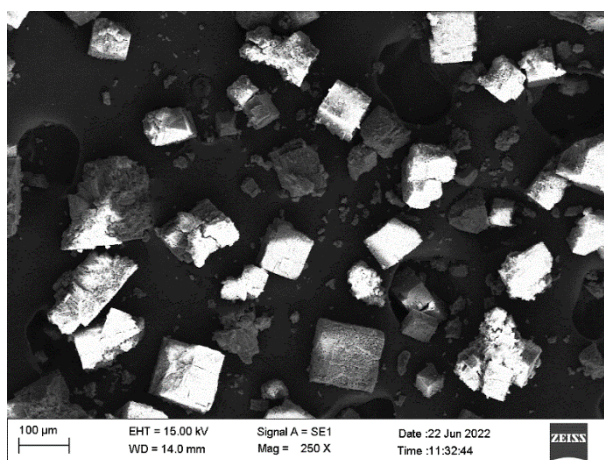

SEM image of MOF-5 at 100μm (Figure 15)
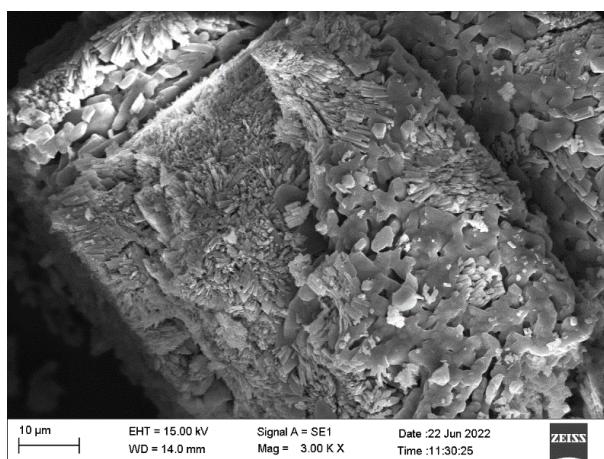
SEM image of MOF-5 at 10μm (Figure 16)
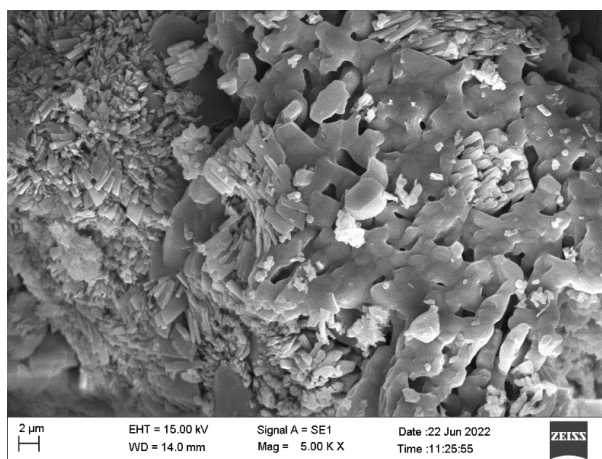
SEM image of MOF-5 at 2μm (Figure 17)

## 5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure (18) represents the FT-IR spectrum of MOF-5. FT-IR confirms the presence of functional groups present in MOF-5. The two sharp peaks obtained at 1577.71 cm^{-1} and 1368.32 cm^{-1} corresponds to the symmetric and asymmetric stretching of C-O bonded to Zn, respectively. Several small peaks occurring in the range of 1250 to 950 cm^{-1} correspond to the in-plane bending of C-H group present in the benzene ring of the BDC linker. Similarly small peaks occurring in the range of 900 to 660 cm^{-1} correspond to the out-plane bending of C-H group of the benzene ring of the BDC linker. Peaks occurring around 500 cm^{-1} are because of the Zn-O stretching. The broad peak observed at 3191.78 cm^{-1} correspond to O-H group of the water and indicates the presence of humidity that is frequently located in the metal coordinates. These all details are comparable with the reviews made by *Sabouni et al ; Coates ;*.Therefore from the details of FT-IR spectrum, the synthesised sample contains MOF-5.
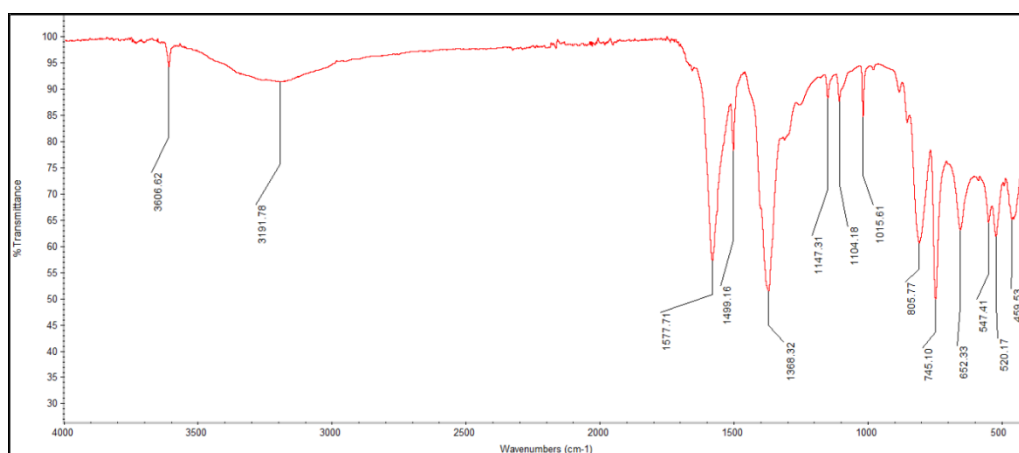
FT-IR spectrum of MOF-5 (Figure 18)

