

Review Article

Design Techniques and Applications of Ionic Liquids Incorporated Metal Organic Frameworks (IL/MOFs)

Olaniran Kolawole Akeremale^{1,*} , Joy Aworetan² , Olamide Aworetan³ 

¹Department of Science and Technology Education, Bayero University, Kano, Nigeria

²Department of Chemistry, University of Benin, Benin City, Nigeria

³Department of Industrial Chemistry, Ado-Ekiti, Ekiti State University, Ado-Ekiti, Nigeria

Abstract

Metal-organic frameworks (MOFs) are an interesting class of materials consisting of central metal ions and organic binders. These are porous crystalline materials in which different organic groups are combined with metal that has been cemented into place to provide a rigid and porous geometry. Green Metal Organic Frameworks (GMOFs) are a novel class of porous materials with a number of distinctive properties, including uniform and tunable pore size, large surface areas, adaptable pore structure, high porosities, acceptable thermal and chemical stabilities, simple production, and structural diversity. In order to alter the physicochemical characteristics and gas affinities of MOFs, ionic liquids (ILs) have recently been inserted as cavity occupants into the pores of metal organic frameworks (MOFs). Recent research has demonstrated that IL/MOF composites outperform pristine MOFs in a variety of applications, including gas storage, membrane-based gas separation, adsorption, catalysis, and ionic conductivity. Ionic liquid-modified MOFs (IL/MOFs) composite materials benefit from the high stability and versatile physical and chemical properties of ILs while retaining the structural characteristics of MOFs. Scholars are particularly interested in them because of their vast potential for usage in the domains of isolation and investigation. In this review, we provide a comprehensive overview of the applications of IL/MOF composites and talk about the latest advancements in their synthesis. The benefits and drawbacks of employing IL/MOF composites in diverse applications were investigated in order to ascertain the future directions in this field.

Keywords

Metal Organic Frameworks, Ionic Liquid, Composite Materials, Adsorption, Gas separation

1. Introduction

Central metal ions and organic binders make up the intriguing class of materials known as metal-organic frameworks (MOFs). These are porous crystalline materials where the metal is fixed into a position to create a stiff and porous geometry coupled by various organic groups. MOFs have numerous uses particularly in areas of gas adsorption and stor-

age, separation, catalysis, sensing, molecular recognition, drug administration, nonlinear optics, luminescence, etc., because of their structural flexibility, huge surface area, and tailorable pore size [1-5, 109, 117]. MOFs are advantageous substances for the separation and storage, or conversion of molecules based on dimension because they have

*Corresponding author: okakeremale.ste@buk.edu.ng (Olaniran Kolawole Akeremale)

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three-dimensionally tunable porous channels. MOFs are members of the coordination polymer class. On the other hand, for porous 2D or 3D crystalline networks, MOFs are more specialized than coordination polymers. The term "porous coordination polymer" (PCP) is also used to describe these [6]. Certain MOFs are susceptible to breaking in the aqueous phase as a result of the tenuous coordination of the metal ion and the ligand molecule; consequently, MOFs have different levels of tolerance to different solvents. Furthermore, if the analytes of interest are rinsed with an acidic or basic solution when MOFs are being utilized as adsorbents, their structure will rapidly collapse. As a result, functional MOF modification, or composite, is a successful strategy to increase MOF stability [7]. Non-molecular solvents known as ionic liquids (ILs) are made up of organic cations and organic or inorganic anion [8]. They are widely employed in separation analysis and other applications because of their many advantages, which include excellent thermal and chemical stability, low vapor pressure, and adjustable physical and chemical properties. [9, 10, 111, 118]. By embedding ILs into the MOF framework, hybrid components with a well-organized framework and a modifiable pore function are produced. These materials possess the high thermal stability of MOFs as well as the distinct dual structure and high thermal stability of ILs.

The combination of metal-organic frameworks (MOFs) and ionic liquids (ILs) has attracted a lot of interest because of the special qualities and improved functions of the resulting IL/MOF composites. By combining the unique physicochemical properties of ILs with the variable porosity and large surface area of MOFs, this synergy creates materials that perform better in a range of applications. In the fields of catalytic processes, gas extraction, separation investigation, and other related subjects, IL/MOF have recently attracted a lot of curiosity and have demonstrated some degree of accomplishment. [11, 12].

Some of the unique properties of IL/MOFs that motivated the study of these materials in recent times include:

1. Enhanced gas adsorption and separations, rendering them potential prospects for operations such as CO₂ recovery and extraction from flue gas blends [13, 109].
2. Improved catalytic activity, providing a flexible framework for chemical processes, such as the breakdown of pollutants and organic changes
3. Increased Stability and Tunability: ILs can provide MOFs more stability, preventing them from degrading in adverse environments. Additionally, ILs' physicochemical characteristics can be precisely adjusted, enabling the creation of IL/MOF composites tailored for particular uses [13, 109].
4. Enhanced ionic conductivity, preventing them from degrading in adverse environments. Additionally, ILs' physicochemical characteristics can be properly modified, enabling the creation of IL/MOF composites tailored to direct applications [14].

The disadvantages of some MOFs (like MOF-5) can be overcome, such as their poor conduction and rapid breakdown in environments with moisture. Combining the flexible design and performance of ILs with permeable MOFs allows for the creation of hybrid materials with diverse species and varied topologies. Furthermore, since the hybrid framework of materials creates novel material features and interaction locations, IL/MOFs are potentially composite materials. This study examines the characteristics and use of IL/MOF hybrid materials in addition to their fabrication techniques.

2. Synthetic Techniques of IL/MOFs Hybrid Materials

2.1. Ionothermal Synthetic Method

Ionothermal synthesis is a technique for synthesizing solid materials using ionic liquid (IL) as the reaction medium. Because IL interacts with MOF pores, it can be easily integrated into MOFs. Furthermore, owing to its low vapor pressure and room temperature liquid state, IL is easily contained in MOF pores, even under vacuum. A variety of methods exist for integrating IL with MOFs, as shown in Table 1. ILs function as a solvent as well as a template and direct the structure of the material during the synthesis of IL/MOFs. According to this process, the basic ingredients, or MOF precursors, are initially dissolved in an IL solution [15-17]. The anions or cations in ILs that act as charge substitutes are firmly anchored in the loaded MOF system as a result of a close host-guest relationship, and the resulting IL/MOF composite materials are electrically neutral. Positively charged components of ILs are incorporated within the MOF structure for the majority of ionothermally created composites [18, 15]. The ionothermal synthesis process is easy to use and safe for the environment. IL properties incorporated into the structure of the MOFs, however, were different from those of the virgin ILs because of the potent interaction between the cations of ILs and MOFs. However, there aren't many MOFs that aren't charged, and there aren't many ILs that can take the place of organic solvents/water as the reaction media. As a result, only a few ILs and MOFs are useful for the synthesis of this hybrid material via this technique, which prevents this approach from being widely used [19, 110].

