JCRS Journal of Chemical Reactivity and Synthesis 2024: 14(2) 127-149

Research Article

Adsorption of organic pollutants by metal–organic frameworks

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ARTICLE INFO:

Received:
9 February 2025

Accepted:
10 April 2025

Available online:
12 April 2025

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ABSTRACT

This review evaluates the effectiveness of metal–organic frameworks (MOFs) in adsorption organic pollution. MOFs are highly effective in dye effluent removal due to their multifunctionality, water stability, and recyclability. They offer exceptional dye removal and degradation capabilities, with significant surface area and adjustable pore size. Among various dye removal techniques (chemical, physical, and biological), adsorption has emerged as a cost-effective and highly efficient method. Characterization studies confirm the effectiveness of MOFs. Conventional adsorbents fall short of industrial dye removal, thus making MOFs a promising alternative. This review assesses MOFs' efficacy in treating dyewastewater, highlighting their superior adsorption capacity over conventional materials. Research into inexpensive and efficient adsorbents from available resources for colour removal is increasingly vital. Studies demonstrate the efficacy of numerous affordable adsorbents in colour removal.

Keywords: Metal-organic frameworks; Adsorption; Organic pollutants; Mechanism

1. Introduction

Metal-Organic Frameworks (MOFs) have emerged as highly effective materials for the removal of organic pollutants from wastewater. Their unique structural properties, including high surface area, tunable pore sizes, and multifunctionality, enable them to outperform conventional adsorbents in various applications.MOFs primarily function through adsorption mechanisms, where pollutants are captured within their porous structures. This process is influenced by the characteristics of both the MOFs and the contaminants. For instance, studies have shown that acid-base interactions play a significant role in the removal efficiency of certain pollutants, such as acids and organic dyes Groundwater sources and external water decay by organic contaminants such as organic dyes, antibiotics, heavy metal ions, and pesticides have become a severe environmental issue. Manufactured dyes have a complex structure and are coloring agents that are nonbiodegradable with heightened resilience[1]. Additionally, organic dyes are broadly utilized for dyeing a variety of products such as leather, textiles, medicine, and plastics[2]. Fabric industries eliminate large quantities of polluted wastewater that possess organic dyes[3]. Coloring reagents are one of the recognized types of water pollutants that should be extracted from wastewater prior to release within aquatic techniques[4,5].Actually, a concentration of 1.0 mg/L provides sufficient coloration and can be unsuitable for consumption by human beings and also contaminate water bodies. There are vast concerns related to the contamination of water by dyes as a kind of organic contaminant due to their persistence and coloration results[6].

Industrial wastewater, such as fabric wastewater, is of primary consideration as this enterprise delivers enormous quantities of wastewater with an intense spectrum of chemical interpretations[7]. In the coloring, printing, and finishing techniques, 10–50% failure of dyes from reactive pigments to the atmosphere is expected due to procedure inadequacy. Unfortunately, all of these contaminants cannot be removed entirely or degraded by traditional wastewater processing manufacturers within the atmosphere due to their continuous character in H_2O and higher potency to rays, temperature, chemicals, and microbes-based invasion[8,9].MOF is a unique three-dimensional (3D) organic–inorganic composite with extremely porous nanostructures containing metal ions/groups and organic linkers[10].

MOF has been carefully studied for several decades and has evolved as one of the magnetic materials for scientists and inventors because of promising components with tunable pore networks, adequate adsorption places, etc. The studies have also shown an in-depth investigation of MOF materials in previous decades, demonstrating their exceptional performance within catalysis[11,12],adsorption, [13,14] and water harvesting[15].

However, conventional catalysts and adsorbents such as activated carbons, clay minerals, zeolites, etc., have poor adsorption and pollutant removal capacity as compared to those of MOF-based NMs[16,17].Investigators have begun to manage the resilience of MOFs within diverse conditions, to comprehend the potential decay pathways, and to endeavor to create more durable framework networks[18].

