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Advances with Metal Organic Framework based nanomaterials in 4th industrial revolution

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Abstract: *Metal Organic Frameworks (MOFs) are expected to become a major player in different industrial sector as a result of biological performance, photocatalysis, adsorption and absorption behavior, capacitance, improved anodic performance in energy storage. In biomedical industries, MOFs utilize antimicrobial characteristics and biosensing, bioimaging, therapeutic, drug delivery capabilities. MOF can be used as a food safety and food packaging agent since they prevent microbes. By photocatalysis MOF can contribute to wastewater treatment. MOFs adsorption and absorption characteristics can remediate groundwater. Improved capacitance and anodic behavior of MOF will contribute to energy storage device improvement. MOFs are also capable of separating gases from mixtures. Thus, MOF will play vital role in biomedical, food, water-treatment industry, oil-gas industry, and energy storage industry. Energy, environment, biomedical applications make MOF important in 4th industrial revolution. This study will focus on special properties along with different industrial application and show the effectiveness of MOF in 4th industrial application.*

Keywords: Biomedical industry; Electronics; Food packaging; Metal Organic Framework; Water treatment.

1. INTRODUCTION

Metal Organic Frameworks (MOFs) are porous hybrids which can be created by mixing organic and inorganic porous materials to create composites that are both stable and structured. They are mainly organometallic crystals where metal ions are coordinated with atoms of organic ligands [1]. The name "MOF" was first used in the scientific literature in 1990 [2]. MOFs are a fascinating new class of hybrid materials that may be utilized to build structures in one, two, or three dimensions. Depending on the need, these structures may be made in one or two dimensions. Secondary building units (SBUs) are smaller building units comprised of functional groups and metal ions that may be used to construct MOFs. These SBUs frequently provide a variety of diverse spatial topologies. Transition metals and lanthanide metal ions are probable linkers in the overall structure. More MOFs have been created, made, and studied now than ever before. Post-synthesis coating of MOFs with diverse functional groups with folic acid or polymers (PEG, PVP, lipid bilayers, and ferrosferric oxide) is common [3]. Due to the structure's versatility, over 7,000 MOF structures have been identified [4]. Many researchers are interested in functionalizing MOF pores to alter their interactions with host and guest molecules by altering their physical and chemical properties [5]. Most MOFs are made of first row transition metals (like iron and cobalt) and organic ligands (such carbon, hydrogen, oxygen, and nitrogen). They may be used to make non-noble catalysts. Including functional species in the framework may result in a lattice with a homogeneous distribution of active centers. The catalyst's design leaves much space for improvement. MOF materials have a highly structured porous structure with a narrow and consistent pore size distribution. MOF materials are used widely. The pore size of MOFs may be reduced to 9.8 nm using an "iso-reticular expansion" approach. Adding additional functional groups to existing ligands may also change their affinity [6]. MOFs may be found in a broad range of fields. Researchers may either functionalize the pre-MOF structure or do it when it is already functional. MOFs may be able to increase the loading capacity of therapeutic ingredients by functionalization. Adsorption, encapsulation, covalent

bonding, and functional molecule insertion are popular ways for functionalizing MOFs. But MOFs may be functionalized in different ways, for instance, solvent exchange, grafting, covalent modification etc. [7]. Early MOF research focused on solvothermal production and characterization to store methane and hydrogen gases. Most MOFs were made at the turn of the century using easily accessible multitopic carboxylic acid ligands. So the research process got easy [8]. MOF-based multifunctional platforms, which integrate the effectiveness of many multifunctional components, may be used to treat a range of ailments. Successful years have been recent [9]. The combination of the physical, digital, and biological worlds is referred to as the fourth industrial revolution. It combines modern technologies in 3D printing, genetic engineering, quantum computing, the Internet of Things (IoT), robots, and artificial intelligence (AI). But to do this feasible we need electrical machines, and we need energy storage devices. MOF can be used in energy storage devices. To generate electricity, we need oil and gas industries in which MOF can be utilized. In many industries we need pure water and water is the part of our environment which is important to us as green chemistry is a part of 4th industrial revolution [10]. Considering these MOFs can be useful in different industries, utilization of MOFs in 4th industrial revolution is our main research objectives.

2. SPECIAL PROPERTIES OF MOF

MOFs are nanoporous materials. They have crystalline powder like structure having high surface area [11]. Some of MOFs shows high hydrolytic stability. e.g. MIL-100 is 12 month stable in water; HKUST-1 is 21 months in 7:1 water : Dimethylformamide (DMF); MOF-505 is 21 month in 5:1 water : DMF ; MOF-5, MOF-177 are also 21 month stable in 1:20 of water-DMF solution [12]. Some MOFs also shows thermal stability at high temperature. e.g., UL-MOF-1 shows extraordinary stability at 610 °C [13]. Cr-MOF, Al-MOF, Zn-MOF, Mg-MOF, ZIF-8-MOF also show higher thermal stability which is up to 450°C [14]. Even Ni₃(BTP)₂ maintains its stability across a wide variety of extreme conditions, including air heating to 430°C and 2 weeks of exposure

with boiling aqueous solution of HCl, HNO₃, NaOH with pH 2 to 14 [15]. HKUST-1(Cu-BTC) shows excellent mechanical stability with ~30.7 GPa Bulk modulus and 117-134 GPa having alcohol guest molecule at ambient temperature and pressure [16]. The nickel bisdithiolene [Ni(S₂C₂Ph₂)₂] complex nanosheet has an electrical conductance of 1.6 10² S cm⁻¹ [17] and a PSM-1 has protonic conductance of 1.64×10⁻¹ S.cm⁻¹ [18]. Certain MOFs have higher photoconductivity, such as MIL-177-HT, which has a conductance of 4 ×10⁻⁴ cm²V⁻¹s⁻¹ under ultraviolet (UV) irradiation because to its lower band gap [19]. MOFs can also show adsorption and desorption characteristics thus these can be used for desalination system [20].

3. INDUSTRIAL APPLICATION

As the 4th industrial revolution is highly focused on the technology, so our major discussion part of MOF based nanomaterials' industrial application will be based on technology-based devices industry, also can be called electronic industry. And also, as this industrial revolution is happening in the era of ending fossil fuel, so environment will be a great issue in this revolution.

