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SYNTHESIS, PROPERTIES AND APPLICATIONS OF COPPER-BASED METAL ORGANIC FRAMEWORKS: A SHORT REVIEW

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***Abstract*— Metal organic framework are a class of compounds consisting of metal ions or clusters that are coordinated to organic ligands to form one-, two, or three dimensional structures. Among the number of metal-organic framework, copper based metal-organic framework are of great interest because of their value as an efficient adsorbent, versatile behavior for toxic gas accumulation, removal of heavy metal from waste water, sensitive colorimetric detection of staphylococcus aureus, for electrochemical energy storage applications and applied for the synthesis of bioactive compounds. All these characteristics have encouraged extensive study of the chemical, physical, biological and industrial properties of metal organic frameworks of copper. So this review article provides a comprehensive overview of synthesis and most of the persists application of metal organic framework of copper.**

***Keywords*-Cu-Metal organic framework, Application of Cu-Metal organic framework**

I. INTRODUCTION

Nearly year of 2000, very small number of the MOFs were known and some of the materials with low porosity could be discussed as most of the MOFs known at that time would easily fit only in one chapter. After the progress of research work in the field of metal organic framework, from the year of 2016 it is possible to create a very long list with MOF structures alone. This significant progress results in the discovery of materials with record large surface areas. Nowadays, near about 10 000 MOFs are in existence, and MOF databases of hypothetical and real MOFs are being developed for managing the enormous amounts of data.[1-3]

Metal–organic frameworks (MOFs) are also proved as useful materials for environmental remediation due to their high surface area, porous structure, and application-specific tailoring of properties. In this regards, metal-organic frameworks based on transition metals are best catalysts and adsorbents for the remediation of gaseous and organic pollutants for the protection of our environment. Transition metal frameworks convert gaseous pollutants into value-added chemicals.[4]

A number of metal organic framework based on transition metals are available. Commonly used transition metals are iron, cobalt, nickel, zirconium, cadmium, copper, zinc, manganese, titanium and vanadium which are capable to link organic linkers and used for the synthesis of metal organic framework.[4-6] Among a large number of MOFs the authors selected copper based metal-organic frameworks for their synthesis and applications in this review study as they are of great interest because of their value as an efficient adsorbent, versatile behavior for toxic gas accumulation, removal of heavy metal from waste water, sensitive colorimetric detection of staphylococcus aureus, for electrochemical energy storage applications and applied for the synthesis of bioactive compounds.

A number of copper based MOFs are ava--ilable at present time. A few of them are as CPL-1 [Cu_2(2,3-pyrazinedicarboxylate)$_2$ (pyrazine)][7], that is mainly used for gas adsorption and separation and stable in air and aqueous solution at about 100^{o}C, Cu_2Cl_2(BBTA) [Cu_2Cl_2(1H,5H-benzo(1,2-d),(4,5-d′)bistriazole)][8] which acts as highly effective catalyst for photodriven hydrogen production; CuBDC [Copper 1,4-benzenedicarboxylate][9] which acts as an efficient and reusable catalyst for one-pot synthesis of benzophenazine derivatives Cu-BDC-(ted)$_{0.5}$ [Cu(1,4 benzenedicarboxylate) (triethylenediamine)$_{0.5}$][10] which is used in the oxidation of benzyl alcohol; CuBTC [Copper benzene-1,3,5-tricarboxylate][11] which is used as an efficient carbon dioxide adsorbents; CuBTC-P [Non-thermal plasma-treated CuBTC][12], which is used in low temperature SCR denitration; HKUST-1 [Cu-based MOF using trimesic acid][13], which is an effective catalyst for highly sensitive determination of ascorbic acid All these characteristics of copper based metal-organic frameworks, have encouraged extensive study of the physical, chemical and biological properties along with their applications.

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II. SYNTHESIS AND APPLICATIONS

Xiangjian Guo et. al., reported 2D and 3D copper-based metal organic frameworks that can be used for the electrochemical detection of hydrogen peroxide[14]. They prepared, two types of Cu-MOFs, a two dimensional (2D) sheet-like structure and other is three dimensional (3D) octahedral structure for the detection of hydrogen peroxide and compared them. They were modified on the glassy carbon electrode for the fabrication of electrochemical sensors. They found the sensor with 3D Cu-MOF modification (HKUST-1/GCE) presented better electrocatalytic performance than the 2D Cu-MOF modified sensor in H_2O_2 reduction. They found that these sensor showed two types of wide linear ranges of 2 μM–3 mM and 3–25 mM and 0.68 μM for low detection limit. It was also observed that the 3D Cu-MOF sensor showed decent stability and selectivity. Furthermore, this type of MOFs was used to detect H_2O_2 in milk samples. So we can say that this work will prove a convenient, practical, and low-cost analysis by using this type of this copper metal organic framework in the field of food industries, agricultural industries, environmental systems, and also in medical area.