The strength of MOFs may be influenced by numerous aspects, such as the working atmosphere, metal ions, organic ligands, metal–ligand organization geometry, hydrophobicity of the aperture texture, etc[19,20].Investigations on the durability of MOFs have permitted us to explain the impact of some aspects and judiciously prepare sturdy framework networks. The somewhat labile coordination binds, which sustain the framework systems, are considered liable for the little resilience of MOFs[21].

Therefore, a steady MOF system should have robust coordination binds to endure the invasion of guest molecules or have steric hindrances to control the intrusion of guests into the metal nodes.MOFs have drawn considerable concentration because of their increased porosity, designable pores, and easy preparation. Some fascinating MOFs are available, including isostructural, isoreticular, isomorphous, or similar types. MOFs with identical crystal systems may be comprised of various metal ions (or groups) and linkers[22].This

Review focused on the synthesis process (such as the traditional, electrochemical, microwave, sonochemical, mechanochemical, and continuous-flow spray-drying methods) of MOF materials.

2. Synthesis of the Metal–Organic Framework

Due to their certain functional and structural properties, MOFs have been presently perceived as an extensive collection of porous compounds. These frameworks are formed by connecting organic linkers and metal ion clusters/metal ions. Beyond question, another perception remarkably associated with MOFs conclusive design and properties is the chosen essential structural blocks known as secondary building units (SBUs)[23].However, various other synthetic approaches and variables like pressure, temperature, pH, time of reaction and solvent should also be scrutinized. Various distinctive synthetic routes viz. hydrothermal/solvothermal, diffusion, electrochemical, mechanochemical, microwave assisted heating and ultrasound can be used to construct MOFs trusting on the subsequent structures and features[24,25].

2.1. Conventional Method

Solvothermal and non-solvothermal methods are included in conventional methods. In the solvothermal method, MOFs are developed in sealednuclear magnetic resonance (NMR) tubes or in vials through conventional electric heating in small intervals.The term“solvo” indicates the solvents, such as ethanol, methanol,formamides, acetones, and water. This method is used by Huang et al[26]. to fabricate Cu3(benzene tricarboxylic acid)2($Cu_3(BTC)_2$) and Cu(benzene dicarboxylic acid) (Cu(BDC))MOFs for the treatment of phenol wastewater. Underneath the identical circumstances, the Cu(BDC) exhibited a higher catalytic performance as compared to that of the $Cu_3(BTC)_2$, which was primarily ascribed to the unique design of the Cu(BDC), directing accessible entry within the holes for the organics. The prepared Cu(BDC) showed a solid capability to adjust to the imitation phenol wastewater of distinct concentrations. Thus, Cu-MOFs would promise heterogeneous catalysts for the catalytic wet peroxide oxidation of organic effluents. Two types of mixtures were prepared, first with 1.94 g of Cu^{2+} nitrate trihydrate mixed in 30 mL of deionized water, and second with 0.84 g of 1,3,5-benzene- tricarboxylic mixed in 15 mL of ethanol and dimethylforma-mide (DMF) each. Both of the solutions are mixed together with stirring until the suspension becomes homogeneous. The obtained solution was then transferred to an autoclave that was sealed and heated to 110 °C. Deep blue crystals were obtained after the reaction was cooled at room temperature. The authors observed a phenol conversion efficiency of 99% Despite numerous benefits, time and temperature must be regulated tightly in the solvothermal approach. For instance,the difference in temperature can influence the particle morphology, and the reaction time extension may direct MOF degradation[27]. Nonsolvothermal techniques are simpler than solvothermal for the synthesis of MOFs. Mechanical, nanoprecipitation, and emulsion are the methods that are involved in a non- solvothermal approach for the fast growth of MOF_s[28].In this strategy, complex equipment is not required; below theboiling point temperature of the solvent, and at atmospheric pressure, MOFs can be fabricated in an open vessel. Modification of pH and temperature is concerned with obtaining the maximum yield of the MOF material. For instance, to synthesize MOF-74 (Zn), Zhang et al[29].carried out an adapted method without the utilization of microwave/ultrasonic treatment, and no extra pressure was provided to the system. In brief, 239 mg of 2,5-dihydroxy terephthalic acid and 686 mg of Zn $(OAc)_2{\cdot}2H2O$ were dissolved in dimethylforma-mide (20 mL). The obtained solution was then added to the salt solution with constant stirring for 18 h at room temperature to produce MOF-74 (Zn). The MOF-74 (Zn) was dried in air and evacuated at 270 °C. Finally, MOF-74 (Zn) was added to 1.14 mL of ethylenediamine and toluene solution, which was dried in air to yield ammoniated MOF-74 (Zn). Ammoniated MOF-74(Zn) byproducts are a lumines- cent sensor for selective tetrabromobisphenol A (TBBPA) detection. The fluorescence enhancement delivered an excellent linear association with the concentrations of TBBPA in the capacity of 50–400 μg/L, and its detection limit could reach 0.75 μg/L. However, traditional methods of MOFs synthesis yield a fine powder, so they are not commercially applicable to much extent.

