



Recent Developments in the Synthesis and Applications of Metal Organic Framework: A Concise Review

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Metal organic frameworks (MOFs) are one of those compounds which have drawn attention in various applications due to their several interesting properties like tunable shape, size, pore size, easy functionalization, high surface area, pore volume, *etc.* Metal organic frameworks due to their uniform structures, tunable porosity, wide variety and stability on various topology, geometry, dimension and chemical functions of the molecular network give a remarkable structural diversity in comparison to other porous materials. This enables scientists to handle numerous framework structures, porosity and functionality effectively. The unique structural architecture and tunable properties of MOF's makes them an interesting hybrid material consisting of organic and inorganic materials. MOF can be randomly constructed like Lego bricks and superior in terms of versatility in comparison to other porous materials. A number of MOFs containing a wide variety of metal *e.g.* zinc, copper, iron, aluminium, magnesium, chromium, zirconium, gadolinium, manganese are gaining rapid growth in commercial markets for gas storage, adsorption, separation and catalytic applications. This concise review emphasizes various synthetic methods *e.g.* solvothermal process, hydrothermal synthesis, electrochemical synthesis, microwave synthesis, sonochemical synthesis, mechanochemical synthesis, of metal organic framework developed in the last few decades. It also addresses various applications of metal organic framework *e.g.* hydrogen storage, gas adsorption, drug delivery systems and bioimaging agents, biocatalysts, biosensors, electrochemical sensors, *etc.* It also comments on various challenges and futuristic applications of metal organic frameworks in various field *e.g.* liquid waste management, gaseous waste management, sunlight assisted catalysis, water purification, building materials, electronic devices, battery technologies, targeted drug delivery, solar cells, *etc.* of science and technology in coming decades.

Keywords: Metal organic framework, Porous materials, Applications.

INTRODUCTION

Metal organic frameworks (MOFs) are the class of compounds consisting of metal ions which are coordinated to organic ligands to form one, two or three-dimensional structures. They have a special characteristics of being porous in nature and also have a high surface area. MOFs composed of various metal ions and ligands having numerous interesting properties and have various applications in many branches of sciences. MOFs are conventionally produced by hydrothermal and solvothermal synthesis in which electronic heating is done in small scales and takes several hours to days to complete the reactions. MOFs are having great importance in the development of modern industries as these porous materials play a vital role in various technical applications.

Organic linkers play an important role in determining the structure and the physico-chemical property of MOF materials [1]. MOF materials have the flexible characters because of these, several types of MOF, by varying ligands and metals ions, have been synthesized which include some classical MOF's such as MOF-5, HQUST-1, MIL-101, UIO-66. As these materials are having high surface area as well as tunable pore size and shapes lead to the more opportunities for the applications in the field of catalysis, chemical sensor, ion exchange, drug delivery, gas separations/storage, energy production/storage and biotechnology [2]. MOFs are enriched with chemical composition and unique architectures which is based upon the variation of coordination modes between numerous metal ions or clusters and organic ligands, which makes them useful in the area of non-linear optics, luminescence, magnetism and others.

In the last few years, some new solvent systems were used for the preparation of crystalline metal organic framework, which consists of ion liquids, eutectic solvents and surfactants. Most of the MOFs contain neutral framework because of the presence of positive charges of metal ion which are often balanced by the negative charges of organic linkers [3]. MOFs are the fast-developing class of organic-inorganic hybrid materials and coordinated metal ions/cluster which are associated with them and acts as nodes. The newly formed porous materials, metal organic framework (MOFs) are different from the other porous materials as they are having high porosity, large surface area, variable chemical functionalities and thermal stability [4]. The preparation of MOFs takes place under mild conditions and simple processes. Many nano-structures are synthesized from MOFs, which are known as NMOFs and act as origin of the nanostructures as well as it sacrifices itself as template which consists of organic components which can act as carbon source for the formation of nanoporous carbon [5]. Some MOFs structures such as Cu-BTC and MOF-5 breaks down during the carbonization process and other MOF structures like ZIF-8 and ZIF-67, which provides a better template and are used for the formation of porous carbon by the evaporation of organic moistures during the process of pyrolysis and leads to the formation of spongy pore system. Pores are the spaces which are formed inside the MOFs (or any porous materials) when the removal of guest molecules takes place and presence of large pores are very much beneficial for conducting host guest relation such as catalysis, so mesoporous or macroporous materials are used. The pores present in the MOFs are occupied by the solvent molecules that is removed for the various applications. Unlike other porous materials, by employing MOFs, unsaturated metal centres (UMCs) can be formed when the removal of the coordinated solvent molecules takes place under vacuum [6]. The MOFs with cage like polyhedral building units can be useful for the storage of small molecules (H_2 , CO_2 , N_2 and CO_2), as the guests, which are adsorbed remain kinetically trapped inside the cages. For the construction of MOFs almost all kind of elements of periodic table *e.g.* alkali and transition metals, lanthanides and actinides are used with different metals which are having adopting different coordination geometries [7]. MOFs contain polar metal ions and non-polar organic ligands which leads to the formation of amphiphilic interior. MOFs have been also synthesized from the edible materials namely cyclodextrins and polysaccharides [8,9].