Yi Jiang et. al., synthesize a copper 1, 3, 5-triamino-2, 4, 6-benzenetriol metal–organic framework[15]. They reported the synthesis and characterization of a two-dimensional (2D) MX_2Y_2-type (M = metal, X, Y = N, S, O, and X ≠ Y) copper 1, 3, 5-triamino-2, 4, 6-benzenetriol metal–organic framework ($Cu_3(TABTO)_2$-MOF. An insulating Cu_3 $(TABTO)_2$-Ar pellet can be used as metallic conductor with an electrical conductivity of 0.78 S cm^{-1} at 300 K after exposure to iodine vapor. This work provides the role of oxygen in the synthesis of redox-active ligand-based MOFs, expands 2D redox-active ligand-based electrically conductive MOFs, and offers more opportunities in sensing, photocatalytic, electronic, and energy-related applications.

Zhi Long Ma et. al., was examined a thermally and chemically stable copper (II) metal–organic framework with high performance for gas adsorption and separation[16]. They prepared (MOF), $\{[Cu(TIA)]\cdot 1.5CH_3OH\}_n$ (Cu-1), by the solvothermal reaction of cuprous (II) salt with the bifunctional ligand 3-(1H-1,2,4-triazol-1-yl)isophthalic acid. They observed that Cu-1 contains an apo three-dimensional skeleton and two types of one-dimensional channels with the help of single-crystal X-ray diffraction. This Cu-1 MOF possess excellent acid-alkali resistance and thermal stability, which is stable at pH = 2–13 aqueous solution and at 260°C air environment. They also found that the microporous copper MOF display very high uptakes of CO_2 (180 $cm^3\cdot g^{-1}$) and C_2H_2 (113 $cm^3\cdot g^{-1}$) at 273 K and displayed better adsorption selectivity for low molecular gases.

Bing An, Zhe Li and coworkers reported cooperative Cu (I) sites on a Zr_{12} cluster of a metal–organic framework for selective hydrogenation of CO_2 to ethanol[17]. In an alkali cation, the Zr_{12}-supported Cu^I centres activate hydrogen by bimetallic oxidative addition and induced C–C coupling for the production of ethanol. This work highlights the potential of using MOFs as a tunable platform to design earth-abundant metal catalysts for CO_2 conversion.

Melvin S Samuel , Kirankumar Venkat Savunthari and Selvarajan Ethiraj synthesize a copper (II) metal-organic framework based on 1,3,5-benzenetricarboxylic acid ($Cu_3(BTC)_2$) by the hydrothermal method[18]. Which exhibited pyramid shaped morphology and showed an average specific area of 32.16 $m^2\ g^{-1}$. They were characterized by using Fourier-transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), field emission scanning electron microscopy-energy-dispersive X-ray spectroscopy (FESEM-EDX), UV-Vis diffusive reflectance spectra, and Brunauer-Emmett-Teller (BET). They examined the photocatalytic activity of $Cu_3(BTC)_2$ on Rhodamine B (RhB) degradation under visible light irradiation and found that $Cu_3(BTC)_2$ photocatalysts can be capable to reduce rhodamine B dye in water[18].

A Team of Yanze Liu, Shuai Li, Lu Dai, Jiani Li, Jianning Lv, Zhejiaji Zhu, Prof. Dr. Anxiang Yin, Prof. Dr. Pengfei Li, Prof. Dr. Bo Wang were synthesized a highly crystalline hexaazatrinaphthylene (HATNA)-based 2D conjugated copper metal-organic framework for highly selective electroreduction of Carbon dioxide to methane[19]. They proposed that this type of MOF can be capable to facilitate the electroreduction of carbon dioxide to methane by synergic effect of HATNA and copper catecholate node, at about 78 % of selectivity and at 8.2 milliamperes current density per square centimetre ($mA\ cm^{-2}$) for 12 hours of long durability.

B. M. Omkaramurthy, G. Krishnamurthy & Sabine Foro were synthesized and characterised mesoporous nanostructure Cu-metal organic frameworks (Cu-MOF-1 and Cu-MOF-2) by a high temperature solvothermal route[20]. They were characterized these product by using X-ray diffraction, Brunauer–Emmett–Teller surface measurement, Thermo gravimetric analysis, Scanning electron microscope and Single crystal XRD methods. They were used cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopic techniques for examine electrochemical properties of these type of Cu-MOFs. They found that Cu-MOF-2 has showed greater specific capacitance than Cu-MOF-1 and both MOFs have significant charge storage capacity when they used 6 M KOH as electrolytes. They proposed that this type of excellent electrochemical properties of Cu-MOFs can be due to the rapid transport of ions into electrolytes/electrodes and also due to the large surface area of structurally fixed electro-active metallic centres. On the basis of these results they concluded that these Cu-MOFs can be used as potentially high-performance electrode materials for super capacitor applications.

Ravi Nivetha et al, repoeted the synthesis of meso-Cu-BTC metal organic framework (Cu-MOF) for electrocatalytic hydrogen evolution reaction[21] in 1 M NaOH solution. They found that meso-Cu-BTC electrocatalyst showed a low overpotential of 89.32 mV and an onset potential of 25 mV

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with an significant current density and proposed that meso-Cu-BTC can be act as a good candidate for electrocatalysis towards hydrogen evolution.