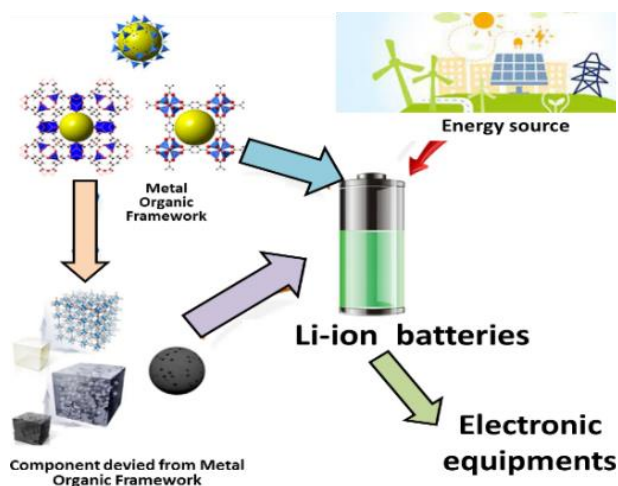


Fig. 1. MOF for Li-ion batteries.

3.1 Electronic industry

In energy storage MOF derivatives can be utilized. Such MOFs are porous carbon and nanostructured metal oxides. Lithium-Ion Batteries (Fig. 1) with alkaline earth metal-based MOF (MC₈H₄O₄, M = Ca, Sr, Ba), anode (MC₈H₄O₄, M = Ca, Sr, Ba) have shown improved ionic bonding with the terephthalate anions in their cationic metal cations and molecular structures. This has resulted in better discharge capacity and less capacity decay when compared to other MOFs [21–23]. MIL-100 (Cr) might be used in Li-S batteries because of its mesoporous structure and its high BET surface area, which is equal to 1485 m² g⁻¹. The notion of melt diffusion was used to inject sulfur into the pores of MIL-100 (Cr). This resulted in large pore volumes (1 cm³ g⁻¹) and small windows, which made possible the use of MIL-100 (Cr) for the encapsulation of sulfur and intermediate polysulfide. In addition, the polar sections of the inorganic moieties that make up MIL-100 (Cr) have the potential to interact further with exceptionally polar polysulfide species. According to the claims, the composite MIL-100

(Cr)/S@155 used as an electrode material had greatly better capacity retention as a result of these properties [24]. RT-MOF-5, solvothermal MOF-5, ZIF-8, and [Zn₃(fumarate)₃(DMF)₂] (ZnFumarate) may all be used to make porous carbon by evaporating Zn atoms, therefore they are all good candidates for making MOF-derived carbon via solvothermal synthesis. Greater mesopore volumes (2–50 nm) in MOF-derived carbon showed larger initial discharge capacities, whereas higher micropore volumes (<2nm) in MOF-derived carbon showed improved cycle stabilities [25]. When used as air cathodes in Li–O₂ batteries, pure MOFs have the potential to produce cleaner air than other cathode materials.

The inside surface of M-MOF-74 had a sizeable number of open metal sites and 1D channels with a diameter of 11.0 angstroms that were both able to host oxygen molecules and function as oxygen reservoirs. This study showed Mn-MOF-74 had the highest significant capacity under 1 atmosphere of oxygen (9420 mAh g⁻¹) [26]. The cathode of a Li–O₂ battery may have a capacity of 9000 mAhg⁻¹ and high stability, with just a minor voltage decrease after 170 cycles when using a Ni-based MOF with a 3D micro-nano structure. Lithium-ion batteries may achieve a capacity of 9000 mAhg⁻¹ and outstanding stability by using a 3D micronano structure based on Ni-based MOF. Despite this, just a minor voltage decrease was seen after 170 cycles [27]. To construct a nanocomposite of ZIF-based nanocomposites with Zn and Co metal inclusions, N-doped carbon hollow tubules (CHTs) with greater interlayer spacing may intercalate Na⁺ using the self-etching approach followed by graphitization. Metal salt may be used to hollow down carbon cores in ZIF composites. Several improvements, including as graphitization, a hierarchical porous structure, a large interlayer spacing, and N doping, may be used to make an effective Sodium Ion Battery (SIB) anode. After 10,000 cycles, the anode retains its original capacity of 346 mAh g⁻¹ [28]. Because of their ability to produce long cycling existences, rapid charging capabilities (210 mAh g⁻¹ at 5000 mA g⁻¹), and very high Coulombic efficiencies of 99 percent, tiny, nanotube-embedded ilmenite FeTiO₃ nanoparticle-encased carbon nanotubes (FTO/CNTs) may be utilized as anodes for solid-iron SIB[29]. The fact that co-based MOFs are such good materials for super capacitors makes them an attractive building block for synthetic molecules. The energy density of a single layer of a Co-based MOF material is 7.18 Whkg⁻¹, and its specific capacitance is 206.76 Fg⁻¹ when measured at 0.6 Ag⁻¹. In addition to this, it causes a capacitance loss of 1.5 percent after 1000 cycles and reverses the electrochemical process of redox switching [30] [31]. ZIF-8 resulted in the porous carbon with a high BET surface area of 3405 m² g⁻¹ and a large pore volume of 2.58 cm³ g⁻¹. As the electrode material for Electric Double Layer Capacitors (EDLCs), the porous carbon material obtained specific capacitances of more than 200 Fg⁻¹ at current densities of 250 mA g⁻¹ [32]. Researchers have used a hydrothermal method to embed -MnO₂ nanoparticles into a MIL-101 (Cr) matrix to prepare a -MnO₂/ MIL-101 (Cr) composite. They reported that the abundant micropores and high surface area that resulted from this process improved the