Recently, MOFs have been tested for various biomedical applications and are used for cancer treatment, drug delivery of various drugs, *etc.* and are useful for the removal of traces of sulphur components from various gases. The structures of MOF are having open metal sites designated for chemisorb electron rich molecules, like amines, phosphine's, oxygenates, alcohols, water, or sulphur containing molecules. In the process of gas separation, the mixture of gas contains the components which are having concentrations in the same order of magnitude. The MOFs having small pores are used to separate the molecules by size or kinetic parameter. MOFs play a vital role in many chemical processes, out of which heterogeneous catalysis is one of the most important applications in chemical industry,

It has been observed that about nine out of ten chemical processes takes place by heterogeneous catalysts [10,11]. There are reliable reports that MOF-enabled technologies may address several of this modern era's main challenges-especially energy and environmental related issues. This involve carbon capture to mitigate climate change, the conservation of low-pressure gases for portable fuels (hydrogen industry) or the catalytic breakdown of toxic chemicals and organisms. Yet several researchers indicate MOFs have made a number of commitments but also given nothing and that the challenges are intractable to the realization of true MOF solutions. Some industries (*e.g.* NuMat Technology, IBM, BASF, Decco) have already shown good design proofs and also developed consumer products based on MOFs recently.

MOF technology is now expanding its solvent-free mechanochemical processing ability for the manufacturing of MOFs to larger scale. Many challenges exist until certain of the most critical targets can be accomplished worldwide. Still, MOF pioneers will definitely be able to take the first steps into the challenging field of technology marketing. In this review article, we summarized the recent synthetic techniques of MOFs and its various applications. This review comprises of three sections, an overview of various methodologies for the synthesis of MOFs followed by a brief discussion on applications of MOFs in various field of science and technology and finally a short comment of future prospects of MOFs is presented [12,13]. We hope that the readers will find in this concise review a new inspirations for their future work and future perspectives on Metal Organic Frameworks.

Synthesis: MOFS are synthesized conventionally by hydrothermal or solvothermal processes in small scales by the process of electrical heating. This reaction takes the time of about an hour to days. Alternative methods are also formed in order to shorten the time of synthesis and to form small crystals. Few methods *e.g.* microwave-assisted, sonochemical, electro chemical and mechanochemical methods are recently implemented for the synthesis of a varieties of MOFs. MOFs structures were prepared by the organic ligand like 1,4-benzene dicarboxylic acid (H_2BDC) and its functionalized form ($H_2BDC-NH_2$; 2-amino-1,4-bezene dicarboxylic acid, $H_2BDC-(OH)_2$; 2,5-dihydroxy-1,4-carboxylic acid) [9,14-16]. In below, brief description of various sythesis techniques are discussed.