2.2. Electrochemical Method

The method is used for the synthesis of MOF powders on an industrial scale. The metal ion is provided by anodic dissolution into reaction mixtures that contain the organic ligands and electrolytes. The major advantages of this method are the slighter temperatures of reaction and extremely quick synthesis under milder conditions, compared to solvothermal method. Several MOFs, such as HKUST-1, ZIF-8, MIL-100(Al), MIL-53(Al), and NH_2-MIL-53(Al), have been synthesized by this method in an electrochemical cell, and the influence of several reaction parameters on their yield and texture properties have been investigated [30].

2.3. Microwave-Assisted Method

The method is often used for the synthesis of organic and nanoporous inorganic materials . More recently, the method was used for the synthesis of metal clusters and MOFs . The advantages of the method are the short reaction time required, the high yield, and the low cost. The microwave-assisted synthesis of HKUST-1 with formula $[Cu_3(BTC)_2(H_2O)_3]$ (BTC^{3-} = 1,3,5-benzenetricarboxylate) gave crystals with improved yield and physical properties, requiring a much shorter reaction time, with respect to its conventional hydrothermal synthesis [31]. Despite the fact that the specific technique cannot produce crystals, the microwaves facilitate the motion of the molecules, leading to nucleation and formation of crystals with a controlled shape and size by appropriately adjusting the concentration and the temperature of the reaction [32].

2.4. Sonochemical Method

Sonochemistry deals with the chemical transformations of molecules under high-energy ultrasonic radiation (20 kHz–10 MHz). The bubbles formed when a reaction solution is irradiated with ultrasound radiation create local hot spots of a short lifetime with a high temperature and pressure, which promote chemical reactions and immediate formation of crystallization nuclei [33]. High quality crystals of MOF-5 and MOF-177 with a size of 5–25 μm and 5–20 μm, respectively, were prepared via the sono-chemical method in the presence of 1-methyl-2-pyrrolidone as a solvent, in a substantially reduced reaction time [34].

2.5. Mechanochemical Method

The method uses mechanical forces, instead of using a solvent, at room temperature, to form coordination bonds by either manual grinding of the reagents or more often in automatic ball mills. In some cases, a small amount of solvent may be added into the solid reaction mixture and succeeded to obtain one-dimensional, two-dimensional, and three-dimensional coordination polymers [35]. The mechanochemical method facilitates mass transfer, reduces particle size, heats, and locally melts the reagents, thus, accelerating the reaction time. It constitutes an environmentally-friendly green chemistry method, which produces materials of high purity and high efficiency at short reaction times [36]. The application of mechanical chemistry to the synthesis of MOFs is additionally attractive because it is an alternative to the high temperature and pressure solvo(hydro)thermal synthesis. The biggest disadvantage of the method is the isolation of amorphous products, unsuitable for single-crystal X-ray structural studies.