accessibility of the reactant to the catalytically active sites, thereby increasing oxygen reduction reaction (ORR) activity in alkaline electrolytes [33]. In addition, the robust interaction between the -MnO_2 and the MOF maintained structural stability, which led to outstanding stability [34]. An intrinsically conductive 2D layered MOF ($\text{Ni}_3(\text{HITP})_2$) can be used as a tunable oxygen reduction electrocatalyst in alkaline solution. This was accomplished by directly growing the $\text{Ni}_3(\text{HITP})_2$ film onto a glassy carbon electrode without the use of binders and conductive additives. In this context, the naturally large surface area and porosity of $\text{Ni}_3(\text{HITP})_2$ may make it very simple to reach the catalytically active sites within the material, which in turn results in significant ORR activities [35]. On build solar cells, the thin layer of MOF-5/DMF paste was applied to an ITO electrode with an area of $1\text{-}1\text{ cm}^2$ and a 50-micrometer-thickness layer. MOF-5 can be used as a photoactive material for photovoltaic cells, as demonstrated by its ability to generate an open-circuit voltage of 0.33 V, a short-circuit current of 0.7 A, and a fill factor of 44%. This proves that MOF-5 can be used as an active component in photovoltaic cells and that MOF-5 can exhibit activity as a photoactive material [36]. To make $\text{Cu}_{2x}\text{S}/\text{CdS}$ photovoltaic cells more stable, Zr-based metal-organic frameworks (MOFs) have been developed as the copper supply. In this case, the as-prepared MOF material, with its inherently high porosity, chemical stability, and density of Lewis basic sites from bipyridine moieties, can effectively store Cu(I) ions to compensate for the diffused Cu ions, and as a result, improve the stability of the $\text{Cu}_{2x}\text{S}/\text{CdS}$ photovoltaic cells. This is achieved by improving the chemical stability of the MOF material [37].

3.2 Water treatment and textile industry

MOFs have shown excellent efficacy in the treatment of polluted water. For industries, water needed to be treated twice. Firstly, before using the water in the industry, the collected water from the source needs to be treated. And then, after the use, again it's needed to be treated. MOFs such as UiO-66 and UiO-66-(SH)_2 remove numerous heavy metals from water effectively and concurrently, including Cd (II), As(III and V), Hg (II), Pb(II), Cr(III and VI), Cu(II). In a continuous-flow column for water filtration, $\text{UiO-66-(SH)}_2@\text{CeO}_2$ may also be employed as packing material [38]. According to a study, Pb^{2+} removal by ZIF-8 is mostly accomplished by adsorption, while Cu^{2+} removal is accomplished through an ion-exchange process [39]. Another zeolite imidazolate framework (ZIF-300 membrane) shows effective removal of Cu^{2+} , Co^{2+} , Cd^{2+} , Al^{3+} heavy metal ion [40]. Because of its high coordination affinity, magnetic Fe_3O_4 -ZIF-8 core-shell composites could adsorb As(III) from water (up to $100\text{ mg}\cdot\text{g}^{-1}$) [41]. Tetracycline could be removed from water by adsorption using a 3D algininate-based MOFs hydrogel. MA-M achieves equilibrium more quickly than the AM-M. Tetracycline adsorption on MA-M has a maximum adsorption capacity of 364.89 mg/g , which is more than that of AM-M (302.32 mg/g). After 10 cycles, the MA-M exhibits a good regeneration property [42]. Polymer/MOF monoliths, such as chitosan/UiO-66, may also be employed as water adsorbents. For the adsorption

of 60 ppm methylchlorophenoxypropionic acid (MCP) from dilute aqueous solution, chitosan/UiO-66 displayed a capacity of $34.33\text{ mg}\cdot\text{g}^{-1}$ [43]. Kinetic hydrate inhibitor (KHI) can be removed from wastewater by incorporating hydrophilic zirconium-based MOF, UiO-66- NH_2 , into dense selective polyamide (PA) layer atop the polyphenylsulfone (PPSU)-graphene oxide (GO) support layer thin film nanocomposite (TFN) membrane [44]. MOFs could be used to degrade the dyes and toxins produced in textile industries. For example- Iodine absorption by porous Zn-BTC MOF is impressive (84%) in water and 74% in hexane medium; under visible light and H_2O_2 , it also shows heterogeneous catalytic activity toward the degradation of rhodamine B (RhB) (85% efficiency), as well as methylene blue (MB) (79%) [45]. Under visible light irradiation, molybdophosphate-based $\text{Fe}^{\text{II,III}}$ -metal organic framework (FeMoP-MOF) also shows outstanding selective degradation for Rhodamine B (RhB) dye as a photocatalyst [46]. In the presence of UV, MOF-199 degrades cationic dye (Basic Blue 41) due to azo band destruction [47]. ZIF-300 shows greater dye rejections for electroneutral rhodamine B (RhB), positively charged methylene blue (MB), and negatively charged methyl orange (MO) [40]. A research showed that, it is also technically feasible that RhB dye can be decomposed by HKUST-1 [48], $\text{Ag}_2\text{CO}_3/\text{UiO-66}$ composite [49], $\text{Bi}_2\text{Mo}_6/\text{UiO-66(Zr)}$ composite [50], double-layered hollow spheres of $\text{Co}_3\text{O}_4@\text{CdS}$ [51], Zr-MOF composite membrane (PCN-224/TA/PVDF) [52] etc. under the influence of visible light. Under the influence of sunlight, CuO NPs/ZIF-8 nanocomposites degrade rhodamine 6G (Rh6G) dye using a pseudo-first-order kinetics model [53]. Under visible-light irradiation, the ZIF-67 micropores can photodegrade methyl orange (MO) with remarkable efficiency. Within one hour of employing ZIF-67 (using 0.5 gL^{-1}), 88% MO degradation is seen. MOFs like MIL-100 (Fe) (40%), AgBr@HPU-4 (92%), MIL-100(Fe)@MIL-53(Fe) (98%), $\text{MoS}_2/\text{MIL(68)-In}_2\text{S}_3$ (80%), $\text{Cu/ZIF-67-H}_2\text{O}_2$ (95%), Ag/AgCl/ZIF-67 (90%), ZIF-8/ZnO (99%) also degrades methyl orange in presence of visible light and Ce-UiO-66 (81%), Zr-UiO-66 (65%), MIL-100 (Fe) (64%), MOF-199 (38%), UiO-67-bpy-Me (92%) in presence of ultraviolet light [54].