Solvothermal process: Solvothermal method can be described as a process in a reaction vessel that generates a breakdown or chemical reaction(s) between precursor(s) at a temperature higher than that of the solvent in the presence of a solvent. In such situations, the pressure may be autogenous or applied. The pressure can be varied from 1 Pa to 10^5 Pa. The solvothermal system can be heterogeneous or homogenous depending on the experimental environments (pressure and temperature). MOFs are prepared by solvothermal process in small scale by the process of electrical heating. Several MOFs are prepared with wide varieties of topology by this method. For example, octahedral Zn_4O are present in MOF-5 and the Zn_4O units are linked with ditopic linear BDC having a chemical formula of $Zn_4O-(BDC)_3$; the diffusion synthesis method is used by the guest molecules at low yield. Diffusion

process takes place in diethylamine in the solution of zinc nitrate and the deprotonation of HBDC takes place, which is present in DMF/chlorobenzene and reaction takes place with Zn^{2+} ions. Now high yield solvothermal process method is used to replace it [17]. IRMOF-3 comes under the isoreticular structures of MOF in which BDC-NH₂ are linked with Zn₄O. IRMOF-3 has the geometry as that of benzene ring which lies in the plane with Zn₄O ring, intramolecular hydrogen bonding between the aromatic amino hydrogen atom and a carboxylate oxygen atom stabilizes this configuration. IRMOF-3 are also prepared under the solvothermal conditions; in brief, the mixture of Zn(NO₃)₂·6H₂O and H₂BD-NH₂ is dissolved in DMF and DEF and the reaction mixture was heated at 90 °C for 24 h in oven.

In large scale synthesis of MOF-5 takes place at room temperature; Zn(OAc)₂·2H₂O is also dissolved in DMF, in the organic solution zinc salt solution. MOFs which are based upon Zn(II) are not very much stable against moisture and the presence of protic solvent decreases its industrial use. The MIF-101 was prepared by hydrothermal process in which chromic salt and H₂BDC and a small amount of HF were used at 220 °C and autogenous pressure conditions of 8 h was required. The Fe-MIL-100 is an iron carboxylate and having large surface area, from the reaction mixture of 10 Fe polycrystalline powder was formed. Corrosion does not take place in zirconium and it has greater affinity towards the hard oxygen donor ligands. In Zr₄ based MOF, UiO-66 consists of octahedral and tetrahedral cages, which are connected to each other by triangular windows and were prepared by using ZrCl₄ and H₂BDC when reacted with PMF at 180 °C for about 24 h. The UiO-66 consist of high thermal and chemical stability, which also shows high stability in polar protic solvents [18,19].

Hydrothermal synthesis: One of the most common methods of MOFs synthesis is hydrothermal synthesis. It is actually a solution dependent reaction and in this type, solvent is water only. These compounds may be produced in a large temperature ranging from room temperature to very high temperatures in hydrothermal synthesis. The morphology of the materials to be prepared depends on the vapour pressure and either low pressure or high-pressure environments should be used. The hydrothermal synthesis process has important advantages over others. MOFs which cannot be manufactured at high temperatures are viable by hydrothermal synthesis. During the synthesis of MOFs [18], the most important clue is the usage of the suitable linker molecules. In the hydrothermal synthesis of copper serine and copper chloride, the reaction was carried in the presence of water, which results in the formation of copper serinates. Similarly, other MOFs like Fe-MOFs, Zr-MOFs, Cu-MOFs and Zn-MOFs were also synthesized by hydrothermal process [20-23].

Electrochemical synthesis: In electrochemical synthesis of MOFs, metal ions frequently supplied through the anodic dissolution on the metal sources are used in place of metal salts and these sources metal react with the dissolved linker molecules as well as with the conducting salt during the reaction. The metals deposited on the cathode surface are resisted by the use of protic solvents and thereby releasing H₂. This process

is used to obtain higher yield solid products as compared to normal batch reactants. Large copper plates act as anode in an electrochemical cell with H₂BTC and dissolved in methanol solvents and copper as cathode. A green colour is obtained by applying a time period of 150 min and 12-19 voltage is given. A dark blue coloured powder is obtained after the activation and the blue powdered having the surface area of about 1.820 m²/g. This process can be extended for ZIF synthesis also.

Electrochemical synthesis of MOF is further applied to synthesize various types of MOFs. Several important MOFs *e.g.* HKUST-1, ZIF-8, A1-MIL-100, AL-MIL-53 and A1-MIL-53-NH₂ were synthesized through this process. During the synthesis of HKUST-1, the ratio of ethanol and water does not affect the solubility of linkers but also solution conductivity and deprotonation of H₃BTC. Solvent ratio plays an important role for the determination of morphology and topology of the synthesized MOFs by this method. The electrochemical MOF synthesis has many advantages over the other methods *e.g.* (i) synthesis is very fast and takes place at low temperature compared to conventional synthesis; (ii) metal salts are not required and the anions such as NO₃⁻ or Cl⁻ are separated from the synthetic solution [24,25].