A team work of Kihak Gwon, Youngmee Kim, Hyunjun Cho, Seonhwa Lee, So-Hyeon Yang, Sung-Jin Kim and Do Nam Lee[22] proposed that polysiloxanes (PSs) which are widely used in different industries as lubricants, varnishes, paints, release agents, adhesives, and insulators, can also be used as a biomedical materials. They embedded a flexible antibacterial Cu-MOF (metal–organic framework) consisting of glutarate and 1, 2-bis (4-pyridyl) ethane ligands in PS via a hydrosilylation reaction of vinyl-terminated and H-terminated PSs at 25 °C. They tested bactericidal activities of the resulting Cu-MOF-embedded PS (PS@Cu-MOF) and the control polymer (PS) against Escherichia coli, Staphylococcus aureus, and methicillin-resistant Staphylococcus aureus. Thay found that PS@Cu-MOF exhibited more than 80% bactericidal activity toward the tested bacteria at a concentration of 100 $\mu g \cdot mL^{-1}$ and exhibited a negligible cytotoxicity toward mouse embryonic fibroblasts at the same concentration. They also observed that Release tests of the Cu(II) ion showed that PS@Cu-MOF was stable in a phosphate-buffered saline solution. On this basis they conclude that PS@Cu-MOF can be used in medicinal applications, like in implants, skin-disease treatment, wound healing, and drug delivery due to the low cytotoxicity and bactericidal activities.

T. Takenaka et al[23], repoeted that a two-dimensional (2D) perfect kagome lattice, has been formed in the $\pi - d$ conjugated 2D MOF $[Cu_3(C_6S_6)]_n$ (Cu-BHT) and it can be a strongly correlated unconventional superconductor with extremely low superfluid density and they observed a nonexponential temperature dependence of superfluid density, which indicates a the possible presence of superconducting gap nodes. They also found that magnitude of superfluid density is much smaller than those in conventional superconductors and follows the Uemura's relation of strongly correlated superconductors. On the basis of these results they suggested that the unconventional superconductivity in Cu-BHT originates from electron correlations related to spin fluctuations of kagome lattice.

Lei Gan, Arunraj Chidambaram and coworkers[24] reported a novel, porous, and hydrophobic MOF which is highly water-stable and based on copper ion and meta-carborane-carboxylate ligands mCB-MOF-1 for butanol recovery. They observed that this mCB-MOF-1 exhibits excellent stability in organic solvents, water, acidic and basic aqueous solutions. They found that mCB-MOF-1 is non-porous to water (type II isotherm), and it has higher affinity for ethanol, butanol, and acetone compared to ZIF-8.

Xiuping Liu, Yijun Wang, Wenwen Liu, Lianming Zhao and Wenyue Guo[25] reported types of novel water stable metal-organic frameworks, $[Cu(L)\cdot(4,4'\text{-bipy})\cdot(ClO_4)]_n$ (1) and $[Cu(L)\cdot(phen)\cdot(ClO_4)\cdot(H_2O)]_2$ (2), have been constructed by HL=[5-Mercapto-1-methyl] tetrazole acetic acid and Cu (II) salt in the presence of assistant N-containing ligands. They found that these MOFs possessed electrocatalytic activity for water oxidation in alkaline solution.

Ehab S. Gad et al[26] were constructed four new type of modified electrodes out of which two were carbon pasted (o-NPOE; electrode I and DOS; electrode II) and another two (o-NPOE; electrode III and DOS; electrode IV) were based on Cu(II)-MOF ionophore to determine concentration of copper ion (Cu(II)). They observed that the prepared electrodes exhibit Nernstian slope and have strong selectivity for Cu(II) ion against a large variety of cations. On the basis of this observations they concluded that the suggested electrodes were effectively used for the identification of Cu(II) ion in various samples of water.

A reserch team of Q. Fu, K. Xie, S. Tan, J. M. Ren, Q. Zhao, P. A. Webley and G. G. Qiao[27] was prepared a reduced copper metal-organic framework (rCu-MOF) containing Cu^{I} ions by reducing raw MOFs (Cu-BTC). They performed a series of polymer functionalization and coupling reactions and demonstrate that rCu-MOFs exhibited high activity, facile recyclability and good structural stability for different types of catalytic applications.

A comparative study of different synthetic methods of copper metal frameworks were done by P.M. Thabede and N.D. Shooto[28]. They prepared metal-organic framework of copper (Cu-MOF) by using the reflux method and microwave method and analysed these products by scanning electron microscopy (SEM), X-ray diffractometry (XRD), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and ultraviolet-visible (UV-Vis) spectroscopy. They observed in the SEM images that the microwave method synthesized particles were cubic while the reflux method produced amorphous material.

Zhao Liu et al[29], proposed that A flexible antibacterial fibrous membrane employing high antibacterial efficiency has great potential in healthcare applications. They prepared a three-dimensional copper(II) metal–organic framework $[Cu_2(CA)(H_2O)_2$, Cu-MOF-1] and poly(lactic acid) (PLA) [Cu-MOF-1/PLA] composite fibrous membrane through a facile electrospinning method. They observed that the Cu-MOF-1/PLA fibrous membrane exhibited outstanding bactericidal activities against E. coli and S. aureus with the antibacterial rates up to 99.3% and 99.8%, respectively. By the mechanism investigation which indicated that the slowly released Cu^{2+} ions could destroy the microenvironment of bacteria cells and destroy the integrity and permeability of the cell membrane, leading to enzyme inactivation, they concluded that prepared flexible fibrous membrane will advance progress toward developing a broad spectrum antibacterial textile for healthcare protection related applications.