3.3 Biomedical industry

MOFs have the potential to play a significant role in the biomedical industry. MOFs have excellent biosensing abilities (Figure 2) like- $[\text{Cu}(\text{dcbp})_2]_n$ can sense HIV DNA as Fluorescence quenching platform. MIL-101, MIL-88A, UiO-66- NH_2 can also sense DNA and RNA as Fluorescence quenching platform. HKUST-1 can also sense Dopamine, H_2O_2 , Protein; MIL-100(Fe) and ZIF-8 can sense Glucose; MIL-121 senses Hippuric acid; MZMOF-3 senses Lysophosphatidic acid; bio-MOF-1 senses Dipicolinic acid; PCN-222 senses Phosphoprotein; $[\text{Cu}(\text{Mal})(\text{bpy})_2]_n$ senses Amino acids [55]. Moreover, MOFs can sense numerous drugs and toxins. In example- Quercetin can be detected by CDs@ZIF-8@MIP , Eu-MOF; various antibiotics can be detected by TMPyPE@bio-MOF-1 ; Berberine by UiO-66. Toxins like Aflatoxins B1 can be sensed by LMOF-241; Nicotine by MB@UiO-66-NH_2 ; CS lachrymator by

TbAg(bpydc)-SH and pesticides like DCN, Glyphosate, OPP, parathion-methyl, Nitenpyram, Glyphosate can be sensed by Zr-MOF, Tetra-pyridyl calix[4]aren-modified Cd-MOF respectively [56].

Table 1. Utilization of MOF in water treatment

MOF	Utilization in water treatment	References
UiO-66	Remove numerous heavy metals [Cd (II), As(III and V), Hg (II), Pb(II), Cr(III and VI), Cu(II).]	[38]
UiO-66-(SH) ₂	continuous-flow column for water filtration	
ZIF-300 membrane	removal of Cu ²⁺ , Co ²⁺ , Cd ²⁺ , Al ³⁺ heavy metal ion	[40]
Fe ₃ O ₄ -ZIF-8 core-shell composites	Fe ₃ O ₄ -ZIF-8 core-shell composites	[41]
3D alginate-based MOFs hydrogel	Remove Tetracycline from water	[42]
Chitosan/UiO-66	Adsorb methylchlorophenoxypionic acid (MCP) from water	[43]
PA-MOF/PPSU-GO membrane	Removing Kinetic hydrate inhibitor (KHI) from wastewater	[44]
HKUST-1	Degradation of Rhodamine B (RhB) dye	[48]
CuO NPs/ZIF-8 nanocomposites	degrade rhodamine 6G (Rh6G) dye	[53]
ZIF-67	degrade methyl orange (MO) in presence of visible light	[54]

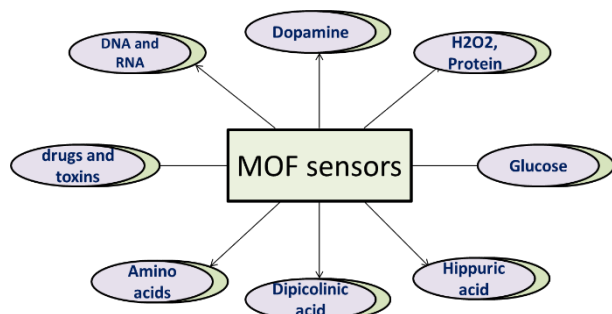


Fig. 2. Biosensing application of MOFs.

MOFs enhance capability of bioimaging applications. Gd MOF, ZIF-90, ZIF-8, UiO-66-F etc. enhances magnetic resonance imaging (MRI) performance. Al-MOF, UiO-66, ZIF-8, Cu-MOF, Fe-MOF etc. improves optical imaging. Zr-UiO, Mn-TCPP etc. improves computed tomography (CT). Hf-UiO-66, PCN-224 improves thermal imaging [3,57]. MOFs show better performance in drug carrying and delivering than other carriers.

Because they are non-toxic, metabolizable, and passive. Some research shows that drugs like Ibuprofen can be delivered safely by MIL-53(Fe), MIL-53(Cr); nicotinic acid by BioMIL-1; Doxorubicin by MIL-100 (Fe); caffeine by UiO-66; Busulfan by MIL-88A (Fe); Procainamide by Zn₈(ad)₄(BPDC)₆O·2Me₂NH₂; phenethylamine by Mg₂(olz) [3]. MOFs also work greatly as therapeutic agent. MOF materials have the potential to be used at every stage of cancer treatment safely. They improve the efficacy of chemotherapy by altering the pharmacokinetics of the medication in the presence of cancer cells. They may also be employed to transport cytotoxic payloads, as well as to mediate photo thermal therapy (PTT) and photo dynamic therapy (PDT) [9,58].

3.4 Food industry

When it comes to the food industry, MOFs may have a significant impact by helping with processes such as food packaging, food safety, food preservation, and food cleaning. For years, MOFs have shown great promise in the realm of food safety and have shown to be adaptable enough to be employed at many stages of the production process. New MOFs are likely to play a significant role in food safety, notwithstanding the progress that has already been done with MOFs. The use of MOF-based materials in food analysis has shown that it is possible to optimize sample preparation, fabricate sensing devices, and increase detection signals using MOF-based materials[59]. Early detection and identification of trace-level pollutants in food is one of the most important steps for assuring food safety and preserving consumer health. Pathogenic microorganisms, heavy metals, unlawful food additives, toxins, persistent organic pollutants (POPs), veterinary medications, and pesticide residue may all be detected quickly and efficiently using MOF-based sensing approaches. Because of its mobility, affordability, dependability, responsiveness, and stability, MOF-based sensing methods might be excellent instruments for evaluating food safety[60]. MOFs may be utilized to regulate toxic levels in foods. In example, Organophosphate insecticides are widely used in agriculture; however, they are very hazardous and may lead to neurological problems. MOFs, on the other hand, can precisely monitor and manage their concentration levels[61]. In the food packaging area, MOFs have shown to be effective in ensuring food safety because of their versatility and ability to adapt into the food supply chain. Even though new MOFs have been developed, it is expected that MOFs will play a vital role in food packaging in the present day by guaranteeing product safety. Fruit and vegetable ripening control, moisture scavengers, food-packing films, sensors/detectors, and bioactive component carriers are all examples of MOF-based active agents in food packaging. As a functional covering for smart food packaging, MOFs and their composite materials have also garnered substantial attention as a means of controlling preservative release and ensuring product safety [62].