Microwave synthesis: Microwave process is widely used for synthesis of non-porous materials under hydrothermal conditions and recently been employed for the preparation of MOFs due to its various advantages *e.g.* short reaction times, rapid crystal growth, low energy consumption, easy control of the MOF properties, *etc.* In this method, a suitable solvent of a substrate mixture is kept in a Teflon vessel, sealed and then placed in the microwave. Heat is given with an appropriate time at the set temperature. In this process, applied oscillating electric field goes in the direction of permeant dipole moment of the molecules, which leads to the formation of molecular rotation. The Cr-MIL-100 is one of the first MOFs which is synthesized by microwave synthesis. Cr-MIL-100 was synthesized at 220 °C for about 4 h and gives yield of 44%, which is equal to that of conventional hydrothermal synthesis. MOF-5 is also synthesized by microwave irradiation. Increases in microwave irradiation time, power level and concentration of substrates beyond an optimum condition leads to the decrease in the synthetic time at the expense of crystal quality. Systematic microwave assisted synthesis of Co-MOF-74 was reported recently which contains cobalt nitrate hexahydrate and H₄DHBDC dissolved in a mixed solvent (DMF:ethanol:water) [26]. This process has been successfully used for the synthesis of an wide varieties of MOFs *e.g.* MOF-5, HKUST-1, MIL-101, NH₂-MIL-101, MIL-100, MIL-53(Al), MIL-53(Cr), MIL-53(Fe), MIL-147(V), MIL-140A, MIL-88B, NH₂-MIL-88B, ZIF-8, MOF-74(Co), CPO-27, UiO-66 [27]. Hence, this method has great potential to be used for industrial synthesis of MOFs.

Sonochemical synthesis: Sonochemical synthesis is the method used for the application of heavy ultrasound radiation (20 kHz-10 MHz) to generate a varieties of nanostructure materials. Sonochemistry can create very high temperatures (5000-25,000 K) and air pressures. It can also achieve very

rapid heating and cooling. Recently, it has been widely used for the preparation of MOFs due to its superiority *e.g.* efficient crystal growth and green synthetic approach over other methods. MOF-5 crystals having a range of 5–25 μm was obtained by sonochemical synthesis using NMP and takes the completion time of 30 min. HKUST was prepared by using DMF/EtOH/ H_2O mixed solution in an ultrasonic bath. The product formed is nanocrystalline powder and takes time of about 5 min, by the increase in the time of reaction results to the formation of larger crystals and higher yields, when again the reaction takes place it produces partial decomposition. The Mg-MOF-74 crystals were also prepared by the sonochemical methods within 1 h after the addition of triethylamine as the deprotonating agent. ZIF-8 was also synthesized in 2 h by a sonochemical method in a pH adjusted conditions using NaOH and triethylamine. The obtained ZIF-8 material consists of excellent structural properties.

In sonochemical method, a substrate solution mixture is introduced in a home type pyrex reactor fitted to a sonicator bar having an adjustable power output with no external support [28–30]. Several MOFs *e.g.* Cu-MOFs, $\text{Cu}_3(\text{BTC})_2$, HKUST-1, one-dimensional Mg(II) MOF $\{[\text{Mg}(\text{HIDC})(\text{H}_2\text{O})_2] \cdot 1.5\text{H}_2\text{O}\}_n$, fluorescent microporous MOFs $\text{Zn}_3(\text{BTC})_2 \cdot 12\text{H}_2\text{O}$ have been synthesized by sonochemical method successfully [30] and this method needs to be explored more to prepare other varieties of MOFs.