2.2. Post-Synthetic Incorporation of ILs into MOFs

A technique known as post-impregnation, whereby ILs are incorporated within the porous structure of the material after its preparation, has been developed in order to solve the issues with ionothermal synthesis. By varying the components, this technique allows the design of IL/MOF composites with various properties and capabilities. Varying techniques, in-

cluding wet impregnation, capillary action, and ship-in-a-bottle procedures, can be used to post-impregnate ILs within the artificial MOF cavities.

2.2.1. Wet Impregnation Method

The most popular post-synthetic technique is wet impregnation because it has easy synthetic processes and a variety of uses. However, composites created by this straightforward impregnation might have a high level of instability. This wet impregnation approach involves dissolving ILs in an inert solvent, adding synthesized MOFs to the ILs mixture, and allowing them to mix for a while at ambient temperature, then removing the inert solvent to produce the IL/MOF. Typically, imidazolium-type ILs like MIL-101 (Cr), NH_2 -MIL-101 (Cr),

MIL-101 (Fe), CUBTC, UiO-66, or ZIF-8 are used in this approach to impregnate the MOFs [20-25]. Submerging 1-butyl-3-methylimidazolium chloride into MIL-101 (Cr) with dichloromethane in the capacity of a solvent, Jhung and colleagues [44] created IL/MIL-101 composite materials. IL/MOF with various properties can be produced by altering the types of ILs and MOFs. The wet impregnation procedure can easily be utilized while the procedure is done in a comfortable environment at room temperature (Figure 1). IL/MOF composites are currently made using this approach, which is common. However, due to the physical interaction that occurs when ILs and MOFs are joined, the hybrid material exhibits low stability [111].



Figure 1. Wet impregnation technique schematic diagram for the impregnation of ILs into MOFs.

2.2.2. Ship-in-a-Bottle Technique

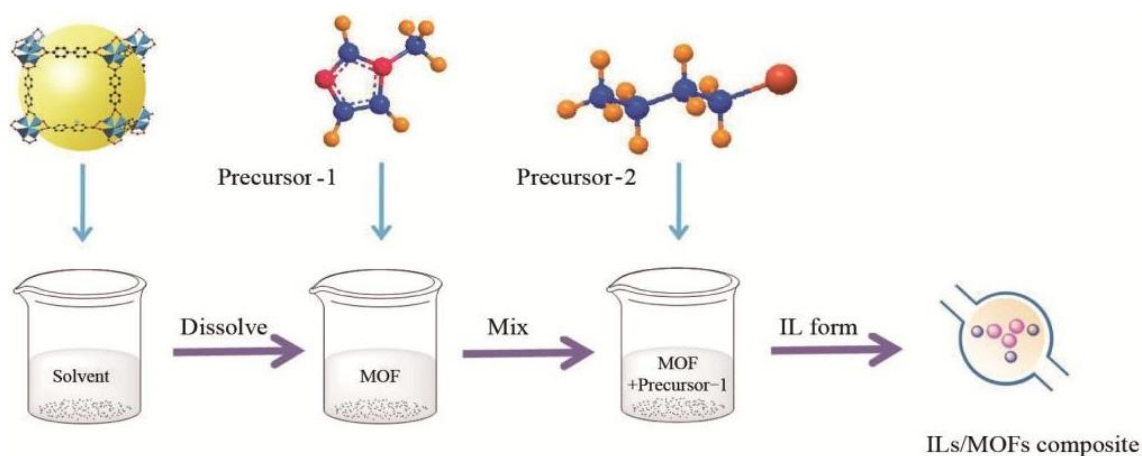


Figure 2. Schematic diagram of Ship-in-a-bottle method of impregnation of ILs into MOFs.

The "ship-in-a-bottle" approach is an additional method. In this procedure, the MOF's porous structure serves as a direct site of IL synthesis. This MOF receives two separate injections of each reactant that makes up the IL. Before the MOF is added, the initial reactant is supplied to it by solvating it into an inert solvent. The mixture is left to permit reactant integration into MOF pores in order to create ideal conditions for the synthesis of IL. This is followed by the addition of the second reactant, which is then left to react to create IL. After the reactants that do not create IL in the MOF and the inert solvent are removed from the mixture, the remaining product is dried. The technique is applicable to MOFs with pores that are smaller than those of the original IL molecule [26]. The starting materials of the synthetic 1-butyl-3-methylimidazolium bromide, 1-methylimidazolium, and 1-bromobutane were loaded into the pores of ZIF-8 and MIL-100 (Fe) by Khan et al. (2018) [27], and the IL@ZIF-8 with IL@MIL-100 (Fe) were subsequently produced. This technique made it possible for tiny IL precursors to permeate and incorporate within the MOF nanopores, which successfully contained ILs in the MOF apertures under geometric restrictions to reduce IL attrition with enhanced IL/MOF

resilience (Figure 2).

2.2.3. The Capillary Action Technique

Prior to the manufacture of the composite, the MOF is warmed up in the absence of oxygen in order to eliminate impurities. Thereafter, MOF and IL are combined and ground into a fine powder. For the purpose of increasing IL diffusion into MOF, the composite is heated for several hours. The pores of MOFs are thought of as capillaries when using the capillary action method. Through annealing treatment, ILs are better distributed and ground into the pores of MOFs [28]. The pre-made EMIMCl and UiO-67(Zr) were ground together to generate the new mixed ion conductor EMIMCl@UiO-67. Heating the resulting mixture improved its dispersion into the UiO-67(Zr) hole. This method is based on capillary action. In order to evenly disperse the ILs into the MIL-101 channel and create an ILs@MIL-101 composite for proton conduction, Chen and Sun [29, 30], adopted a similar strategy. Since no solvent is employed, as seen in Figure 3, the capillary action approach is more cost-effective and environmentally benign than the alternatives.

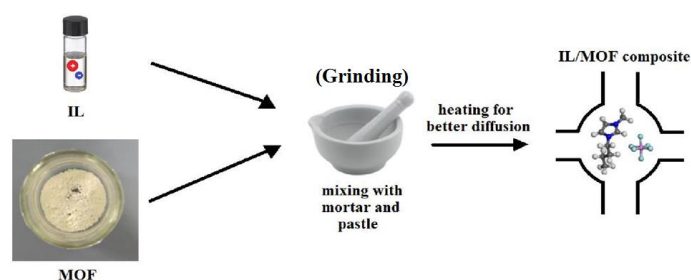


Figure 3. Schematic diagram of Capillary action method of impregnation of ILs into MOFs.