3.5 Oil and Gas Industry

In terms of global concerns, crude oil spills constitute a

major problem. There is a lot of promise in the superparamagnetic γ -Fe₂O₃/ZIF-7 composite for removing crude oil and other hydrocarbon (such as acetone and toluene) contaminants from water [63]. It is possible to separate oil (dichloromethane, ether, dodecane, gasoline) from water using the UiO-66-NH₂/chitosan composite membrane, even under extreme conditions [64]. Excellent oil absorption capabilities were shown using ZIF-67 coated hydrophobic melamine sponges (HMS-ZIF-67). The adsorption capacity of HMS-ZIF-67 was practically invariable after 20 adsorption-desorption's trials because of its strong elasticity and structural stability. The residual oil rate was less than 22%, and the adsorption capacity remained almost constant [65]. Moreover, MOFs can also be used in the edible oil industry. Free fatty acid (FFA) and β -carotene (β -CA) can be absorbed by MOFs like Ti-MOF, γ -CD-MOF, Cr-MOF, Al-MOF, Zn-MOF, Mg-MOF, ZIF-8-MOF effectively at ambient temperature [14]. With an outstanding separation efficiency of over 99 percent and a moderately high flux (829-1542 Lm⁻²h⁻¹bar⁻¹) the Zr-MOF composite membrane (PCN-224/TA/PVDF) is able to efficiently separate various water-insoluble emulsified oils from water [52]. As a catalyst, polyoxometalate acid enclosed in the metal-organic framework UiO-66 (PW₁₂@UiO-66) accelerates in the conversion of soybean oil into biodiesel (over 90% production increase) [66]. Cs_{2.5}H_{0.5}PW₁₂O₄₀@UiO-66 also works as catalyst in the conversion of soybean oil into low-calorie structured lipids [67]. Gas sensing is also an important factor for miscellaneous industries. MOFs are used for sensing volatile organic compounds (VOCs). e.g. Zn₃(Fe(CN)₆)₂·xH₂O, Fe(III)MOF-5, Ni₃(Fe(CN)₆)₂·xH₂O, Pd loaded ZIF-67, MOF-5, Fe^{III}-MOF-5, ZIF-8, Au/ZIF-8, Au@MOF-5, Pd loaded ZIF-67, Fe^{III}-IRMOF-3, ZIF-67/Ni-Co LDH, Zn₃(Fe(CN)₆)₂·xH₂O can detect acetone; ZIF-67, CPP-3 can detect ethanol; Pd@ZIF-8/PVP/AMH can detect toluene and ZIF-8/Co-Zn hydroxide, ZIF-8/Ni-Zn LDH, ZIF-67 rhombic dodecahedra can detect xylene [68]. At ambient temperature, a zeolitic imidazolate framework-8 (ZIF-8) particle-loaded ZnO nanorod hybrid demonstrates better sensitivity and selectivity for H₂S as a gas sensor [69]. MOFs are also used to detect inorganic gases like- for NO₂ detection Tb-MOF, Eu-MOF, MOF-A, Y-DOBDC, Ni-MOF-74, In₂O₃/ZIF-8, Cu₃(HHTP)₂/Fe₂O₃, Pd@Cu₃(HHTP)₂, Pt@Cu₃(HHTP)₂, Cu₃(HHTP)₂, ZIF-8; for H₂S detection MIL-100(In), fum-fcu-MOF, ZIF-8/ZnO, MOF-5/CS/IL, Cu₃(HHTP)₂, Ni₃(HHTP)₂, NiPc-Ni, NiPc-Cu; for SO₂ detection MOF-5-NH₂, Eu-BDC-NH₂, UiO-66-NH₂, MFM-300(In), NH₂-UiO-6, Ni-MOF/-OH-SWNTs; for CO₂ detection ZIF-8, Mg-MOF-74, NH₂-UiO-66(Zr), Cu₃(HIB)₂, SnO₂@ZIF-67; for NH₃ detection MIL-124@Eu³⁺/Al₂O₃, NDC-Y-fcu-MOF, NiPc-M, Cu-BHT, Cu₃(HITP)₂, Cu-HHTP, Pd-Co@IRMOF, Zn (NA), SNNU-88, Cu₃(BTC)₂/GO is used [70].

4. CONCLUSION

MOF has several industrial uses. Due to their properties, they are useful for efficient applications. MOFs are utilized in industry to enhance consumer products. Food

manufacturers used it to generate better-smelling and tasting items for customers. MOFs have been employed by the pharmaceutical and medical industries to create novel medications and improved treatment choices for patients. MOFs enhance healthcare. Energy, water, and environmental industries, as well as oil and gas, are improving their products to solve problems. MOF nanoparticles may reduce the number of regular materials used in industry by displaying developing materials and saving energy. The industrialization of modern technologies uses MOF nanoparticles. MOF nanotechnology still needs a lot of effort to make a major influence on nanomaterials, but thus far, the results have been outstanding. Discoveries are astounding. MOF nanoparticles are transforming several industries, including gas and oil, food and health, and the environment.

Table 2. Utilization of MOF in oil and gas industry.

MOF	Utilization in oil and gas industry	References
UiO-66-NH ₂ /chitosan composite membrane	separate oil (dichloromethane, ether, dodecane, gasoline) from water	[64]
HMS-ZIF-67	oil absorption	[65]
Ti-MOF, γ -CD-MOF, Cr-MOF, Al-MOF, Zn-MOF, Mg-MOF, ZIF-8-MOF	Free fatty acid (FFA) and β -carotene (β -CA) absorption	[14]
PCN-224/TA/PVDF	separate various water-insoluble emulsified oils from water	[52]
PW ₁₂ @UiO-66	conversion of soybean oil into biodiesel	[66].
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ @UiO-66	conversion of soybean oil into low-calorie structured lipids	[67]
Zn ₃ (Fe(CN) ₆) ₂ ·xH ₂ O	Detection of acetone	
Fe(III)MOF-5	Detection of ethanol	
ZIF-67	Detection of ethanol	
CPP-3	Detection of toluene	[68].
Pd@ZIF-8/PVP/AMH	Detection of toluene	
ZIF-8/Co-Zn hydroxide	Detection of xylene	
ZIF-8/Ni-Zn LDH		
ZIF-67 rhombic dodecahedra		
ZIF-8	H ₂ S sensing	[69]
MIL-100(In)		[70]
fum-fcu-MOF		
Tb-MOF	NO ₂ detection	
Eu-MOF		[70]
MOF-A		
Y-DOBDC		
MOF-5-NH ₂	SO ₂ detection	[70]
ZIF-8	CO ₂ detection	[70]
MIL-124@Eu ³⁺ /Al ₂ O ₃ ,	NH ₃ detection	[70]