Mechanochemical synthesis: Due to its simplicity, absence of toxic solvents, high temperature, removal of corrosive reagents and uniform particle size distribution, mechanochemical synthesis is an excellent method for preparing nanosized MOF powders. In addition, certain *in situ* synthesis routes contribute to the development of powdered materials with a more homogenous microstructure than those synthesized through traditional *ex-situ* techniques have also been developed. At room temperature mechanochemical reactions can occur and solvent-free conditions are required. Small MOFs are obtained in very short time of reaction. Metal oxides as the starting material are preferred, which leads to the formation of water as by-product by introducing the small amount of solvents in liquid assisted grinding, which results in the acceleration of the mechanochemical reaction due to the passage of reactants on the molecular levels. Mechanochemical synthesis is applicable for only some MOFs types but also very difficult to obtain the product in large amount. Using the mechanochemical synthesis HKUST-1 was produced using in H_3BTC and copper acetate successfully with no usage of solvent. Nowadays, the synthesis of ZIF becomes more possible due to the presence of ammonium ions and reaction time takes about 30–60 min in the presence of $\text{NH}_4\text{CH}_3\text{SO}_3$ and DMF is used as solvent. However, if the reaction takes place with the addition of ZnO and HETLM in presence of NH_4NO_3 , then the products were formed within 5–10 min [31–33]. Mechanochemical synthesis have been utilized for the preparations of various MOFs *e.g.* MOF-5, eMOF-14, UiO-66- NH_2 , HKUST-1, MOF-74, pillared MOFs, ZIF-67, ZIF-8, UiO-66, copper(II) isonicotinate MOF, MIL-78, MIL-68, MIL-53(Al), MIL-100(Fe), PCN-250(Fe), *etc.* [32].

Applications

Hydrogen storage: Various forms of hydrogen storage medium, such as metal-organic frameworks (MOFs), basic alloys, carbon nanotubes, graphene, borohydrides, aluminates and ammonia boranes were also investigated. Billions of dollars were spent in research into storage materials, resulting in tens of thousands of papers. It is therefore difficult to track how much efforts by types of material has been committed and how the field has been developed over the years. Measures provided by the application of bibliometric and text analysis to research articles will contribute to this mission.

As the MOFs is having special structure as like absence of dead volume, because if it increases in volumetric specific gas storage becomes possible. MOFs are able to store the amount of hydrogen at very low temperature. Hydrogen adsorption takes place by the physisorption at very low temperature of 77 K and involves the weak van der Waals forces. Hydrogen adsorption properties of MOFs having a small amount of effect when the metal ions are fully coordinated. The sequence of the unsaturated metal sites related to the hydrogen molecules plays an important role [28]. The power of the interaction which takes place between hydrogen molecules and a MOF is identified by the isosteric heat of hydrogen adsorption. Hydrogen makes the interaction with Mn(II), Sc(III), Mg(II), the third coordination sites in MOF has been observed.

An adsorption isotherm of hydrogen shows an abrupt rises at the low pressure in the Mn(II) MOF, which is porous in nature. The sudden rise in the hydrogen adsorption during low pressure is due to the interaction between hydrogen and exposed Mn(II) centres. The interaction of hydrogen molecules with the metal-framework can be increased by the microporous of MOFs [34]. Tetrazine rings which are present in the organic ligands lead to the formation of the powerful interaction between the molecules of hydrogen and MOF; since tetrazine contains more electrons in order to create electron rich conjugated π -system to produce excellent interaction with hydrogen MOFs. Several MOFs *e.g.* IR-MOF-3 [IRMOF = isorecticular metal organic framework], UMCM-1- NH_2 [UMCM = University of Michigan crystalline materials] and DMOF-1- NH_2 [DMOF = DABACO metal organic framework]; DABACO = 1,4-diazabicyclo (2:2:2) were modified by the series of anhydrides or isocyanates. The two modified IRMOF-3-AMPH and IRMOF-3-URPH leads to the higher hydrogen uptakes at 77 K and 1 bar, as compared to the unmodified IRMOF-3 [35]. These results showed that the addition of aromatic moieties have the positive effect on the binding ability on hydrogen. When the adsorbent contains small porous, the potential energy of the opposite walls overlaps and the potential interaction can be increased [36].