Gahlot, Swat; Rajput, Abhishek and Kulshrestha, Vaibhav[30], repoeted Fabrication of composite membranes using copper metal organic framework for energy application. They synthesize the nanocomposite polymer electrolyte membrane (PEM) based on copper based metal organic framework (Cu-

MOF) and sulfonated poly ether sulfone (SPES), for fuel cell application. They analyzed prepared material and composite membrane through XRD, FTIR and TGA technique. They concluded on the basis of these measurement that the successful synthesis and thermal stability of MOF and also reported that prepared membranes exhibited good physicochemical properties and good ionic conductivity which can be utilized as PEM for fuel cell application.

Jia Liu, Shen-long Jiang and Qun Zhang[31], published an article related to doping copper ions in a metal-organic framework (UiO-66-NH_2): location effect examined by ultrafast spectroscopy. According to which they prepared two types of copper-doped metal-organic framework (MOF), [Cu@UiO-66-NH22] and [Cu-UiO-66-NH22]. In the former, Cu_{2+} 2+ ions are impregnated in the pore space of the amine-functionalized, Zr-based UiO-66-NH22; while in the latter, Cu_{2+} 2+ ions are incorporated to form a bimetal-center MOF, with Zr_{4+} 4+ being partially replaced by Cu_{2+} 2+ in the Zr--O oxo-clusters. They predicted on the basis of ultrafast spectroscopy, that the photoinduced relaxation kinetics associated with the ligand-to-cluster charge-transfer state is found to be in a sequence of Cu-UiO-66-NH22 >> Cu@UiO-66-NH22 >> UiO-66-NH22. Which also referred to the effect of copper-doping location in this Zr-based MOF system and the rational engineering of the specific metal-doping location in alike MOF systems to promote the photoinduced charge separation and to improve performances in photocatalysis based on copper-MOFs.

Lan Xue, Yi Yang, Shuai Wu, Yue Huang, Jinlong Li, Yang Xiang and Genxi Li[32], proposed in-situ reduction of porous copper metal–organic frameworks for three-dimensional catalytic click immunoassay. In this work, they fabricated reduced metal–organic frameworks (MOFs) for the development of the immunoassay. In their study, MOFs with well-defined porosity are accessible to the substrates of CuAAC, while the substrates can diffuse in the pore channel and these MOFs are beneficial for integration of copper ions into the three-dimensional lattice. After reduction, the copper nodes in MOFs are transformed from Cu^{II} to Cu^{I} in situ and they achieved spatiotemporal control to eliminate the primarily dissolution procedure. They also observed that the reduced MOFs can serve as a powerful catalyst to facilitate the CuAAC click reaction, which can be reduce time and improve the reaction efficiency and this proposed immunoassay showed high analytical performance for hepatitis B virus surface antigen (HBsAg) quantification in the linear range of 0.03–2.0 ng mL^{-1} with a detection limit down to 11.2 pg mL^{-1}. On these observations they conclude that the new immunoassay has been challenged in detection of clinical serum sample.

Chengxiang Chu et al[33] were successfully developed a fluorescent sensor for detection of L-histidine using Cu-MOFs/Fe3+3+ sensor. They proposed that the Cu-MOFs with blue emission served as the identification unit and signal source, and Fe3+3+ played the role of "quencher" in this system. Fe3+3+ induced the fluorescence quenching of Cu-MOFs to form Cu-MOFs/Fe3+3+ sensor due to the effect of photoinduced electron transfer (PET). After the addition of L-histidine, Fe3+3+ was captured by L-histidine to form L-histidine-Fe3+3+ complex, which inhibited the PET effect from Cu-MOFs to Fe3+3+, resulting in the fluorescence recovery of Cu-MOFs. With such a design, L-histidine detection was realized with a wide linear range from 1μμM to 190μμM. The limit of detection (LOD) was calculated as low as 0.156μμM. These results indicated the real applications and potential diagnostic value of Cu-MOFs/Fe3+3+ system.

V. Gómez, J. Benet-Buchholz, E. Martin and J. R. Galán-Mascarós[34] proposed an architectures in copper MOFs from 4-substituted anionic 1,2,4-triazoles. They synthesized three new copper-MOFs, $[Cu_3(L1)_2(OH)_4]_n$ (1), $[Cu(L1)(Cl)]_n$ (2), and $[Cu(H_2O)(L2)(Cl)]_n$ (3), under hydrothermal conditions by reaction of 4-substituted 1,2,4- triazole derivative ligands [L1 = 4-(1,2,4-triazol-4-yl) ethanesulfonate and L2 = 4-(1,2,4-triazol-4-yl)benzenesulfonate] with Cu^{2+} salts. They observed that prepared Cu-MOFs have a new type of unique crystal structures. They analysed magnetic properties of the three compounds and found that all these copper_MOFs showed antiferromagnetic interactions.