5. REFERENCES

- [1] I. Jahan, Bidyut Baran Saha, Thermal Conductivity Enhancement of Metal-organic Frameworks Employing Mixed Valence Metal Doping Technique, *Proc. Int. Exch. Innov. Conf. Eng. Sci.*, 6 (2020) 20–26.
- [2] Z. Pinar Gumus, M. Soylak, Metal organic frameworks as nanomaterials for analysis of toxic metals in food and environmental applications, *TrAC - Trends Anal. Chem.*, 143 (2021) 116417.
- [3] Z. Luo, S. Fan, C. Gu, W. Liu, J. Chen, B. Li, J. Liu, Metal-Organic Framework (MOF)-based Nanomaterials for Biomedical Applications, *Curr. Med. Chem.*, 26 (2018) 3341–3369.
- [4] D. Jiang, C. Huang, J. Zhu, P. Wang, Z. Liu, D. Fang, Classification and role of modulators on crystal engineering of metal organic frameworks (MOFs), *Coord. Chem. Rev.*, 444 (2021) 214064.
- [5] K.K. Tanabe, S.M. Cohen, Postsynthetic modification of metal-organic frameworks—a progress report, *Chem. Soc. Rev.*, 40 (2011) 498–519.
- [6] A. Mahmood, W. Guo, H. Tabassum, R. Zou, Metal-Organic Framework-Based Nanomaterials for Electrocatalysis, *Adv. Energy Mater.*, 6 (2016).
- [7] M.R. Saeb, N. Rabiee, M. Mozafari, E. Mostafavi, Metal-Organic Frameworks (MOFs)-Based Nanomaterials for Drug Delivery, *Materials (Basel)*, 14 (2021) 3652.
- [8] Z. Wang, S.M. Cohen, Postsynthetic modification of metal-organic frameworks, *Chem. Soc. Rev.*, 38 (2009) 1315–1329.
- [9] L. He, Y. Liu, J. Lau, W. Fan, Q. Li, C. Zhang, P. Huang, X. Chen, Recent progress in nanoscale metal-organic frameworks for drug release and cancer therapy, *Nanomedicine*, 14 (2019) 1343–1365.
- [10] T. Philbeck, N. Davis, The Fourth Industrial Revolution: Shaping a New Era: Discovery Service for University of Johannesburg, *J. Int. Aff. Editor. Board*, 72 (2019) 17–22.
- [11] T.H. Rupam, M.L. Palash, I. Jahan, B.B. Saha, Adsorption Characterization of Aluminum Fumarate Metal-organic Framework, *Proc. Int. Exch. Innov. Conf. Eng. Sci. (IEICES)*, 5 (2019) 34–35.
- [12] K.A. Cychoz, A.J. Matzger, Water Stability of Microporous Coordination Polymers and the Adsorption of Pharmaceuticals from Water, *Langmuir*, 26 (2010) 17198–17202.
- [13] D. Banerjee, S.J. Kim, J.B. Parise, Lithium based metal-organic framework with exceptional stability, *Cryst. Growth Des.*, 9 (2009) 2500–2503.
- [14] E. Yilmaz, A. Erden, M. Güner, Structure and properties of selected metal organic frameworks as adsorbent materials for edible oil purification, *Riv. Ital. Delle Sostanze Grasse*, 96 (2019) 25–38.
- [15] V. Colombo, S. Galli, H.J. Choi, G.D. Han, A. Maspero, G. Palmisano, N. Masciocchi, J.R. Long, High thermal and chemical stability in pyrazolate-bridged metal-organic frameworks with exposed metal sites, *Chem. Sci.*, 2 (2011) 1311–1319.
- [16] K. Yang, G. Zhou, Q. Xu, The elasticity of MOFs under mechanical pressure, *RSC Adv.*, 6 (2016) 37506–37514.
- [17] T. Kambe, R. Sakamoto, T. Kusamoto, T. Pal, N. Fukui, K. Hoshiko, T. Shimojima, Z. Wang, T. Hirahara, K. Ishizaka, S. Hasegawa, F. Liu, H. Nishihara, Redox control and high conductivity of nickel bis(dithiolene) complex π -nanosheet: A potential organic two-dimensional topological insulator, *J. Am. Chem. Soc.*, 136 (2014) 14357–14360.
- [18] S. Mukhopadhyay, J. Debgupta, C. Singh, R. Sarkar, O. Basu, S.K. Das, Designing UiO-66-Based Superprotonic Conductor with the Highest Metal-Organic Framework Based Proton Conductivity, *ACS Appl. Mater. Interfaces*, 11 (2019) 13423–13432.
- [19] S. Wang, T. Kitao, N. Guillou, M. Wahiduzzaman, C. Martineau-Corcus, F. Nouar, A. Tissot, L. Binet, N. Ramsahye, S. Devautour-Vinot, S. Kitagawa, S. Seki, Y. Tsutsui, V. Briois, N. Steunou, G. Maurin, T. Uemura, C. Serre, A phase transformable ultrastable titanium-carboxylate framework for photoconduction, *Nat. Commun.*, 9 (2018) 1–9.
- [20] N. Riaz, M. Sultan, Investigation of Adsorption and Desorption Characteristics of Metal-Organic Frameworks for The Development of Desalination Systems, *Proc. Int. Exch. Innov. Conf. Eng. Sci. (IEICES)*, 7 (2021) 261–267.
- [21] F. Containing, L. Rectangular, Hydrothermal synthesis of a Metal-Organic Framework containing large rectangular channels, *J. Am. Chem. Soc.*, 117 (1995) 10401–10402.
- [22] S. Qiu, G. Zhu, Molecular engineering for synthesizing novel structures of metal-organic frameworks with multifunctional properties, *Coord. Chem. Rev.*, 253 (2009) 2891–2911.
- [23] L. Wang, C. Mou, Y. Sun, W. Liu, Q. Deng, J. Li, Structure-property of metal organic frameworks calcium terephthalates anodes for lithium-ion batteries, *Electrochim. Acta*, 173 (2015) 235–241.
- [24] R. Demir-Cakan, M. Morcrette, F. Nouar, C. Davoisne, T. Devic, D. Gonbeau, R. Dominko, C. Serre, G. Férey, J.M. Tarascon, Cathode composites for Li-S batteries via the use of oxygenated porous architectures, *J. Am. Chem. Soc.*, 133 (2011) 16154–16160.
- [25] K. Xi, S. Cao, X. Peng, C. Ducati, R.V. Kumar, A.K. Cheetham, Carbon with hierarchical pores from carbonized metal-organic frameworks for lithium sulphur batteries, *Chem. Commun.*, 49 (2013) 2192–2194.
- [26] D. Wu, Z. Guo, X. Yin, Q. Pang, B. Tu, L. Zhang, Y.G. Wang, Q. Li, Metal-organic frameworks as cathode materials for Li-O₂ batteries, *Adv. Mater.*, 26 (2014) 3258–3262.
- [27] X. Hu, Z. Zhu, F. Cheng, Z. Tao, J. Chen, Micro-nano structured Ni-MOFs as high-performance cathode catalyst for rechargeable Li-O₂ batteries, *Nanoscale*, 7 (2015) 11833–11840.
- [28] Y. Chen, X. Li, K. Park, W. Lu, C. Wang, W. Xue, F. Yang, J. Zhou, L. Suo, T. Lin, H. Huang, J. Li, J.B. Goodenough, Nitrogen-Doped Carbon for Sodium-Ion Battery Anode by Self-Etching and Graphitization of Bimetallic MOF-Based Composite, *Chem*, 3 (2017) 152–163.