Table 1. IL/MOF Integration Techniques.

IL	IL Full Name	MOF	Method	Ref
[emim][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	ZIF-8	Capillary action	[31, 32]
[emim][TfO] ⁺ [em-imLi][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate with an additional charge Lithium 1-ethyl-3-methylimidazolium trifluoromethanesulfonate	ZIF-8	Capillary action	[33]
EMIMCl	1-ethyl-3-methylimidazolium chloride	Uio-67(Zr)	Capillary action	[28]
EMIM DCN EMIM TCB	1-ethyl-3-methylimidazolium dicyanamide 1-ethyl-3-methylimidazolium tetracyanoborate	MIL-100(Al)	Capillary action	[34]
EIMS-HTFSA	1-ethyl-3-isopropylimidazolium bis(trifluoromethanesulfonyl)amide	MIL-101(Cr)	Capillary action	[30]
EIMS	1-ethyl-3-isopropylimidazolium	MIL-101	Capillary action	[29]
[emim][EtSO ₄]	1-ethyl-3-methylimidazolium ethyl sulfate	Cu-BTC	Capillary action	[35]

IL	IL Full Name	MOF	Method	Ref
[emim][TfO]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	ZIF-8	Capillary action	[32]
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate	ZIF-8	Impregnation	[36]
[C ₃ NH ₂ bim][NTf ₂]	1-(3-aminopropyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide	NH ₂ -MIL-101(Cr)	Impregnation	[37]
ABIL-OH	Aminopropyl-imidazolium-based ionic liquid (hydroxyl functionalized)	HKUST-1	Impregnation	[38]
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate	Cu-BTC	Impregnation	[24]
[NH ₂ -bim][Br]	1-(aminoalkyl)-3-methylimidazolium bromide	Cu-BTC	Impregnation	[21]
[SO ₃ H-(CH ₂) ³ HIM][HSO ₄]	1-(3-sulfopropyl)-imidazolium hydrogen sulfate	MIL-100(Fe)	Impregnation	[39]
[bmim][NTf ₂]	1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide	ZIF-8	Impregnation	[40]
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate	ZIF-8	Impregnation	[26]
[bmim]Cl	1-butyl-3-methylimidazolium chloride	MIL-101(Cr)	Impregnation	[41]
ABIL	Aminopropyl-imidazolium-based ionic liquid	HKUST-1	Impregnation	[42]
Dicarboxylic Acid IL	dicarboxylic acid functionalized ionic liquid	MIL-101(Cr)	Impregnation	[43]
[NMP][CH ₃ SO ₃]	N-methylpyrrolidinium methanesulfonate	MIL-101(Cr)	Impregnation	[20]
Polymeric IL based on vinylimidazole	polymeric ionic liquids (PILs) derived from vinylimidazole,	MIL-101(Cr)	Ship-in-a-bottle	[40]
[bmim][Br]	1-butyl-3-methylimidazolium bromide	MIL-101(Cr)	Ship-in-a-bottle	[44]
IMIZ-BAIL	imidazolium-based bioavailable ionic liquid	MIL-101(Cr)	Ship-in-a-bottle	[45]

3. Characterization of IL/MOFs Composite Materials

In order to evaluate the effects of material qualities on human health and the environment, assess quality control during production, and design regulatory frameworks for their usage, the physical chemical characterization of IL/MOF is essential. Several physicochemical techniques should be employed to further characterize them, utilizing different procedures. Not to mention its stability in water, determining its electrical and optical capabilities, examining the homogenic condition, and comprehending the texture, structure and properties, particularly when it comes to adsorption-based water treatment. Each of these characteristics is essential. These include specific surface areas determined by gas adsorption, thermal stability with thermogravimetric analysis (TGA), elemental analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), particle shape and size distributions from transmission electron microscopy (TEM), crystalline phase and crystallite size determined by powder X-ray diffraction (PXRD), scanning electron mi-

croscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. Strong absorption bands at 1597 cm⁻¹ and 1406 cm⁻¹ have been connected to O–C–O asymmetric and symmetric stretching vibrations based on the evidence that is currently available from FTIR data in the literature, whereas bands around 1504 cm⁻¹ have been reported to show C=C vibrations of a benzene ring. Furthermore, bands of 1626 cm⁻¹ have been suggested to represent stretching vibrations of C=O. SEM and TEM images of the produced IL/MOF reflect its surface shape. Materials can have various morphologies based on a variety of parameters, such as the molar ratio of doped metals and ionic liquids. Consequently, the performance of the resulting MOF is determined by its structure. For instance, Fe-MOFs that were synthesized by Liang and colleagues in 2015 [46] were demonstrated to have a lattice structure, a homogeneous spindle-like shape, and a consistent microstructure. They were also described by high-resolution TEM (HRTEM) and field emission SEM (FE-SEM) (Figure 4).

By using EDX to analyze the chemical composition, mapping data for each element were obtained, enabling the determination of the homogeneity of the synthesized MOFs.

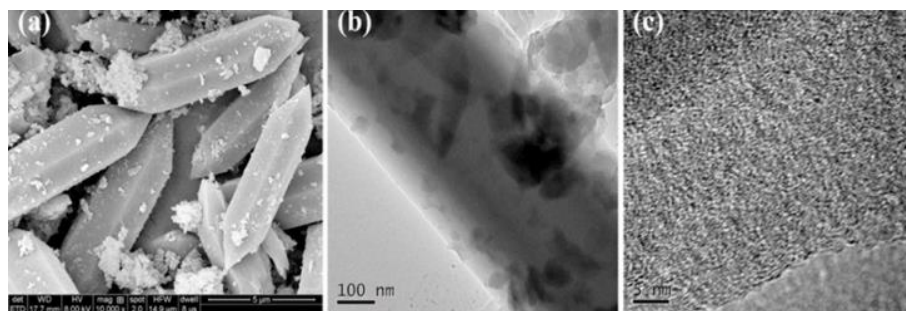


Figure 4. (a) Field Emission Scanning Electron Microscopy (FE-SEM) image of Fe-MOF; (b) Transmission Electron Microscopy (TEM) image of Fe-MOF; (c) High-resolution TEM (HRTEM) image of Fe-MOF. [47].