Gas adsorption: For several industrial uses, gas separation is highly necessary. The method typically uses porous solid materials as adsorbents, for example, zeolites, activated carbons or silica gel. Adsorbents with tailor-made structures and tunable surfaces must be sought, considering the increasing need for a more reliable, energy-saving and environmentally sustainable gas separation process. Such a novel type of porous

material are metal-organic frameworks (MOFs) consisting of metallic knots joined by organic bridges. Because of their wide surfaces, variable pores and tunable properties and reasonable thermal stability, such materials are gaining interest for gas separation adsorbents. The material which are chosen for the adsorption of selective gas are considered on the basis of same criteria like the capability of adsorption by the adsorbent and the selection of the adsorbent for an adsorbate. The interactions which takes place in the surface of adsorbent plays a vital role during the selective adsorption of oxygen over nitrogen. For example, Cu(bdc) MOF contains double and triple bonded metal coordination site and shows the greater affinity towards the oxygen. The materials which are used for selection of gas adsorption is based on the MOF adjustable molecular sieve. A number of MOFs are prepared during the last 20 years from aluminium, chromium, zinc, iron, nickel for the adsorption and selective separation of a varieties of gases [37-39].

MOF as drug delivery system and bioimaging agents:

MOF has been introduced to overcome some of the inherent limitations of soft drug delivery systems *e.g.* liposomes, polymersomes, dendrimers, *etc.* The ability to tune the size, shape, structure and surface modifications of MOFs offers a great advantage over other materials. As the MOFs consist of tunable pore size, indicates themselves as the suitable materials for drug delivery. This has significant benefits in terms of using the MOFs because both the organic and inorganic materials are used. Iron and zinc MOFs are already used for the delivery of doxorubicin under different external stimuli *e.g.* pH, micelle, liposome, *etc.* ZIFs (ZIF-7 and ZIF-8) have also been developed to deliver an anticancer drugs (doxorubicin) under various external stimuli [40-42]. Recently, MOF-silica nanocomposites are used for the controlled delivery of doxorubicin in presence of various external stimuli [43-45].

The technologies of bioimaging provide a device which establishes the characteristics of pathology and also the functions of the metabolites of the biological tissues, which increases the diagnosis of diseases. In order to create the signals or to increase the signals contrast in the targeted tissues imaging agents are used such as fluorescent small molecules and the agents of imaging contrast. As the MOFs having a soft functionalization, diversiform structures, compositions and porosity, the MOFs based nanocomposites are used in fluorescence imaging (FL), computed tomography (CT), magnetic resonance imaging (MRI) and positron emission tomography (PET) imaging. In monomodal, bioimaging imaging method is universally used [46-52]. Till now, various MOFs that contains Gd, Mn, Fe, iron oxide and also the derivation of these metals are used for the development of contrast agents of MRI in order to get the high-resolution MRI effects.

MOFs as biocatalyst: Biocatalytic MOFs applications are still in its primitive phase, with many studies focused on the function of MOFs for the bioprotection. In order to facilitate the separation and the maintenance of high catalytic activity of enzymes during the catalytic process, enzymes need to be immobilized on the solid support and MOFs are already being used. For the effective diffusion of any substance, the pore structures are very much beneficial. Surface bioconjugation,

infiltration and encapsulation strategies lead to the formation of MOF enzyme biocomposites. The loading of superoxide dismutase and catalase in MOFs is reported [53,54]. The first artificial cell which is stable, active and give response to stimuli was prepared by Liang & Liang [55] and the cell consists of metal phenolic network. Marti-Gastaldo *et al.* [56] prepared a mesoporous MOF based composite in order to increase the stability of enzymes and also its recyclability under extreme conditions.

MOFs as biosensors: Compared to inorganic nanomaterials (*e.g.* graphene, graphene oxide, gold nanoparticles and MoS₂), MOFs are potentially beneficial for the biological applications due to their inherent biodegradability and the ability to use biocompatible building blocks. Several types of MOFs have recently been used to detect DNA, RNA, enzyme activity and small biomolecules, as well as magnetic resonance imaging (MRI) and computed tomography (CT), which are useful tools for clinical diagnosis [57]. Two GOX/Lactate oxidase (LOX) loaded MOF based biosensors having a high sensitivity and AUNPS into MIL-101 are selectivity formed *in situ* and are used to measure glucose and lactic acid in living tissues [59]. Surface Immobilized GOGOX based MOFs biosensors for the ultrasensitive detection in human serum was reported by Zhu *et al.* [59]. GOX is immobilized on Fe-MIL-88B-NH₂ to form Fe-MOF-Gox *via* EDC/NHS induced covalent binding and this takes place after hydrothermal synthesis of Fe-MIL-88B-NH₂ [60].