A team of Supaporn Bouson, Atiweena Krittayavathananon, Nutthaphon Phattharasupakun, Patcharaporn Siwayaprahm and Montree Sawangphru[35], reported antifungal activity of water-stable copper-containing metal-organic frameworks. They investigated antifungal activity of copper-based benzene-tricarboxylate MOF (Cu-BTC MOF), against Candida albicans, Aspergillus niger, Aspergillus oryzae and Fusarium oxysporum. They concluded that the Cu-BTC MOF can be capable to control the growth rate of C. albicans and it also reduce the the spore growth of A. niger, A. oryzae and F. oxysporum. On these results it can be say that Cu-BTC MOF can be used as a strong biocidal material against yeasts and moulds found in the agricultural and food processing industries.

Synthesis and characterization of structure for copper terephthalate metal-organic frameworks were reported by cantwell g. et al[36]. they reported a high-throughput (gram quantities) solvothermal method for the synthesis of copper terephthalate metal-organic frameworks in dmf. after applying a number of analytical technuqes, they cocluded that cu-tpa also exhibits reversible solvent-exchange properties which make this material can have potentially applications in gas storage and catalysis.

Y Uozumi, and A Tazawa[37], reported some work on the oxidation and reduction of olefins on copper/metal–organic framework catalysts.

Tresia Pangestua, Yosafat Kurniawana, Felycia Edi Soetaredjoa, b, Shella Permatasari Santosoa, Wenny Irawatya, Maria Yulianaa, Sandy Budi Hartonoa and Suryadi Ismadjia[38] repoeted the synthesis of biodiesel using copper based metal-organic framework as a catalyst. They reported that the metal-organic framework (MOF) produced from the coordination of

benzene-1, 3, 5-tricarboxylic acid (BTc) and divalent copper (Cu) used as a heterogeneous catalyst for biodiesel production. They also observed that the prepared CuBTc-MOF is applied to produce biodiesel from palm oil. They concluded on the basis of GC, optimal FAME yield in biodiesel of 91%, that the CuBTc-MOF exhibited potential catalytic activity in the production of biodiesel.

Some experimental and molecular study on dye removal from water by a graphene oxide-copper-metal organic framework nanocomposite were reported by Mostafa Dadashi Firouzjaei et al[39]. In this study, they were immoobilized a novel copper-based metal-organic framework (Cu-MOF) on graphene oxide (GO) and synthesized GO-Cu-MOF was used as an adsorbent. They were investigated kinetics data for the removal of dye molecules. In order to evaluate the performance of the adsorbent in removing a model contaminant based on the real-world water treatment conditions, they performed various parameters such as solution temperatures and pH, dye, and adsorbent concentrations. The synthesized adsorbent was characterized using different analysis techniques. These characterization results showed full exfoliation of GO in Cu-MOF. The adsorption kinetic results followed the rapid adsorption process with a pseudo-second-order characteristic. The GO-Cu-MOF exhibited higher adsorption capacity. They concluded on the basis of these dye removal experiments that the acidic condition and the higher temperature (65 °C) favours the adsorption of methylene blue (MB) on GO-Cu-MOF compound.

Camille Petit, Jacob Burress and Teresa J. Bandosz[40] collectively proposed the synthesis and characterization of copper based metal organic frameworks/graphite oxide composites. They prepared new types of composites by using a copper-based metal–organic framework and graphite oxide, with different ratios of HKUST-1 (also called MOF-199) and graphite oxide. X-ray diffraction, sorption of nitrogen, FT-IR spectroscopy, thermal analyses, scanning electron microscopy, and sorption of hydrogen techniques were used to characterizing the prepared compounds and parent materials. They found that these composites exhibit features similar to HKUST-1 as well as an increased porosity compared to the parent materials. They observed that some new small pores were also prepared as there observed an increase in the hydrogen uptake. They concluded on the basis of the obtained results that the building process of the composites occurs via the reaction/binding of the copper dimers from the HKUST-1 with/to the functional groups in graphite oxide.

Synthesis, Characterization and Comparative Study of Copper and Zinc Metal Organic Frameworks were also repoeted by Ezekiel Dixon Dikio and Abdullahi Mohamed Farah[41]. They were synthesized Metal organic frameworks (MOFs) of copper and zinc with 1, 4- benzenedicarboxylic acid and N,N-dimethylformamide at room temperature by solvothermal method. The prepared MOFs were characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

A team of M F M Fadli, H Misran, S Z Othman, A M S Bahari, N A Samsudin, S A Rosli, Z Lockman, A Matsumoto and N Ami[42] reported room temperature synthesis and characterizations of Cu-MOF using natural polysaccharide as organic linker. In this study, copper-based metal-organic framework was successfully synthesized using natural polysaccharide, gum Arabic (gA, Acacia Senegal) as potential organic linker by adopting the synthesis method from Misran et al. with some modifications. These studies indicated the possibility of natural polysaccharide as new, non-toxic, water soluble linker. Thermogravimetric Analysis (TGA) analyses of as-synthesized Cu-MOF exhibited three different weight losses when heated to ca. 600^{o}C. They concluded on the basis of FTIR that these natural polysaccharide can be employed as a new, non-toxic, renewable linker for the MOF materials.