3.1. Powder X-Ray Diffraction (PXRD)

PXRD is widely utilized to determine the crystallinity and structural properties of the MOFs. A simulated pattern created by single crystal X-ray and stored in a database, a diffractogram already published in the literature, or computer modeling can all be used to compare the synthesized MOF's diffractogram [47]. The crystallinity of the structures, various polymorphic forms, and an estimation of the crystallinity percentage can all be determined using this method. The determination of the crystallographic details, which include the size of the crystallite, unit cell size, and lattice parameters, are all feasible once the crystalline structure of the MOF has been discovered. The size of the crystallite can be estimated with Scherrer's equation after its diffraction peaks have been found, often using the sharpest non-overlapped peak [48]:

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

D being the crystallite size, K the equipment-dependent size factor (usually between 0.84 and 0.98), β the peak's full width at half maximum height (FWHM), and θ the Bragg angle for the peak located on the diffraction graph. In order to understand how a MOF crystallizes as well as to confirm the development of a novel MOF, heterojunction, or composite, researchers studying MOFs frequently use this characterization technique. The MOF's stability in adsorption applications is also assessed using the XRD method. After the reaction, the spent MOF will be removed from the solution, cleaned, then dried off. In order to check for potential differences and determine whether the MOF structure is stable, the pattern of the diffraction graph is recorded and then compared with the unspent MOF [49]. Since X-ray diffraction requires complex synchrotron radiation facilities, other X-ray absorption-based techniques are less frequently used in MOF characterization. Extended X-ray absorption fine structure (EXAFS or XAFS) analyzes the different classes and also accounts for the exact amount of particles in the surroundings of the absorbing species with the distance between the absorber and its neighbor through oscillatory modulation in the X-ray absorption coefficient on the high-energy side of an absorption edge [50]. The band width energy, bond angles, and valence state are

revealed by X-ray absorption near-edge structure (XANES); on the other hand, [51].

3.2. Nitrogen Adsorption-Desorption at -196 °C (Surface Area Measurement)

Because it enables the determination of textural characteristics such as average pore size, specific surface areas, pore volumes, and pore size distributions, it is frequently employed in MOF characterization. The adsorption of nitrogen (N_2) across the material's surface at the liquid nitrogen boiling temperature, producing an adsorption isotherm. The isotherm's shape reveals details on the solid's homogeneity. Six categories of physisorption isotherms were established by the International Union of Pure and Applied Chemistry (IUPAC) in 1985 [52]. The material must be sufficiently heated and dried without air before N_2 adsorption/desorption isotherm in order to collect pertinent data. This pretreatment does, however, occasionally result in a reduction in surface areas because of framework collapse [53]. It was often believed that this collapse was caused by the elevated surface strain as well as capillary forces which formed at the point of transition between the gas and the confined solvent molecules. [54]. The bulk of microporous materials in MOFs exhibit type I isotherms and have high surface areas ($>2000 \text{ m}^2\text{g}^{-1}$). The Brunauer-Emmett-Teller (BET) method [55] is the method most frequently used to determine the surface area of MOFs and allows for relating it with other porous materials. Nevertheless, due to the fact that this model was created for even surfaces and accurate MOF adsorption data may not be accurately captured, particular consideration must be given to three-dimensional (3D) MOFs with high porosity [56]. Data from the isotherm of adsorption of a permeable and impermeable material are related using the t-plot technique. [57] is typically used to detect the presence of microporous materials. The N_2 adsorption isotherm can be used to obtain the pore volume and pore size distribution, much like in BET modeling. It is worthy to note that the Barrett-Joyner-Halenda (BJH) technique is effective for mesopores alone, while the Horwath-Kawazoe (HK) method is only used for micropores. The density functional theory (DFT) model [58] is commonly utilized for assessing the MOFs distribution of its pore size ranging from meso- to micropores. The availability of

equipment, particularly in the analysis of micropores and adsorption data is required in extremely low relative pressures, where the accuracy of the experimental data that can be fitted is determined by the porosity of the MOFs. For instance, the DFT technique is dubious when MOFs with flexible holes or organized randomly are investigated because it presupposes that the pores are stiff and have a clearly defined geometry [59].

3.3. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

Scanning electron microscopy (SEM) is a method that is frequently employed for MOF characterization. This method produces images that are two-dimensional (2D) in nature with great resolution, which shows the spatial fluctuations of the material as well as its shape, providing details on its exterior morphology, dispersion, and phase mixture. As a result of the porous nature of MOFs, a variety of morphologies, including cubes, bars, rhombohedra, and others, are produced. Based on the SEM apparatus being used and the insulating properties of particular MOFs, the SEM characterization may require a previous pretreatment by covering the surface with a conductive material, frequently gold [56]. In order to overcome the limitation, the field emission scanning electron microscopes (FESEM) can be utilized by researchers. This device uses a field emission cannon that generates extremely concentrated electron beams, which enhances the depth of field at minimal potentials. The aforementioned characteristic reduces the impact of charging on insulators and even shields certain delicate MOFs from electron beam damage. However, the use of TEM to measure the size of the grain/particle, and obtaining information like plane indices from its crystallography has become more common. The images from the microscopy can be analyzed using a variety of software tools (such as ImageJ and Cell Profiler). In the use of these instruments, there is feasibility of calculating the distance between crystallographic planes as well as the particle size by measuring various particles and generating a histogram. Because the gathered images provide information on the size and dispersion of those nanoparticles (NPs), this technique is highly helpful for characterizing MOFs changed by the incorporation of NPs [60]. The elemental analysis of MOFs (quantitatively and qualitatively) can be ascertained using these microscopies in combination with energy dispersive spectroscopy (EDS) or energy dispersive X-ray analysis (EDX or EDAX).

3.4. Thermogravimetric Analysis (TGA)

TGA analyzes a material's mass loss as a function of temperature in a controlled environment. This method can be used to calculate the MOF's solvent-accessible pore volume and assess its thermal stability. Depending on the carrier gas utilized for the TGA (N_2 , air, or O_2), the MOF breakdown differs. The TGA curve in a typical study shows the percent loss of weight in the MOF with respect to temperature. The graph typically shows firstly, the loss of mass between 40 and 110

degrees Celsius, which corresponds to the removal of solvent molecules, and a second loss between 300 and 600 degrees Celsius, which is typically assumed to be the structural modification of the MOF framework, producing the corresponding metal oxides. Remembering that this weight loss does not necessarily indicate a structural change, it is required to supplement this research with an examination of the change in structure using XRD at various temperatures [56].

3.5. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

This technique is used to detect and count the elements that are present in a particular sample (elemental analysis) and the sample's emission spectra are used in the process. ICP-OES usually determines how pure the MOFs are and the type of relationship that exists among the molecules that make them up since it can identify the majority of components at very low concentrations. However, this method demands that the sample to be analyzed must be well dissolved (digested) before examination rather than analyzing the chemical composition directly over the solid materials. Even when using harsh treatments like HNO_3 , H_2SO_4 , followed by H_2O_2 or even HF digestions, the total dissolution of MOFs is not always straightforward. Because it is important to make sure that the dissolution is thorough, these procedures for the ICP-OES analysis are challenging [61, 56]. As a result of this hindrance, other methods that enable understanding the fundamental analysis are sought after. One cutting-edge method for elemental analysis applications is Wavelength Dispersive X-ray Fluorescence (WDXRF). In WDXRF, all elements are concurrently stimulated, resulting in their distinct radiation emissions, which are then each recognized by a detector. In contrast to ICP-OES, which necessitates a laborious process of solid dissolution, this approach can be used immediately on solid materials [62-64].