2.6. Continuous-Flow Spray-Drying Method

For the production of MOFs on a large scale for the industrial exploitation and continuous synthesis of MOFs in the form of NPs, composites, and spherical structures, the continuous-flow spray-drying technique attracted much attention due to its cost-effectiveness and environmentally friendly process[37]. This technique is a combination of both spray-drying and continuous-flow techniques. Several members of the MOFs family involving UiO-66 and Fe-BTC/MIL-100 were synthe- sized by Garzó n-Tovar et al.91 Briefly, they introduced a continuous-flow reactor at the nozzle of the spray dryer. Initially, in a continuous flow reactor, the precursor solution was injected, which contains metal salt and organic linker, and it was heated to a temperature that promotes nucleation. The outlet of the flow reactor was directly connected to the entrance of the spray dryer; the solution was automatically injected into the spray dryer. Here, the growth of the MOFs was confined to the atomized droplets and collected as micro spherical beads. In addition, the utilized solvent could be recovered, making the process cost-effective and waste- efficient. UiO-66-NH2 and Zr-fumarate beads were synthesized by Avci-Camur et al[38].Briefly, a mixture of 2-amino-terephthalic acid with H2O and CH3COOH in an equimolar ratio with ZrOCl2·8H2O was inserted into the coil-flow reactor and placed in a silicone bath. The resulting yellow-colored slurry was spray-dried, and the beads were collected and dried at 75 °C. The surface area of UiO-66-NH2 was 840 m2/g. This synthesis method is integrated as a green approach in many industrial sectors for the continuous one-step preparation of MOF beads.

3. Properties of the Metal–Organic Frameworks

The adsorptive and catalytic properties of the MOF-based materials have great potential in drug delivery[39,40]. lumines-cence,95,96 sensing and degradation,[41], and in the removal of toxic pollutants from wastewater. They possess tunable pore sizes, outstanding thermo-chemical stability, and large amounts of surface area. We briefly explain the adsorptive and catalytic properties of MOF-based materials in separation, sensing, and environmental remediation. Figure 1 shows the proposed properties of the MOFs

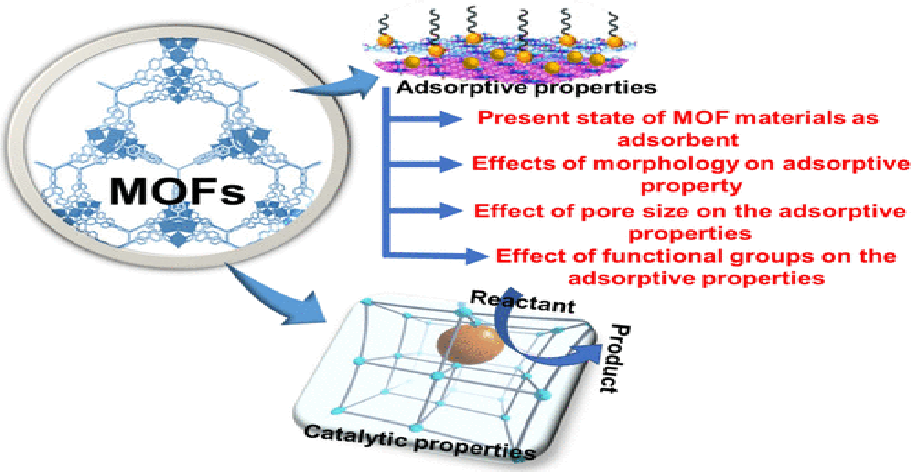

Fig. 1. Properties of the MOFs materials.

3.1. Adsorptive Properties

Adsorptive elimination of poisonous contaminants from wastewater is considered to beone of the most challenging and outstanding research areas toward the protection of the environment and management of water due to cost-effectiveness, user and eco-friendly synthesis, waste, and industrial rivulets have been supposed to produce low-price adsorbents. In contrast, adsorbents with extraordi- nary capability or selectivity have also been developed. MOFs are classified as engineering materials with porous organic networks that make them unique with extraordinary perform- ance as nonconventional adsorbents.