Kritika, Narang, Kaiser, Farid and Akhtar[43] reported a copper MOF synthesized using a facile solvothermal synthesis. They found that the Cu-MOF crystals were of cuboid-shaped of 300-500 nm in size and also demonstrated that a BET surface area of 756 m^2/g for the prepared Cu-MOF. The prepared Cu-MOF showed carbon dioxide uptake capacity of 2.1 mmol/g at 273K and 100 kPa and 1.8 mmol/g at 293 K and 100 kPa. The gravimetric high-pressure adsorption was carried out for both CO_2 and CH_4 gases at 10 bar. The Cu-MOF showed 3.7 mmol/g uptake of CO_2 and 2.5 mmol/g for CH_4 at 10 bar and 293 K. The isosteric heat of adsorption (Q_{st}) using Van't Hoff equation was 18 kJ/mole for CO_2 adsorption, which describes the low energy penalty for the regeneration cycles. To investigate CO_2 separation performance from CH_4, the Cu-MOF powders were structured into mechanically strong hierarchically porous pellets and breakthrough adsorption and desorption cycles were measured. The breakthrough data was used to obtain mass transfer coefficient and diffusivities value[44-47].

Robert R. Tuttle et al[48] reported about copper metal-organic framework surface catalysis to discuss about catalyst poisoning, IR spectroscopic and kinetic evidence to determine the nature and number of the catalytically active sites.

Sheta M. Sheta, Said M. El-Sheikh and Mohkles M. Abd-Elzaher[49] were prepared novel copper metal–organic framework nanoparticles Cu-MOF-NPs (C1) via two simple alternative methods and confirmed by analytical characterization using mass, IR, Raman, XRD spectrum, HR-TEM and TGA-DSC. On the basis of these analysis techniques they indicated that Cu-MOF-NPs (C1) were successfully used as biosensors for the assessment of the triiodothyronine hormone (T3). They also observed that the Cu-MOF-NPs (C1) show more enhanced biological activity against various pathogens (five strains of bacteria: Gram positive and Gram negative) when compared to an antibacterial agent and the effectiveness of Cu-MOF-NPs increases with increasing particle dose.

Özlem H. Demirel, Timon Rijnaarts, Patrick de Wit, Jeffery A. Wood, Nieck E. Benes[50] reported the electroforming of a metal-organic framework on porous copper hollow fibers and the porous copper hollow fibers have been used. They were focused on the effects of the presence of a supporting electrolyte and the magnitude of the applied electrical potential on the formation and the morphology of the films. They also observed the formation of more uniform film with smaller particles at low potential and in the absence of a supporting electrolyte. They suggested that this is due to the more pronounced electric-field driven mass transport of the organic ligand from the liquid bulk towards the surface of the electrode combined with the slower dissolution of copper due to the lower overpotentials. They concluded that in the presence of a supporting electrolyte, the ligand transport is much slower and copper dissolution is higher due to higher overpotentials which is responsible for the formation of less homogeneous films and the growth of metal-organic framework crystals in the liquid bulk and also suggested that the localized formation of thin metal-organic framework films on metal porous hollow fibers with high surface area to volume ratio can have a towards various applications in the field of membranes, microfluidic devices, sensors and heterogeneous catalysts.

Mar´ıa Albert-Soriano and Isidro Manuel Pastor[51] reported that Metal-organic framework based on copper and carboxylate-imidazole as robust and effective catalyst in the oxidative amidation of carboxylic acids using formamides and developed a protocol for the synthesis of amides was developed by using an oxidative coupling reaction of carboxylic acids and formamides in the presence of an oxidant and a metal–organic framework (MOF) based on copper and 1,3-bis(carboxymethyl)imidazole (bcmim) as the catalyst. The reactions gave good conversions with good selectivity, and the $Cu(bcmim)_2$ heterogeneous catalyst was easily recovered. A metal–organic framework (MOF) based on copper and 1,3-bis(carboxymethyl)imidazole (bcmim) was prepared on a gram scale by using a precipitation method at room temperature.

III. CONCLUSION

Metal organic framework are a class of compounds consisting of metal ions or clusters that are coordinated to organic ligands to form one-, two, or three dimensional structures. Among the number of metal-organic framework, copper based metal-organic framework are of great interest because of their value as an efficient adsorbent, versatile behavior for toxic gas accumulation, removal of heavy metal from waste water, sensitive colorimetric detection of staphylococcus aureus, for electrochemical energy storage applications and applied for the synthesis of bioactive compounds. All these characteristics have encouraged extensive study of the chemical, physical, biological and industrial properties of metal organic frameworks of copper. So this review article provides a comprehensive overview of synthesis and most of the persists application of metal organic framework of copper. This review highlighted research work of many researchers reported in literature for synthesis, properties and different application. From this review it may be concluded that the modification in Zn-MOFs displayed valuable physiochemical and pharmacological activities and these modifications can be utilized to develop potentially biologically active agents for future investigations. This review can be helpful to develop various new compounds possessing Zn-MOFs moiety that could be better in terms of efficiency and safe therapeutic agents of clinical importance**.**