3.6. Aqueous Stability Testing

Testing the aqueous stability of these materials is crucial because they should be robust when in contact with water containing (aqueous) solutions in order to effectively exhibit their characteristics in the adsorption processes for the removal of emerging contaminants from water. Since most MOFs include basic or acidic functional groups in their structures, the pH of the water must be evaluated both before and after the MOF is added. Determining the MOF's zeta potential, which is the measure of the total effective electric charge on the MOF's surface in the aqueous solution, may also be of interest. Exposing the substance to an aqueous solution with a specified pH is an easy technique to evaluate the stability of MOFs in water. After some time has passed, the material can then be sieved, cleaned, and dried. By comparing recovered mass to the starting mass, it is possible to determine the stability yield. The structure and porosity must first be controlled, and the N_2 adsorption isotherm and XRD must be measured both before and after the water testing [49]. The bulk

of MOFs are microporous materials, as was previously mentioned, and their gas adsorption experiment suited the anticipated type I isotherm model. The specific adsorption isotherm's shape revealed information about its nature together with the strength of the relationship that exists at the interface of the water molecules and the MOFs surface. XRD characterization needs to go along with these investigations. While the majority of MOFs exhibit water adsorption isotherms that are comparable with the ones reported in literature using other porous materials, some MOFs do show unique adsorption capabilities because their structural design is flexible.

3.7. Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-vis DRS)

UV-vis DRS offers details on the optical characteristics and makes it possible to determine the range of wavelengths at which MOFs absorb light in the electromagnetic spectrum; hence, it is commonly employed to characterize these adsorbents. By using this method, an absorption spectrum that appears in the absorption band will be displayed on the readout device of the machine at the UV-visible wavelength range, typically between 190 to 900 nm. Due to their ability to exhibit inorganic, organic, or hybrid behavior depending on their composition, MOFs are a very intriguing kind of sorbent. The electrons in an inorganic compound can become excited and transit between the valance band (VB) and conduction band (CB) when sufficiently stimulated by light, creating a vacuum in the VB. Organic compounds use very similar principles, but their electronic transitions take place between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the molecule. MOFs can undergo e^- transitions between the valence band and the conduction band of the central metal atom. This transition can also occur between the HOMO and LUMO of the organic linker when excited by light of the right energy [65]. As a result, depending on which component encourages electronic transitions, the absorption spectrum can consist of different bands. A helpful method for figuring out a material's band gap energy (E_g) is also the UV-vis DRS. The Tauc plot approximation is typically used for this purpose [66, 67].

4. Influence of Interaction Between IL and MOFs on the Properties and Performance of IL/MOFs Composites

The combination of metal-organic frameworks (MOFs) with ionic liquids (ILs) produces composite materials whose performance and characteristics are greatly impacted by the interactions between MOFs and ILs. It is essential to comprehend these interactions in order to customize IL/MOF composites for particular uses.

Types of interactions existing between IL and MOFs:

1. **Physical Encapsulation:** Via morphological encapsulation, ILs can be contained inside MOF pores, improving their adsorption capabilities. For example, it has been demonstrated that encapsulating ILs within ZIF-8 MOF improves CO_2/CH_4 selectivity. This is because the ILs stabilize the aperture configuration of the MOF [68].
2. **Chemical Bonding:** By establishing chemical connections between the metal nodes or organic binders of MOFs, functional groups in ILs can create composites that are more stable and functional. The IL/MOF composites' adsorption capabilities and thermal stability limits may be improved by this interaction [69].
3. **Electrostatic Interactions:** The ionic conductivity of the composite and its appropriateness for uses such as solid electrolytes in batteries can be affected by electrostatic interactions between the charged ILs and the MOF framework. The possibility of IL/MOF composites becoming solid electrolytes in lithium-ion batteries has drawn attention [70].

Some of the influence of these interactions on their properties and application performance are highlighted below;

1. **Enhanced Gas Adsorption and Separation:** By adding ILs to MOFs, gas adsorption capabilities and selectivities can be improved. For instance, when compared to virgin MOFs, IL/MOF composites have demonstrated better performance in gas capture applications [26].
2. **Improved Catalytic Activity:** Because ILs and MOFs work in concert, IL/MOF composites can have improved catalytic qualities. The interactions between ILs and MOFs are mostly determined by the interionic interaction energy of ILs, which can be adjusted to maximize catalytic activity [69].
3. **Increased Stability:** IL interactions stabilize the MOF structure; hence, their presence can stop MOFs from breaking down and speed up processes like melting. For example, it has been demonstrated that ILs help the ZIF-8 MOF melt by stopping its breakdown [69].
4. **Enhanced Ionic Conductivity:** IL/MOF composites are appropriate for use in energy storage devices due to their high ionic conductivity. MOFs and ILs have been combined to create composite materials that can be used as solid electrolytes in batteries and supercapacitors [14].

5. The Uses of IL/MOFs Hybrid Materials in Separation Studies

5.1. Using IL/MOFs For Segregation and Retention

5.1.1. Using IL/MOFs in Adsorption-based Gas Segregation and Retention

The use of MOFs and ILs together in creating blended structures is becoming more popular in adsorption-based gas