- [29] L. Yu, J. Liu, X. Xu, L. Zhang, R. Hu, J. Liu, L. Ouyang, L. Yang, M. Zhu, Ilmenite Nanotubes for High Stability and High Rate Sodium-Ion Battery Anodes, *ACS Nano*, 11 (2017) 5120–5129.
- [30] D.Y. Lee, S.J. Yoon, N.K. Shrestha, S.H. Lee, H. Ahn, S.H. Han, Unusual energy storage and charge retention in Co-based metal-organic-frameworks, *Microporous Mesoporous Mater.*, 153 (2012) 163–165.
- [31] M. Du, M. Chen, X.G. Yang, J. Wen, X. Wang, S.M. Fang, C. Sen Liu, A channel-type mesoporous In(iii)-carboxylate coordination framework with high physicochemical stability for use as an electrode material in supercapacitors, *J. Mater. Chem. A*, 2 (2014) 9828–9834.
- [32] H.L. Jiang, B. Liu, Y.Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong, Q. Xu, From metal-organic framework to nanoporous carbon: Toward a very high surface area and hydrogen uptake, *J. Am. Chem. Soc.*, 133 (2011) 11854–11857.
- [33] Y. Jia, J. Qian, B. Pan, Dual-Functionalized MIL-101(Cr) for the Selective Enrichment and Ultrasensitive Analysis of Trace Per- And Poly-fluoroalkyl Substances, *Anal. Chem.*, 93 (2021) 11116–11122.
- [34] F. Yin, G. Li, H. Wang, Hydrothermal synthesis of α -MnO₂/MIL-101(Cr) composite and its bifunctional electrocatalytic activity for oxygen reduction/evolution reactions, *Catal. Commun.*, 54 (2014) 17–21.
- [35] E.M. Miner, T. Fukushima, D. Sheberla, L. Sun, Y. Surendranath, M. Dincă, Electrochemical oxygen reduction catalysed by Ni₃(hexaiminotriphenylene)₂, *Nat. Commun.*, 7 (2016) 1–7.
- [36] F. Xamena, A. Corma, H. Garcia, Applications for metal-organic frameworks (MOFs) as quantum dot semiconductors, *J. Phys. Chem. C*, 111 (2007) 80–85.
- [37] V. Nevruzoglu, S. Demir, G. Karaca, M. Tomakin, N. Bilgin, F. Yilmaz, Improving the stability of solar cells using metal-organic frameworks, *J. Mater. Chem. A*, 4 (2016) 7930–7935.
- [38] G. Boix, J. Troyano, L. Garzón-Tovar, C. Camur, N. Bermejo, A. Yazdi, J. Piella, N.G. Bastus, V.F. Puntes, I. Imaz, D. MasPOCH, MOF-Beads Containing Inorganic Nanoparticles for the Simultaneous Removal of Multiple Heavy Metals from Water, *ACS Appl. Mater. Interfaces*, 12 (2020) 10554–10562.
- [39] A. Tanihara, K. Kikuchi, H. Konno, Insight into the mechanism of heavy metal removal from water by monodisperse ZIF-8 fine particles, *Inorg. Chem. Commun.*, 131 (2021) 108782.
- [40] J. Yuan, W.S. Hung, H. Zhu, K. Guan, Y. Ji, Y. Mao, G. Liu, K.R. Lee, W. Jin, Fabrication of ZIF-300 membrane and its application for efficient removal of heavy metal ions from wastewater, *J. Memb. Sci.*, 572 (2019) 20–27.
- [41] J.B. Huo, L. Xu, J.C.E. Yang, H.J. Cui, B. Yuan, M.L. Fu, Magnetic responsive Fe₃O₄-ZIF-8 core-shell composites for efficient removal of As(III) from water, *Colloids Surfaces A Physicochem. Eng. Asp.*, 539 (2018) 59–68.
- [42] Y. Zhuang, Y. Kong, X. Wang, B. Shi, Novel one step preparation of a 3D alginate based MOF hydrogel for water treatment, *New J. Chem.*, 43 (2019) 7202–7208.
- [43] Q. Fu, L. Wen, L. Zhang, X. Chen, D. Pun, A. Ahmed, Y. Yang, H. Zhang, Preparation of ice-templated MOF-polymer composite monoliths and their application for wastewater treatment with high capacity and easy recycling, *ACS Appl. Mater. Interfaces*, 9 (2017) 33979–33988.
- [44] M. Golpour, M. Pakizeh, Preparation and characterization of new PA-MOF/PPSU-GO membrane for the separation of KHI from water, *Chem. Eng. J.*, 345 (2018) 221–232.
- [45] A. Sarkar, A. Adhikary, A. Mandal, T. Chakraborty, D. Das, Zn-BTC MOF as an Adsorbent for Iodine Uptake and Organic Dye Degradation, *Cryst. Growth Des.*, 20 (2020) 7833–7839.
- [46] W. Zhu, X. Yang, Y. Li, J. Li, D. Wu, Y. Gao, F. Yi, A novel porous molybdophosphate-based Fe II, III -MOF showing selective dye degradation as a recyclable photocatalyst, *INOCH*, 49 (2014) 159–162.
- [47] N.M. Mahmoodi, J. Abdi, Nanoporous metal-organic framework (MOF-199): Synthesis, characterization and photocatalytic degradation of Basic Blue 41, *Microchem. J.*, 144 (2019) 436–442.
- [48] J. Zhang, C. Su, X. Xie, P. Liu, M.E. Huq, Enhanced visible light photocatalytic degradation of dyes in aqueous solution activated by HKUST-1: performance and mechanism, *RSC Adv.*, 10 (2020) 37028–37034.
- [49] Z. Sha, H.S.O. Chan, J. Wu, Ag₂CO₃/UiO-66(Zr) composite with enhanced visible-light promoted photocatalytic activity for dye degradation, *J. Hazard. Mater.*, 299 (2015) 132–140.
- [50] J. Ding, Z. Yang, C. He, X. Tong, Y. Li, X. Niu, H. Zhang, UiO-66(Zr) coupled with Bi₂MoO₆ as photocatalyst for visible-light promoted dye degradation, *J. Colloid Interface Sci.*, 497 (2017) 126–133.
- [51] H. Yang, J. Fan, C. Zhou, R. Luo, H. Liu, Y. Wan, J. Zhang, J. Chen, G. Wang, R. Wang, C. Jiang, Co₃O₄@CdS Hollow Spheres Derived from ZIF-67 with a High Phenol and Dye Photodegradation Activity, *ACS Omega*, 5 (2020) 17160–17169.
- [52] J. Xue, M. Xu, J. Gao, Y. Zong, M. Wang, S. Ma, Multifunctional porphyrinic Zr-MOF composite membrane for high-performance oil-in-water separation and organic dye adsorption/photocatalysis, *Colloids Surfaces A Physicochem. Eng. Asp.*, 628 (2021) 127288.
- [53] A. Chakraborty, D.A. Islam, H. Acharya, Facile synthesis of CuO nanoparticles deposited zeolitic imidazolate frameworks (ZIF-8) for efficient photocatalytic dye degradation, *J. Solid State Chem.*, 269 (2019) 566–574.
- [54] N.T. Tran, L.G. Trung, M.K. Nguyen, The degradation of organic dye contaminants in wastewater and solution from highly visible light responsive ZIF-67 monodisperse photocatalyst, *J. Solid State Chem.*, 300 (2021) 122287.
- [55] H.S. Wang, Metal-organic frameworks for