3.1.1 Effects of Morphology on the Adsorptive Property

It is clearly understood that the structural morphology and orientation could significantly impact the performance of MOFs as adsorptive materials. In regard to this, Oliver et al[42].showed the effect of high order structurization on the adsorptive characteristics of MOFs. Significantly, from an essential viewpoint, the high order structurization of MOFs delivers the option for unique effects to occur that are self- sustaining of the molecular arrangement and system configuration of the MOF. In the molecular range, the modular manufactured process authorizes the metal and organic ingredients to be rationally chosen, such that their positions are comprised into the resultant framework. It permits parameters, for example, the chemical functionalities and pore dimensions, to be finely adjusted according to the chosen substance characteristics. On the nanoscale, the characteristics of particular crystals are managed, for example, crystal dimensions and morphology that may show benefits, such as the adsorption kinetics. Individual crystals may be employed as assembling unions to make big groups at the mesoscale, directing refined architectures, for example, hollow spheres, thin layers, and monolithic designs. Ultimately, structuralization on the macroscale delivers ways to shape the MOF designs into the preferred structure. These scales provide many fascinating possibilities to increase the adsorptive effects of MOF techniques for the mesoscale and nanoscale structuralization of MOF[43].

3. 1. 2.Effect of Pore Size on the Adsorptive Properties

The pore size and geometry of the MOF-based materials are crucial for the adsorptive removal of dyes. Because of their higher surface area, porous MOFs can absorb more significant quantities of dyes than can nonporous MOFs. Flexible or adjustable design results in several MOF frameworks with multiple pore sizes, dimensions, and geometries. An exhaustive review by Cai et al[44].provides insights into this aspect, where they considered composites and MOF derivatives to explain the effects of mesopores on the microporous structures. For instance, MOFs such as IRMOF-01 and PCN-222 have square grid channels, while PCN-224 and MOF-74 have hexagonal channels[45,46]. If the pore size of the MOF-based composites is larger than the size of the dye molecules, then a considerable amount of dye can be adsorbed on the surface of the MOF. However, if the size of the molecules of dyes is more significant as compared to the MOF frameworks, then the adsorption of dye molecules is ruled out within the pores of MOF[47]Also, Cui et al[48]. reported the regime upon the pore chemistry and size within metal coordination systems with hexafluoro silicate and organic linkers toward preferential binding, as well as the tidy group of acetylene molecules via combined host−guest and guest−guest relations. The significance of these binding relations affords high adsorption ability and selectivity for acetylene at room temperature. Experimental breakthrough curves exhibit their efficiency in separating acetylene/ethylene combinations.

3.1.3. Effect of Functional Groups on the Adsorptive Properties

The adherence of adsorbates is promoted by particular functional groups present in MOF-based materials, such as amino groups interacting with acidic dyes and sulfonic acid interacting with basic dyes and pore geometries of porous MOFs[49]. Dyes can facilely be degraded via the oxidation process. The Fenton advanced oxidation process is considered a potential method for removing dyes.115 Li et al[50]. fabricated magnetic porous Fe3O4/carbon octahedra via two-step calcination of Fe- based MOF to eliminate methylene blue. Within 1 h, this material shows 100% removal efficiency in the presence of H_2O_2 by a Fenton-like heterogeneous reaction.