separation technologies [71, 26, 72]. Sezginel and associates [24] published some of the first investigations of MOFs with IL integrations in 2016. The experiment involved adding [BMIM][BF₄] to CuBTC, and the resultant hybrid material exhibited optimum selectivity for CH₄ ahead of H₂ and N₂ that were almost 1.5 times better than those of virgin MOF at lower pressures. These improvements were attributed to altered pore environments, newly formed adsorption sites, and improved guest molecule interactions with IL-MOF interfaces. In a similar vein, Yang's group also reported one of the earliest contributions to this subject, which demonstrated how adding [BMIM][NTf₂] to ZIF-8's nanocages improved the material's ability to adsorb CO₂ [73]. Due to its high solubility and affinity for IL molecules, CO₂ has more favorable adsorption sites than other gases, which results in its preferred adsorption. In order to get additional insight into the impact of IL incorporation on the performance of IL/MOF composites in terms of selective gas adsorption and separation, [BMIM][PF₆] was added to another MOF, ZIF-8 [23]. When [BMIM][PF₆] was integrated, ZIF-8's optimum CO₂/CH₄ and CO₂/N₂ selectivity were enhanced by over twofold at minimal pressure. Additionally, [PF₆]⁻ has a greater preference for CO₂ than other gases, and this combination of properties allowed for more adsorption sites within ZIF-8. After that, Henni and colleagues observed that adding [BMIM][Ac] to ZIF-8 boosted its CO₂ uptake by seven times, and adding [EMIM][Ac] to ZIF-8 at 0.1 bar increased its CO₂/N₂ selectivity by eighteen times [74]. These gains in carbon dioxide adsorption and separation efficacy were found to be caused by the inclusion of IL particles within ZIF-8 scaffolds as highly beneficial CO₂ adsorption sites that subsequently enhance CO₂ adsorption and separation capacity [75]. It should be further pointed out that there may be various sorption mechanisms where gas molecules are not only adsorbed on their outermost layer but can also be absorbed through the IL layer, when the IL is present in many layers, particularly at large IL loadings. The important finding is that ILs containing acetate anions can potentially increase a composite material's capacity to absorb CO₂ since the acetate ion functions as a potent Lewis base, generating more CO₂ adsorption sites [76, 77]. In summary, these results show that the CO₂ collection and separation performance of the IL/MOF composite are significantly affected by altering the anion type of IL. In conclusion, research published in the literature shows that adding ILs to MOFs greatly improves the parent material's ability to separate and adsorb gases. Given that MOFs and ILs are both extremely adjustable and have an almost infinite number of possible configurations, more research is needed to gain a basic understanding of the structural elements influencing performance in order to rationally design innovative hybrid materials with significantly higher separation potentials.

5.1.2. The Application of IL/MOFs in Liquid Phase Segregation and Retention

Hybrid materials are being employed in liquid phase separation and adsorption operations due to the ever-growing

volume of contaminants generated in the paper, steel, chemical, food, pharmaceutical and petrochemical sectors [78]. Adsorptive materials with adjustable architectures and strong adsorption capacities, such as IL/MOF material composites, are therefore required to achieve the selective removal of dangerous chemicals from water [79, 80, 44]. Because task-specific synthesis is made easier with IL/MOF composites, there has been a documented increase in the diversity of adsorbed molecules in the domain of separation and adsorption in liquid phases available in the literature. Similar to selective gas phase adsorption, research has been done in the literature where organic pollutants, such as dyes [81, 82], pesticides [83], antibiotics and drugs [84, 85, 86], and heavy metals such as hexavalent chromium [87], are taken out of their solutions and adsorbed selectively. In these tests, the maximal potential for adsorption and discrimination of IL/MOF composites is nearly invariably higher than that of their pristine equivalents. Inhibiting the usage of hydrophobic ILs and water-stable substrates because of polar solvents and solutions containing water can be characterized as the primary issue of this topic. Consequently, careful consideration should be given to the pairing of IL/MOF materials in order to maintain the composite's integrity during the adsorption process. Modification with ILs becomes important to boost affinity towards target compounds with the right partnering selection. Kulak and colleagues recently proposed the IL/functionalized MOF (IL/fMOF) idea to the field of liquid adsorption in order to improve the adsorption of methylene blue from an aqueous solution [81]. This study investigated the effects of implantation of hydrophobic and water-stable IL, [BMIM][PF₆], on the methylene blue uptake of amine-functionalized UiO-66 and water-stable MOFs. The maximal adsorption values of the hybrid material were higher than those of their pristine equivalents. According to this research, selecting the appropriate IL/porous substance with respect to the solid or liquid contamination and accounting for any chemical, adsorptive, and electrostatic relationships between the pollutant and the material may be crucial to a successful liquid-phase separation process.

5.2. The Application of IL/MOFs in Catalysis

Because catalysts feature active sites that can speed up reactions and reduce activation energy, catalysis is crucial for increasing reaction rates and saving energy. A few different kinds of catalysts, such as homogeneous, heterogeneous, and biological catalysts, have been applied in numerous fields. Every one of these catalysts has benefits and downsides of their own. MOFs are classified as heterogeneous catalysts and have been shown to have catalytic potential. They can tolerate high temperatures and have high densities in their catalytic sites, respectively. These materials have good selectivity [88], higher recyclability [89], and strong catalytic activity [90, 91]. Because of these exceptional qualities, MOFs can be combined with other species or materials to increase their catalytic activity. One of the earliest

reports of an IL/MOF composite being used as a catalyst for the cycloaddition of propylene oxide and CO₂ was made by Ma et al [73] on MIL-101(Cr), a salt of quaternary ammonium along with a phosphorus salt, IL, were modified through post-synthesis modification. The resulting composites had more [Br]⁻ anions of the IL than previous benchmark MOFs. These anions reacted with Cr³⁺ Lewis sites that were acidic to increase the formation of propylene carbonate. Sun and his fellow researchers investigated the cycloaddition of CO₂ with epichlorohydrin (ECH) using an IL/MOF as a heterogeneous catalyst [92]. IL/MOF was synthesized via the acid-base reaction pathway by treating an IL functionalized with amine, 1-methyl-3-(2-amino-ethyl) imidazolium bromide, [2-aemim] [Br], with MIL-101-SO₃H. In their report, both precursor synthesis steps were described in detail. The IL/MOF system was created in an atmosphere of room temperature and pressure, with water serving as the solvent. A strong crystalline structure with initial MOF mother mimicry was seen in XRD diffractograms, suggesting how the addition of [2-aemim] [Br] failed to alter the MIL-101-SO₃H framework's original configuration. The presence of an amino group was confirmed by FTIR and X-ray photoelectron spectroscopy (XPS) analyses. Both the former and the latter supported the notion that the N and S elements in IL and MOF, respectively, were involved in the acid-base reaction. The former produced the vibrational stretching of the imidazole ring at 1575 cm⁻¹, which corresponded to a slim [2-aemim] [Br] spectrum. The latter showed evidence of a N component in the IL/MIL-101-SO₃H specimen that was missing in the initially prepared sample of the MOF. Sun and colleagues [92] evaluated the catalytic efficacy of the produced IL/MIL-101-SO₃H by cyclizing CO₂ alongside a compound called epichlorohydrin and comparing the transformation rate of epoxide to carbonate using ¹H NMR measurements from a blended ratio of peaks. The use of an IL/MIL-101-SO₃H (N, 3.5 wt%) catalyst resulted in an excellent epichlorohydrin to chloropropene carbonate transformation rate. This was contrasted with an untreated sample (0% yield) and MIL-101-SO₃H that was not added to IL (58% yield). A hybrid material created by mounting [AmPy][I] over ZIF-90 by post-covalent transformation was a further catalyst that was tried for the cyclic addition of propylene oxide and CO₂ in the absence of a solvent. Under the same conditions, the composite (IL/ZIF-90) produced a yield for propylene carbonate that was about twice as high as the pristine counterpart [93]. Cui and colleagues (2019) [94] have reported that the addition of Lewis base binders, namely -NH₂, -OH, or -S=O, can significantly improve the catalysis efficiency in the framework during the process of cycloaddition between epoxides and CO₂. The cycloaddition of CO₂ and propylene oxide without the need for a substrate or co-catalyst was made possible by grafting [AeM-IM][Br] onto the aldehyde-functionalized ZIF-8 through post-synthetic modification [95]. The coordinated unsaturated Zn sites had the opposite effect as Lewis base sites as the Br⁻ ions did. It was found that the catalytic activity produced by the IL-grafted ZIF specimen is enhanced by the Zn²⁺ and Br⁻ sites cooperating in lowering the energy boundary for propylene ox-