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5.3 X-ray Diffraction (XRD)

Figure (17) shows the XRD pattern of the synthesised MOF-5. The peak at $2\Theta = 9.7^{\circ}$ corresponds to MOF-5 crystal plane confirming the successful synthesis of MOF-5. The MOF-5 framework is also confirmed due to the presence of peak near $2\Theta = 13$. The splitting of the peak at $2\Theta = 9.7^{\circ}$ is an indication of the distortion in the cubic symmetry. An intense peak of MOF-5 at $2\Theta = 8.9^{\circ}$ is due to the decomposition of MOF-5 which may be due to exposure to air. The XRD pattern look similar to that of work of Ata-ur-Rehman and co-workers [109]. However, one key peak $2\Theta = 6.9^{\circ}$ was missing in the present study, probably due to some alterations of atomic orientation in crystal plane by solvent and other adsorbate molecules that fill the mesopores of MOF-5. Several unidentified peaks are also present which may be due the presence of some impurities within the pores. By analysing the peaks obtained in the diffractogram, size of the particle can be achieved by using Scherrer's equation by calculating fwhm, so that the crystallite size of MOF-5 is 38.17nm.
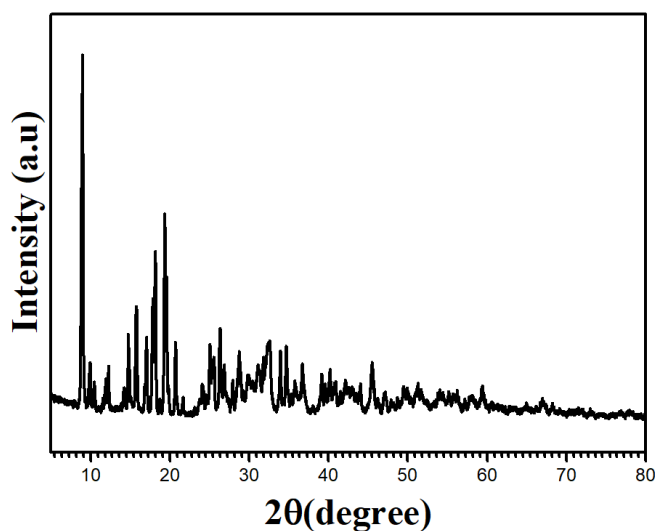

XRD image of MOF-5 (figure 19)

5.4 UV-Visible spectroscopy for CuO nanoparticle analysis

The formation of CuO nanoparticles can be detected from UV-visible spectrum and here figure (20) represents the UV-Visible spectrum of the synthesised CuO nanoparticles. UV-visible spectral analysis was done in the wavelength range of 200 to 800nm. The UV-visible spectra of the CuO nanoparticles exhibit the maximum absorption peak between 350 to 400 nm

suggesting the CuO nanoparticle formation. In the spectra, maximum peak is attributed to the shift in surface plasmon resonance resulted by the absorption of metal oxide nanoparticle.
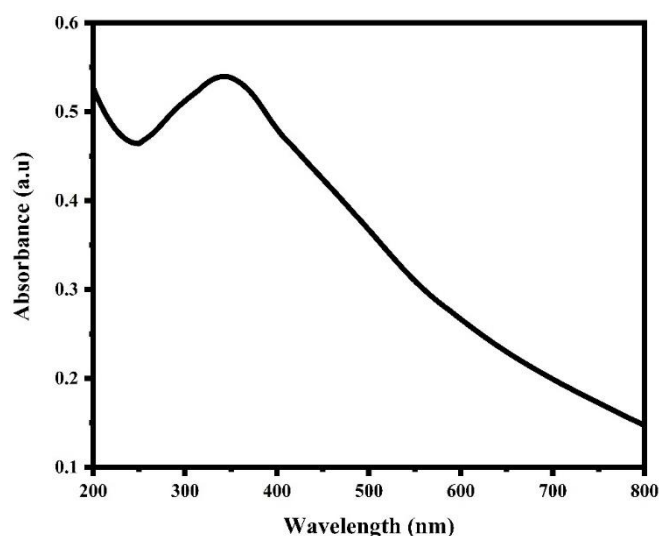