4. Mechanism of MOF-Based Materials in the Removal of Pollutants from Water

The mechanism of the removal of toxic elements utilizing MOFs most commonly uses π−π interactions, ion exchange, H-bonding, acid−base interactions, and electrostatic inter-Actions[51]. Electrostatic interactions are crucial in adsorption processes between surface charges on pollutants (adsorbates) and oppositely charged MOFs (adsorbents). Net surface charges lead to protonation and deprotonation, which favors the electrostatic interactions between the MOFs and pollutants. Further, the interactions between hydrogen atoms in N−H, F−H, and O−H bonds and lone pairs of electronegative atoms are known as H-bonding. Studies have revealed that MOFs contain −OH groups and make H-bonds with adsorbates. Acid−base interactions are other mechanisms for the adsorptive removal of MOFs. For instance, removal naproxen and clofibric acids from an aqueous solution using MIL-101 functionalized with acidic (−SO3H) and basic (−NH2) groups. The results revealed that acid−base interactions were dominant and performed better for eliminating acids than did bare MIL-101. Adsorptive mechanisms of MOFs in removing contaminants from wastewater are described in Figure 2. Relatively higher surface areas of MOFs facilitate the adsorption of pollutants. Adsorption capacity depends on the characteristics of MOFs as well as on the contaminants. The dominant interactions significantly influence the adsorption mechanism. Therefore, the actual adsorption mechanism is complex, and further investigations are required for exact predictions. In the adsorption mechanism, toxic pollutants only transfer to the surface of MOFs, and their desorption may result in secondary contaminants [52]. Therefore, for the degradation of pollutants from wastewater, catalysts, oxidizing agents, and some reactants are utilized by sewage treatment plants and factories. [53]. Over the past few years, MOFs have attracted much attention for degrading contaminants from wastewater. n catalytic processes, MOFs are combined with highly reactive species such as sulfate radicals (SO_4•−) and hydrogen peroxide (H_2O_2) to promote the oxidation of pollutants into less toxic products. NbCo-MOF was synthesized to remove tetracycline from wastewater via SO_4•− oxidation. The catalytic mechanism of the removal of tetracycline is shown in Figure 2. The observed removal efficiency was 99.7% within 30 min. Because of the unique structures of MOFs, closer contacts are provided between pollutants and active sites of MOFs, which enhance the reactions between them. MOFs have several advantages, such as high flexibility, highly selective and relatively higher degradation due to rational design, and different pore structures over other catalysts.