ide ring-opening. As the previously described instances show, grafting ILs onto metal organic frameworks prevents IL leaching and has benefits including structural stability and appropriate catalyst recovery. Conversely, many of them necessitate complex modification processes. In order to immobilize ILs through coordination bonds, implantation of ILs into MOF frameworks is a simple yet effective technique [96, 107 108].

5.3. IL/MOFs Application in Solid Phase Extraction

When treating complicated samples, IL/MOF composites exhibit a remarkable capacity for enrichment and superior selectivity. With respect to their improved adsorption, stability, and selectivity, they have become cutting-edge materials in solid-phase extraction (SPE). Numerous benefits of these composites have been emphasized by recent studies and this makes them useful for solid-phase extraction analyses of toxic compounds found in food, medicine, and wastewater. A pyridine ionic liquid-functionalized bimetallic MOF was developed in 2022 by Jun and colleagues [97] for the solid-phase extraction of sunset yellow, a synthetic dye frequently found in food products. The modified MOF demonstrated high selectivity and adsorption capacity for sunset yellow, highlighting the useful benefits of IL modification in improving the performance of MOFs for solid-phase extraction applications. Additionally, in a study by Wei and coworkers (2018) [98], they described the creation of IL-modified magnetic MOFs for α -chymotrypsin extraction, demonstrating enhanced adsorption capacity and selectivity.

This review goes into length on a number of aspects of its use in solid-phase extraction, including dispersed solid-phase extraction, magnetic solid-phase extraction, and solid-phase microextraction [99].

5.3.1. IL/MOFs Hybrid Materials in Magnetic Solid-Phase Extraction

By incorporating magnetic nanoparticles (such as Fe₃O₄) into IL/MOF hybrid material, a magnetic solid-phase extracting agent can be produced. Two types of extraction drivers, ILs adapted to magnetized zeolite imidazolate framework-8 (IL/Fe₃O₄/ZIF-8), as well as ILs adapted to magnetized multi-walled carbon nanotubes/zeolite imidazolate framework-8 (IL/MM/ZIF-8), were produced with the aim of determining the dichlorodiphenyltrichloroethane level in water from environmental sources and the four pyrethroids in tea [100, 101]. These extraction agents created a simple and effective non-hazardous magnetic solid-phase separation technique, which was then combined with GC-MS. To identify aflatoxin in milk samples, Gao and colleagues used a combination of UHPLC-MS and magnetic solid-phase extraction. According to Gao et al. (2019) [102], the results of the experiment indicate that an altered MOF exhibits superior performance during extraction and also has increased discrimination. Comparing the composites composed of a magnetic compound and

IL/MOF, the latter had a greater specific surface area and a shorter diffusion distance. It is possible to achieve effective microextraction at low concentrations with a short equilibrium period and just a small quantity of extraction agent, resulting in an effective extraction rate and capacity that are very high.

5.3.2. IL/MOFs Composites Used for Solid-Phase Microextraction

Once the IL/MOF hybrid materials have been coated on their outermost layer to form solid-phase micro-extractants utilizing fused silica fibers or a different material for supportive substrate, the item that will be assessed is taken out, enhanced, injected, and evaluated by either the direct or headspace approach. After the fiber has been loaded with the analyte, it is directly sent to the apparatus (GC or HPLC) to undergo specific desorption before being separated and analyzed. A suitable microextraction solid-phase fiber covering material, ILs/IRMOF-3/PDMS, has been developed by properly cultivating IRMOF-3 over the surface of stainless-steel cables while coating them using ionic liquids (ILs) and polydimethylsiloxane (PDMS) [103]. In addition to having a rougher surface, the framework becomes more porous, possessing an extended service life (100-fold) than IRMOF-3. The ILs/IRMOF-3/PDMS coating could effectively avoid significant moisture-induced cracking of IRMOF-3. Utilizing gas chromatography-mass spectrometry in conjunction with the fiber allowed for the accurate and sensitive detection of polycyclic aromatic hydrocarbons in rainfall. An easy-to-use in situ solvothermal growing technique was used by Wu et al. (2016) [104] to install MOF/IL-doped graphene (ILG/MOF-5) hybrid materials on scratched stainless-steel cables. The covalent bond across the amino group of IL alongside the carboxyl pair of MOFs improves the mechanical stability and structural homogeneity of the crystallites. The resultant composite combines the benefits of both MOF and IL with a large surface area as well as improved removal ability. The removal effectiveness

of thiamphenicol and chloramphenicol in the water-based solution was preconcentrated using gas chromatography-flame ionization detection. Solid-phase microextraction significantly accelerates analysis and detection by integrating sampling, extraction, concentration, and sampling. The extraction efficiency is further increased by adding IL/MOFs composites to the solid-phase microextraction agent.

5.3.3. IL/MOFs Composites Used for Dispersive Solid-Phase Extraction

In order to extract the analyte from the sample aqueous solution, dispersive solid-phase extraction involves dispersing the solid-phase extraction agent. The extraction agent is added to IL/MOF to give it the better qualities of these hybrid materials, namely excellent stability, a large specific surface area, with accessible sites for adsorption. Yohannes and Yao [105] combined a group of permeable materials known as MOF together with tropine-based ILs, which shared structural characteristics with naturally occurring tropine alkaloids, for the quantitative research of Huashan biochips. To create a compound using tropine-based ILs (N-propyl substituted tropine hexafluorophosphate, $[C_3tr][PF_6]$), three different metal organic frameworks (MIL-101, HKUST-1, and ZIF-8) were employed. Chromatographic analysis was performed to assess the potential adsorbent value of the IL/MOF composite for dispersive solid-phase extraction-based propane alkaloids enrichment. The outcome demonstrated the high recovery rate and good adsorption capacity of $[C_3tr][PF_6]/MIL-101$. The process is basic and quick, and the extraction efficiency can be further increased by adding IL/MOF composites to the dispersive solid-phase extraction agent. It is capable of efficiently eliminating metal ions from environmental water samples and pesticides from samples of fruits and vegetables. The summary of the synthesis and major applications of IL/MOFs in shown in figure 5 below.