In the biological process, MOF based biosensors are used for the detection of biomacromolecules like proteins and nucleic acid [61,62]. Three types of electrochemical Zr-MOF based biosensors for the detection of proteins was designated by Du *et al.* [63] and also Zr-MOF-BA was constructed for the detection of lysozyme [64]. Stable and sensitive luminescent MOF-bacteriophage based was formed from NH₂-MIL-53 and based on the photoluminescence stoppage method in order to detect *S. aureus* [65]. Electrochemical polyaniline/Cu-MOF based biosensor in order to detect the *E. coli* is also developed [66].

MOF as electrochemical sensors: MOFs have a diverse array of redox behaviours to be implemented in a number of fields (*e.g.* microporous conductors, electrocatalysts, energy storage systems and electrochemical sensors). Numerous MOF composite systems have been developed as efficient electrochemical sensors for various applications *e.g.* environmental, biochemical targets [67]. In particular, the redox and catalytic active sites introduced by the use of active metal ions and/or ligands provide MOFs with the functions needed for electrochemical sensing [68,69]. Furthermore, the detailed chemical modification of functional molecules and the immobilization of metal nanoparticles, carbon nanomaterials and biomolecules may improve their electrical and chemical efficiency.

Carbon, metal oxides derivatives and their composites are applicable in super capacitors. Co-MOF derived nanostructures have the largest specific capacitance and large surface area is possessed by ZIF-8 [70,71]. Hollow porous ZnO-MOF is recently formed by Song *et al.* [72] at the moderate pyrolysis temperature of about 500 °C. ZnO was distributed on the nanocages of carbon. For the applications of laser-induced breakdown spectroscopy (LIBS), it has been investigated that

various nanostructured materials such as carbon nanotubes, graphene composite, metal oxides are used [73].

Challenges and future prospects of MOF: Although MOFs have been used in numerous applications for the last few decades, but a large number of MOFs are still unexplored for applications and needs to be investigated thoroughly to use them in several fields in science and technology. Thousands of MOFs are prepared over the last few years and only few of them have found the space for actual applications. A great commercial market of MOF is awaiting and thus, more research is needed. A number of areas can be explored *e.g.* liquid water management, gaseous waste management, sunlight assisted catalysis, water purification, building materials, electronic devices, battery technologies, targeted drug delivery, solar cells *etc.* where MOFs can be applied. But it must be noted that lots more challenges are also there in terms of the bulk scale preparation of MOFs in environmentally friendly manner. For biological applications, little is known about the details of long term and short-term toxic effects of MOFs and enormous amount data is required to be analyzed before it finds practical applications and for that more systematic investigation is required.

MOF chemistry has entered the next generation and various potential modifications to MOFs are available, *e.g.*, improvements of the surface by the coating or greasing of polymers, small molecules such as lipid, enzymes or proteins and use of nanoparticles as core composites to improve biostability and selectivity. Two emerging trends support this transformation *e.g.* attempts to build composites with MOFs have been especially fascinating, with synergistic effects anticipated on combined materials and new features such as ferromagnetism or quantum luminescence, or more interestingly, upgraded nanoparticles found in non-usable MOFs. New processing techniques and the use of various processes suited to the plastics and metallurgy industries appear vital and are the basic steps to accomplish nearly endless possibilities. Nano-MOFs are not only significant because of their remarkable chemical reactivity, which can be used to function with a wide variety of molecules.

Conclusion

The applications of metal organic frameworks are increasing day-by-day and so does their demand which needs easy and cost-effective preparation method. In this concise review, various recent developments of the MOFs and their applications discussed in a stepwise and systematic manner. One of the fundamental difficulties confronting the industrialization of MOFs for catalysis is the absence of real data about catalysis in industries. This factor has restricted the commercialization of MOFs for industrial catalyst and more research in this field is required. Selectivity is another significant issue for the commercialization of MOFs as catalyst; accomplishing close to 100% selectivity is a critical test in catalysis that isn't completely tended to. For biological applications of MOFs, the concrete data of toxicity of MOF and nano-MOFs are still ambiguous and thus restrict their uses for various biomedical applications. The modern era demands the industrial scale cost effective production of MOFs to fulfil the application of MOF in real world. Nonetheless, the full acknowledgment of these

materials, their industrialization is prevented by many drawbacks which needs the corrected and yet to be totally comprehended and examined.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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