UV-Visible spectrum of CuO nanoparticles (Figure 20)

5.5 Comparative antibacterial study of MOF-5 and CuO@MOF-5

The synthesised MOF-5 and CuO@MOF-5 are tested for antibacterial activity using *Escherichia coli* (a gram-negative bacteria) and *Staphylococcus aureus* (a gram-positive bacteria) shown in figure (21), (22), (23) and (24). T_1 is the 50μl of sample from 10 mg/ml and T_2 is 100μl of sample from 10 mg/ml are being used for antibacterial study. Both MOF-5 and CuO@MOF-5 show no inhibition zone on *E. coli* for T_1. MOF-5 and CuO@MOF-5 show small and almost same inhibition zone on *E. coli* for T_2 (13mm and 12mm respectively). Hence, MOF-5 and CuO@MOF-5 shows almost same antibacterial activity against *E. coli*. The average diameters of inhibition zones of MOF-5 and CuO@MOF-5 on *Staphylococcus aureus* were 17mm and 20mm respectively at T_1 and 19mm and 23mm respectively at T_2. This shows that CuO@MOF-5 show much more antibacterial activity than CuO@MOF-5 against *Staphylococcus aureus.*
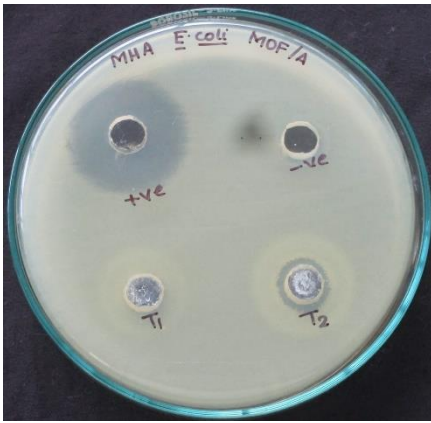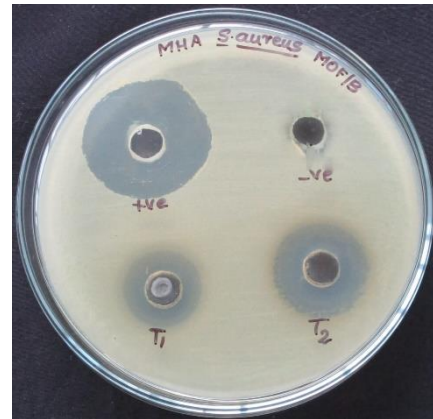
MOF-5 on E. coli (Figure 21)
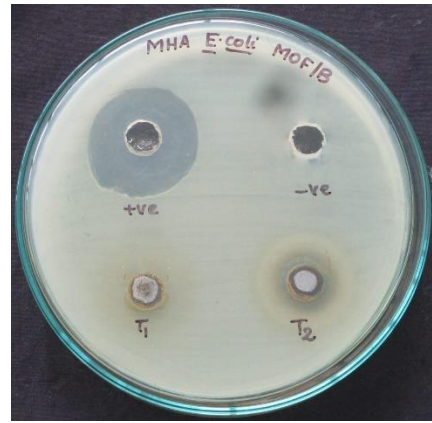
CuO@MOF-5 on E. coli (Figure 22)

MOF-5 on S. aureus (Figure 23)

CuO@MOF-5 on S. aureus (Figure 24)

CHAPTER – 6

CONCLUSION

MOF-5 materials have been known for their crystalline and porous structure that have several applications including storage of several molecules. In this study, MOF-5 was successfully synthesised by hydrothermal approach and was characterised using XRD, FT-IR and SEM analyses. Formation of MOF-5 and its crystalline nature was confirmed by XRD and FTIR studies. FT-IR study also confirmed the structure of MOF-5 and major two peaks obtained at 1577.71 cm^{-1} and 1368.32 cm^{-1}. SEM images showed the morphology and porous, crystalline and cubic structure of the synthesised MOF-5 powdered particles. The analysis techniques such as Power diffraction pattern gives the particle size of 38.17nm based on Scherrer equation. These data proves that the structure of the synthesised MOF-5 is similar with the literature reviews. This particular MOF-5 material can be used in the studies of applications. Copper oxide nanoparticles have been synthesised by chemical method and its formation was confirmed using UV-Visible spectrum giving maximum absorption peak between 350-400nm. The synthesised CuO nanoparticle was incorporated into the synthesised MOF-5 by hydrothermal method. Comparative antibacterial study between MOF-5 and CuO@MOF-5 was done with gram-negative *E. coli* and gram-positive *Staphylococcus aureus* bacteria. Antibacterial activity of MOF-5 and CuO@MOF-5 against *E. coli* was almost the same. But CuO@MOF-5 showed much more antibacterial activity than MOF-5 against *Staphylococcus aureus.* The antibacterial nature both MOF-5 and CuO@MOF-5 can be further studied for their applications.

CHAPTER - 7

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