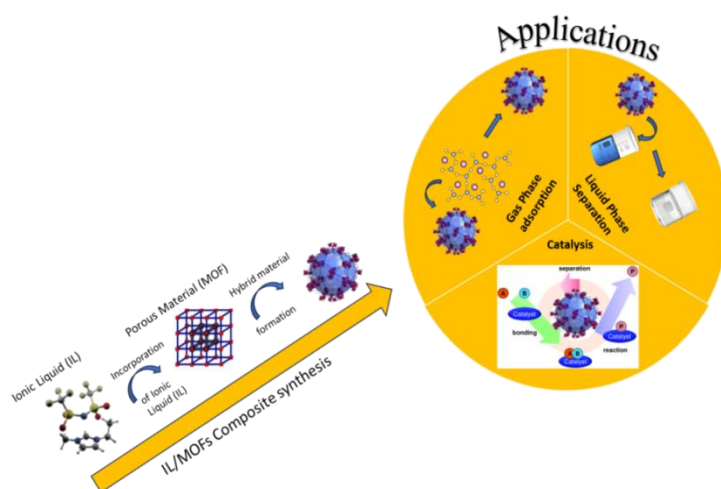


Figure 5. Schematic Diagram of the Formation and Major Applications of IL/MOFs Composite Materials, Inspired by Ozce et al., 2022 [106].

6. Challenges in IL/MOF Synthesis

Ionic liquids (ILs) have the potential to improve effectiveness, conductance, and catalytic efficiency when added to metal-organic frameworks (MOFs). Recent research, however, has brought to light a number of difficulties related to this integration, namely with regard to the environmental implications, operational stability and scalability, and synthesis complexity.

6.1. Pore Blockage and Reduced Surface Area

When ILs are integrated into MOFs, they may cause pore blockage, which reduces the surface area and, in turn, the adsorption capacity of the material. Studies on IL-hybrid materials for CO₂ capture, for example, have demonstrated that IL inclusion can lower the sorbent's heat capacity but also cause pore blockage, which affects adsorption effectiveness [112].

6.2. Problem Associate with Compatibility

It is essential that ILs and MOFs be chemically compatible. For instance, the fundamental strength of MOFs' susceptibility to moisture may be jeopardized by hydrophilic ILs. It is crucial to choose the right ILs that don't negatively impact the MOF structure [113].

6.3. Cost and Complexity of Synthesis

IL/MOF composite synthesis can be difficult and expensive. Because of the complexity of their synthesis methods, it is still very difficult to scale up the manufacturing of these composites for industrial purposes [114].

7. Ionic Liquids Related Environmental Concerns

7.1. Ecotoxicity of Ionic Liquids

Ionic liquids have adjustable characteristics and very little vapor pressure, but they are not always "green." Concerns about their extensive use, particularly in IL/MOF systems, are legitimate given their toxicity, low biodegradability, and environmental persistence. Ionic liquids can be extremely harmful to aquatic life, including fish, algae, and *Daphnia*, both acutely and over time. The cationic structure of the IL (such as imidazolium or pyridinium) and the length of the alkyl chains, which influence lipophilicity and membrane permeability, are major factors in this toxicity. In aquatic life, ILs can interfere with metabolic processes and cell membranes. Some ILs may bioaccumulate via food chains and are resistant to degradation [115].

7.2. Biodegradability and Persistence

The majority of traditional ILs do not biodegrade easily. Microbial degradation is resisted by the ionic character of cationic moieties, particularly those with long alkyl chains or aromatic groups. This leads to long environmental half-lives and contributes to soil and groundwater contamination issues. Among the elements that contribute to ILs' biodegradability include; Cation core structure; pyridinium and imidazolium cores are more resistant, Alkyl chain length; Longer chains are more poisonous and hydrophobic, Anion selection; Because of their endurance, fluorinated anions (such as PF₆⁻ and BF₄⁻) are especially challenging. [116]

8. Conclusion

ILs are one of the agents that exhibit potential for modifying the physical and chemical properties of the virgin target material. We focused on the possible characteristics of IL/MOF hybrids in this review, where the initial addition of ILs alters the structural dynamics of the pure material. We looked into IL/MOF material composites in terms of their application areas, characterization methods, and preparation processes. The advantages of each component are integrated into IL/MOF composites, and the infinite combinations of these components considerably expand the range of materials available. Furthermore, MOFs and ILs are good extraction agents, and the mixtures that combine them enhance their application as extractants efficacy even further. The performance of the pure material is improved by IL inclusion in a number of applications, including liquid phase adsorption and separation, solid phase adsorption and separation, gas adsorption and separation, and catalysis. These enhanced outcomes were explained by the relationships that occur between porous substances and the IL. Performance of the IL/MOF material composites may be hampered by a number of possible issues, such as choosing the right preparation method, designing IL/MOF material composites rationally, the reusability of IL/MOF, and ensuring the material composites thermal and chemical stability. The drawbacks of each material can be solved by the composite of MOF and IL, improving application performance. Nevertheless, because present research focuses on binary gas mixtures and synthetic conditions rather than actual commercial mixtures and conditions, the technique has not yet reached industrialization. Thus, more study and industrial application of the IL/MOF combination as a composite are required. Future research directions on these composites should also be directed towards expanding material diversity, advanced characterization techniques, enhancing the stability of the materials, explorations of new applications, investigation of the environmental impact of IL/MOFs, and green/scalable synthesis.

Abbreviations

Mofs	Metal Organic Frameworks
GMOFs	Green Metal Organic Frameworks
ILs	Ionic Liquids
IL/MOFs	Ionic Liquid Modified Metal Organic Framework
PXRD	Powdered X-Ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV-vis DRS	Ultraviolet- Visible Diffuse Reflectance Spectroscopy
DFT	Density Functional Theory
FESEM	Field Emission Scanning Electron Microscope
NPs	Nanoparticles
EDS	Energy Dispersive Spectroscopy
WDXRF	Wavelength Dispersive X-ray Fluorescence
VB	Valence Band
CB	Conduction Band
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
FTIR	Fourier Transform Infrared Spectroscopy
SPE	Solid Phase Extraction.

Clinical Trial

Authors declare that clinical trial is not applicable in this manuscript.

Ethics Statement

Not Applicable.

Ethics and Consent to Participate Declaration

Not Applicable.

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Conflicts of Interest

The authors declare no conflicts of interest.

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