- biosensing and bioimaging applications, *Coord. Chem. Rev.*, 349 (2017) 139–155.
- [56] Y. Zhao, H. Zeng, X.W. Zhu, W. Lu, D. Li, Metal-organic frameworks as photoluminescent biosensing platforms: Mechanisms and applications, *Chem. Soc. Rev.*, 50 (2021) 4484–4513.
- [57] Y. Liu, T. Jiang, Z. Liu, Metal-Organic Frameworks for Bioimaging: Strategies and Challenges, *Nanotheranostics*, 6 (2022) 143–160.
- [58] J. Yang, Y.W. Yang, Metal–Organic Frameworks for Biomedical Applications, *Small*, 16 (2020) 1–24.
- [59] P.L. Wang, L.H. Xie, E.A. Joseph, J.R. Li, X.O. Su, H.C. Zhou, Metal-Organic Frameworks for Food Safety, *Chem. Rev.*, 119 (2019) 10638–10690.
- [60] A. Hitabatuma, P. Wang, X. Su, M. Ma, Metal-Organic Frameworks-Based Sensors for Food Safety, *Foods*, 11 (2022).
- [61] P. Kumar, K.H. Kim, A. Deep, Recent advancements in sensing techniques based on functional materials for organophosphate pesticides, *Biosens. Bioelectron.*, 70 (2015) 469–481.
- [62] P.S. Sharanyakanth, M. Radhakrishnan, Synthesis of metal-organic frameworks (MOFs) and its application in food packaging: A critical review, *Trends Food Sci. Technol.*, 104 (2020) 102–116.
- [63] M. Shahmirzaee, A. Hemmati-Sarapardeh, M.M. Husein, M. Schaffie, M. Ranjbar, Magnetic γ -Fe₂O₃/ZIF-7 Composite Particles and Their Application for Oily Water Treatment, *ACS Omega*, 7 (2022) 3700–3712.
- [64] X. Zhu, Z. Yu, H. Zeng, X. Feng, Y. Liu, K. Cao, X. Li, R. Long, Using a simple method to prepare UiO-66-NH₂/chitosan composite membranes for oil–water separation, *J. Appl. Polym. Sci.*, 138 (2021).
- [65] Y. Zhang, N. Zhang, S. Zhou, X. Lv, C. Yang, W. Chen, Y. Hu, W. Jiang, Facile Preparation of ZIF-67 Coated Melamine Sponge for Efficient Oil/Water Separation, *Ind. Eng. Chem. Res.*, 58 (2019) 17380–17388.
- [66] Y. Zhang, X. Song, S. Li, B. Zhao, L. Tong, Y. Wang, Y. Li, Two-step preparation of Keggin-PW12@UiO-66 composite showing high-activity and long-life conversion of soybean oil into biodiesel, *RSC Adv.*, 11 (2021) 38016–38025.
- [67] W. Xie, X. Yang, P. Hu, Cs₂₅H₀₅PW₁₂O₄₀ Encapsulated in Metal–Organic Framework UiO-66 as Heterogeneous Catalysts for Acidolysis of Soybean Oil, *Catal. Letters*, 147 (2017) 2772–2782.
- [68] X.F. Wang, X.Z. Song, K.M. Sun, L. Cheng, W. Ma, MOFs-derived porous nanomaterials for gas sensing, *Polyhedron*, 152 (2018) 155–163.
- [69] X. Wu, S. Xiong, Y. Gong, Y. Gong, W. Wu, Z. Mao, Q. Liu, S. Hu, X. Long, MOF-SMO hybrids as a H₂S sensor with superior sensitivity and selectivity, *Sensors Actuators, B Chem.*, 292 (2019) 32–39.
- [70] X. Chen, R. Behboodian, D. Bagnall, M. Taheri, N. Nasiri, Metal-organic-frameworks: Low temperature gas sensing and air quality monitoring, *Chemosensors*, 9 (2021) 1–33.