IV. REFERENCES

[1]. "The chemistry of metal organic framework"(2016) Stefan Kaskel, Wiley – VCH Verlag GmbH & company KGaA
[2]. "Metal - Organic Framework Material', (2014) Wiley John Wiley & Sons Ltd.
[3]. "Metal-Organic Framework" (2015) Taylor & Francis group, LLC.
[4]. Yeisy C. L. et al, Environmental Chemistry Letters (2021) 19, 1295-1334.
[5]. Qiannan Liang, Jianmin Chen, Fengliang Wang, Yingwi Li, Coordination Chemistry reviews, (2020) 424, 213488.
[6]. Xiang - Long Qu, Xiao - Li Zheng and Xia Li, RSC Advances, (2016) 73, 69007-69015.
[7]. CD Bioparticles Drug Delivery
[8]. Ning-Yu Huang, Hai He, Hao Li, Pei-Qin Liao and Xiao-Ming Chen (2020) Electronic Supp- lementary Material (ESI) for Chem Comm. This journal is © The Royal Society of Chemistry.
[9]. Salman Taheri, Hoda Mollabagher & Amir Hossein Seyed Mousavi, Taylor Francis Online (2021) doi.org/10.1080/10406638.2021.1984951.
[10]. Ling Peng, et al, RSC Advances (2016) Issue 76
[11]. Yuanyuan Liu, Pramila Ghimire, Mietek Jaroniec, Journal of Colloid and Interface Science(2019) 535, 122-132.
[12]. Shu Hao, Liu Yuling, Jia Yang, science of the Total environment (2022) 820, 152984.
[13]. Tianyang Shen, et al, RSC Advances (2020) 10 (39) 22881-22890.
[14]. Xiangjian Guo et al, Front Chem, 07 October 2021, doi.org/10.3389/fchem.2021.743637
[15]. Yi Jiang et al, J. Am. Chem. Soc. 2020, 142, 43, 18346–18354 Publication Date: October 6,2020, doi.org/10.1021/jacs.0c02389.
[16]. Zhi Long Ma et al, Inorg. Chem. 2021, 60, 9, 550–6558, Publication Date: April 16, 2021, doi.org/10.1021/acs.inorgchem.1c00357.
[17]. Bing An et al, Nature Catalysis volume 2, pages 709–717 (2019).
[18]. Melvin S Samue, Kiran kumar Venkat Savunthari and Selvarajan Ethiraj, 7, 2021 Aug;28

(30) 40835-40843. Epub 2021 Mar 26 doi:10.1007/s11356-021-13571-9.

[19]. Yanze Liu, Shuai Li, Lu Dai, Jiani Li, Jianning Lv, Zhejiaji Zhu, Prof. Dr. Anxiang Yin, Prof. Dr. Pengfei Li, Prof. Dr. Bo Wang, 07 May 2021, doi.org/10.1002/anie.202105966

[20]. B. M. Omkaramurthy, G. Krishnamurthy & Sabine Foro, S N Aapplied Sciences, (2020) Volume 2, Article number 342.

[21]. Ravi Nivetha et al, 2020 Mater. Res. Express, 7, 114001 doi.org/10.1088/2053-1591/abb056

[22]. Kihak Gwon, Youngmee Kim, Hyunjun Cho, Seonhwa Lee, So-Hyeon Yang, Sung-Jin Kimand Do Nam Lee Nanomaterials 2021, 11(3), 719; doi.org/10.3390/nano11030719.

[23]. T. Takenaka et al, Science Advances, 17 Mar 2021, Vol 7, Issue 12, doi: 10.1126/sciadv.abf3996

[24]. Lei Gan, et al, 2020, J. Am. Chem. Soc. 2020, 142, 18, 8299-8311, April 27, 2020.doi: 10.1021/jacs.0c01008

[25]. Xiuping Liu, Yijun Wang, Wenwen Liu, Lia-nming Zhao and Wenyue Guo, METEC WebConf. Vol 142, 2018, International Conference on Materials Applications and Engineering 2017 (ICMAE2017), Article Number 01004, doi.org/10.1051/matecconf/201814201004.

[26]. Ehab S. Gad et al, Int. J. Electrochem. Sci., 15 (2020) 11904 – 11919,doi: 10.20964/2020.12.21.

[27]. Q. Fu, K. Xie, S. Tan, J. M. Ren, Q. Zhao, P.A. Webley and G. G. Qiao, 2016, Chemical communications, Vol. 52, 82, 12226-12229,doi: doi.org/10.1039/c6cc06890a

[28]. P. M. Thabede and N. D. Shooto, Assian J. Chem. 2021, 33 (100) 2360-2364, doi.org/10.14233/ajchem.2021.23323.

[29]. Zhao Liu et al, Biometric science, 9, 2021, 3851-3859, doi: doi.org/10.1039/D1BM00164G

[30]. Gahlot, Swat; Rajput, Abhishek and Kulshre-stha, Vaibhav AIP Conference Proceedings, Volume 1942, Issue 1, id.050079, April 2018, doi:10.1063/1.5028710.