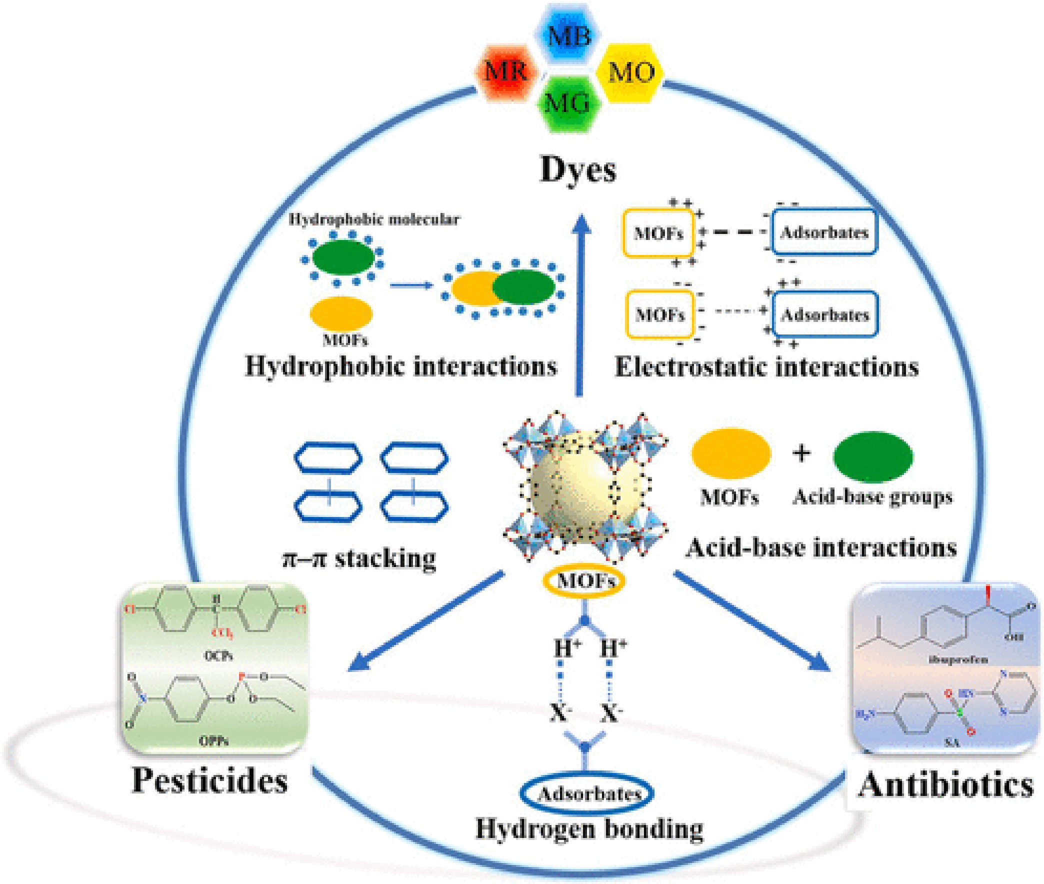

Fig. 2. Adsorptive mechanisms of MOFs in removing contaminants

5. Application of Metal–Organic Framework for Removal of Organic Dyes

MOFs can be applied to pollutant purification, including organic dyes, as one of the primary sources of water contamination. Some characteristics of MOFs make them appropriate materials for dye adsorption from wastewater with preferable performance over other conventional adsorbents [54]. These characteristics include crystalline, porous structure, large surface area, multifunctional capabilities, structural diversity, flexible structure, and very active sites for dye adsorption [55,56].The porosity of the MOF structure improves the adsorption of pollutants into adsorption sites and facilitates the saturation of adsorption [57]. MOFs are superior materials for water treatment as their structural ligands provide a high density of adsorption sites and their ultrahigh porosity improves the extraction of pollutants from contaminant sources [58] The mechanisms of dye adsorption by MOFs are similar to other adsorbents, except that the presence of ligand functional groups and the presence of metal ions or metal clusters in the structure of MOFs in some cases cause two or several interactions between dye and MOF, and performance improvements in the adsorption processes. The most common interaction is the electrostatic interaction that occurs between two species with different surface charges. The electrostatic interaction is observable between a wide range of dyes and MOFs [59,60].The π–π interaction is usually observed in the removal of compounds containing aromatic rings. Dyes such as MG, MO, and CR, which contain multiple aromatic rings, can interact with MOFs that have aromatic rings in their structure [61,62].Hydrogen bonding is also observed between dyes and MOFs that can bond between hydrogen atoms and electronegative atoms. Adding functional groups such as NH_2 to the structure of MOFs can create and improve the hydrogen bonding between dye and MOF [63,64].

6. Conclusion and Future Prospects

Metal–organic frameworks with superior advantages over other conventional sor- bents in removing dyes from the aquatic environment have attracted much attention in recent years. Extensive structural diversity, the possibility of using different structures with different metal clusters and/or organic linkers according to the purpose, is one of the most important characteristics of MOFs in the field of wastewater treatment, which distinguishes them from other adsorbents. MIL-type MOF structures with adjustable properties for selective adsorption, ZIF structures with high surface area and high adsorption capacity, and zirconium-based MOFs with excellent stability in aqueous and acidic environments are categorized as the most studied structures in dye removal applications. The removal of various dyes such as methylene blue, methyl orange, Congo red, acid orange 7, malachite green, acid chrome blue K, acid red 1, orange G, methyl red, basic blue 41, rhodamine B, neutral red, fuchsin basic, safranine T, alizarin red S, eosin, fuchsin acid, reactive black 5, xylene orange, fluorescein sodium, and sunset yellow have been studied using MOF-based sorbents. The existence of some challenges such as stability in aqueous and acidic environments, reusability, and improvement of adsorption performance through increasing the adsorption capacity has led researchers to modify and structurally improve metal–organic frameworks. Synthesis of magnetic MOF-based composites for easy recycling and reuse, introduction of amine functional groups, and preparation of graphene–MOF composites to increase the adsorption capacity and improve the stability of the framework in the aqueous medium are some of the proposed and applied solutions to address the above-mentioned challenges. Amine-functionalized MOF structures aim to increase the adsorption capacity by creating and improving hydrogen bonds and electrostatic interactions between the dye molecules and the adsorbent framework. Use of graphene–MOF composites also aims to increase the adsorption capacity by improving electrostatic and π–π interactions. These composites also have high thermal stability due to their sandwich-shaped structures and the presence of graphene in the structure.

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