[31]. Jia Liu, Shen-long Jiang and Qun Zhang, 2020 33(4) 394-400, doi: 10.1063/1674-0068/cjcp2005070.

[32]. Lan Xue, Yi Yang, Shuai Wu, Yue Huang, Jinlong Li, Yang Xiang and Genxi Li, Analytical chemistry 2020 v.92 no.4 pp. 2972-2978, ISSN: 1520-6882

[33]. Chengxiang Chu et al, Nano Vol. 16, No. 02, 2150015 (2021) BRIEF REPORT Free doi: doi.org/10.1142/S1793292021500156.

[34]. V. Gómez, J. Benet-Buchholz, E. Martin and J. R. Galán- Eur. J. Inorg. Chem., 2014**,** 3125-3132.

[35]. Supaporn Bouson, Atiweena Krittayavathana-non, Nutthaphon Phattharasupakun, Patchara-porn Siwayaprahm and Montree Sawangphru Royel Society Open Science, 11 October 2017doi: doi.org/10.1098/rsos.170654

[36]. Cantwell G. Carson, Kenneth Hardcastle, Just-in Schwartz, Xiaotao Liu, Christina Hoffmann , Rosario A. Gerhardt, Rina Tannenbaum, European Journal of Inorganic Chemistry, Issue 16, 2338-2343, 2009

[37]. Y Uozumi, and A Tazawa, Synfacts 2017, 13 (02): 0220 doi: 10.1055/s-0036-1589852.

[38]. Tresia Pangestua, Yosafat Kurniawana, Felyc- ia Edi Soetaredjoa, b, Shella Permatasari Santosoa, Wenny Irawatya, Maria Yulianaa, Sandy Budi Hartonoa and Suryadi Ismadjia Journal of Environmental Chemical Engineer-ing, Volume 7, Issue 4, August 2019, 103277, doi; doi.org/10.1016/j.jece.2019.103277.

[39]. Mostafa Dadashi Firouzjaei et al, 2020, Journal of Water Process Engineering, Vol. 34, Published April 2020, Article number; 101180. doi: doi.org/10.1016/j.jwpe.2020.101180.

[40]. Camille Petit, Jacob Burress and Teresa J. Bandosz, Elsevier, Volume 49, Issue, 2nd Feb,2011, Pages 563-572, doi: doi.org/10.1016/j.carbon.2010.09.059.

[41]. Ezekiel Dixon Dikio and Abdullahi Mohamed Farah, Chem Sci Trans., 2013, 2(4), 1386-1394 Chemical Science Transactions doi:10.7598/cst2013.520

[42]. M F M Fadli, H Misran, S Z Othman, A M S Bahari, N A Samsudin, S A Rosli, Z Lockman A Matsumoto and N Ami, International Journ-al of Recent Technology and Enginnering (IJRTE) ISSN: 2277-3878, Volume-8, Issue-4, November 2019. doi:10.35940/ijrte.D5163.118419.

[43]. Kritika, Narang, Kaiser, Farid and Akhtar Conference Presentation, Conference Type: AIChE Spring Meeting and Global Congress on Process Safety, Presentation Date: August 19, 2020.

[44]. I Angelidaki, L Treu, P. Tsapekos, G Luo, S Campanaro, H Wenzel, et al, Biogas upgrading and utilization: Current status and perspectives, Biotechnology Advances. 36 (2018), 452-466.

[45]. Chaemchuen, NA Kabir, K. Zhou, F Verpoort, Metal - Organic Frameworks for upgrading biogas via CO_2 adsorption to biogas green energy,Chem. Soc. Rev. 42 (2013) 9304-9332.

[46]. B Yuan, X Wu, Y Chen, J Huang, H Luo, S Deng, Adsorption of CO_2, CH_4, and N_2 on Ordered, mesoporous carbon: Approach for greenhouse gases capture and biogas upgradi- ng, Environ. Sci. Technol., 47 (2013) 5474-5480.

[47]. K Zhou, S Chaemchuen, F Verpoort. Alterna- ative materials in technologies for Biogas upgrading via CO_2 capture, Renewable Sustai- nable Energy Rev. 79 (2017) 1414-1441.

[48]. Robert R. Tuttle et al, 6 August 2020, Chemis-try, ACS applied materials & interfaces, doi:10.1021/acsami.0c08961.



[49]. Sheta M. Sheta, Said M. El – Sheikh and Mohkles M. Abd-Elzaher, Dalton Transaction, 2018.
[50]. Özlem H. Demirel, Timon Rijnaarts, Patrick de Wit, Jeffery A. Wood, Nieck E. Benes, Membrane Science and Technology, Journal of Materials Chemistry A , 12616-12626,11,2019.
[51]. Mar´ıa Albert - Soriano and Isidro Manuel Pastor, Eur. J. Org. Chem., 18 August, 2016, 10.1002/ejoc.201600991, Link to VoR: http://dx.doi.org/10.1002/ejoc.201600991

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