



Removal Methods of Pesticides and Their Improvement Using Metal-Organic Frameworks

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Abstract

The safety of the environment is a major global concern that has grabbed the attention of many researchers. Multiple variables can lead to food and water contamination. Pesticide is one of the hazardous variables that pollute water and affect negatively living organisms. Therefore, pesticide disposal is a big challenge. There are various treatment methods, such as biological, chemical, and physical methods used to remove pesticides. Metal-organic frameworks (MOFs) are hybrid materials, which composed of organic and inorganic units. They are widely utilized for wastewater remediation. This review sheds light on the different types of pesticides and the various techniques used in removing pesticides including biological, chemical, and physical treatments. Furthermore, the definition and the most common stable MOFs are also discussed. Thus, the advantages and disadvantages of using MOFs in wastewater treatment are explained in this article. The synthetic procedure for the preparation of MOFs is illuminated in this review as well. Food safety has become a challenge. The applications of MOFs as sensors and as stationary phase extraction for the detection and removal of pesticides are intensively debated. Finally, this study gives insight on MOFs composites that utilized for pesticides removal and water purification.

Keywords: pesticide, removal, biological, chemical, adsorption, MOFs sensor, extraction

Abbreviations; (AOPs) = Advanced Oxidation Processes; (MOFs) =Metal-organic frameworks; DDT= dichlorodiphenyltrichloroethane; EPA = Environmental Protection Agency; EDB= ethylene dibromide; AFB = anaerobic fluidized bed; AF = anaerobic filter; UASB = up flow anaerobic sludge blanket; SCOD = soluble chemical oxygen demand; MBR = membrane bioreactor; HRT = hydraulic retention time; PCNB = pentachloronitrobenzene; WWTP = wastewater treatment plants; AOPs = advanced oxidation process; AC = Activated carbon; MW = Microwave irradiation; EC=Electrochemical synthesis; ECL = Electrochemiluminescence; SPME = solid-phase microextraction; UiO = University of Oslo; GC-FID = gas chromatography-flame ionization detector; MCPP = methylchlorophenoxypropionic acid; BET =

Brunauer-Emmett-Teller; MWCNT=multi-walled carbon nanotube; GO = Graphine oxide.

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1. Introduction

Environmental pollution is gradually increasing, causing a negative impact on ecosystems, biodiversity and living organisms including humans by polluting soil, air, and water worldwide [1,2]. Water is a precious and indispensable resource for life on Earth. Water pollution affects all life on Earth [3]. Water pollution with harmful substances leads to a decrease in water quality [4]. Recently, fertilizers and pesticides have been widely used to improve food quality, crop productivity and protection [5]. Pesticides are chemical or natural substances used to control or kill weeds and harmful pests that cause plant diseases [6]. About 4.1 million tons of pesticides were used in the world in 2016 [7]. Pesticides have disadvantages including their toxicity to humans, beneficial plants, animals, and aquatic ecosystems and their long persistence in the environment, causing risks to both the environment and public health [8]. Exposure to pesticides causes human serious diseases such as asthma, allergies, blood diseases, immune system damage, liver damage, leukemia, brain cancer, ovarian cancer, endocrine disorder, etc [9,10]. Pesticides must be removed from the environment and water to eliminate their negative effects on human health, living organisms, and food quality.

There are techniques such as biological, chemical, and physical methods for treating water from pesticides [11]. The biological process is characterized by the biodegradation of organic pollutants into less harmful substances such as methane, carbon dioxide and water [12]. Photodegradation, chemical and microbial processes can be used to degrade pesticides in the environment

[13]. Advanced Oxidation Processes (AOPs) are chemical techniques for pesticide removal that use oxidant agents (as hydroxyl radicals) to oxidize contaminants. AOPs degrade organic pollutants into harmless products. In general, AOPs are categorised into ultraviolet (UV)-based treatment, ozone-based treatment, photo advanced oxidation processes (pAOP), catalytic advanced oxidation processes (cAOP), and electrochemical advanced oxidation processes (eAOP) [11]. Thus, removing pesticides from water becomes a challenge. Adsorption is used to extract biological, soluble and insoluble pollutants with adsorption efficiency of up to 90-99% [14]. Adsorption is widely used among these methods due to its ease of operation, no sludge formation, simplicity, versatility, and harmless by-product. The efficiency of adsorption is based on the possible interactions with pollutants, surface area, available sites, and porosity [11, 15].

Metal-organic frameworks (MOFs), also known as porous coordination polymers, were composed of organic linkers and metal ions [16]. Due to their exceptional porosity, high surface area, and stable framework, MOFs have been applied in various applications including catalysts, sensors, drug-delivery agents, storage, separation systems and others [17]. MOFs have been used as sensors to detect nutritional risk factors, such as pesticide residues, mycotoxins, veterinary drugs, illegal additives, pathogens, heavy metals, and food additives. Where the conventional methods used to assess food safety, such as chemical and chromatography methods, have some limitations including requiring expensive equipments, skilled laboratory personal, and time consuming. Therefore, MOFs have been applied as sensors, including surface enhanced Raman scattering (SERS), colorimetric, electrochemical, luminescent, electrochemiluminescence sensors and etc, to overcome the limitations of conventional methods [18].

The unique features and structure of MOFs make them very attractive materials for various applications including sorbents for sampling, stir bar sorptive extraction, magnetic solid-phase extraction, solid-phase microextraction, and stationary phases for chromatography [19]. MOFs have been used for the adsorption removal of hazardous compounds from water. Due to their excellent properties, MOF

matrices can effectively remove hazardous compounds from aqueous solutions [20]. Common MOFs, such as ZIF-8 (Zn), ZIF-67 (Co), MIL-53 (Cr) and MIL101 (Cr), Cu-BTC, UiO-67 (Zr), UiO-67(Zr)/GO, have efficiently removed pesticides from aqueous solutions [21].

Here, the nature of pesticides and their harmful effect on the environment and living organisms are discussed. Removal of pesticides in different methods such as biological, chemical, and physical treatments is reported. Definition, preparation, properties, and applications of MOFs are described. The applications of MOFs for the detection, extraction, and adsorption of pesticides are also discussed.

2. Pesticides

2.1. Environmental Issue of Pesticides

Organisms that have a negative impact on humans and the environment are called pests. Pests are animals, insects, fungi, and bacteria. They attack humans, animals, and plants and can carry diseases. In agriculture, pests attack crops, both in the field and during storage, infecting or dying plants. Therefore, pests affect the production or growth of crops by losing or reducing the amount of the crop. The level of damage to agricultural products caused by pests is high. [22] So, the harmful pests must be controlled to protect the plants. Biological, chemical, and physical methods are used to control pests. The chemical and biological quality of the soil may be compromised by the use of chemical or physical treatment techniques [23].

Pesticides are chemicals, natural or synthetic, that is used to target and eliminate harmful organisms. The reduction or completely elimination of weeds, pests, and diseases is the goal of using pesticides [24]. These pollutants have a negative impact on soil properties and enter food chains, leading to risks to human health [23]. Pesticide cause critical toxic effects and remain for a long time. The ecological balance is disturbed by killing unharmed insects, fishes, and animals. The pests have also modified their genes by creating resistance against these pesticides [25]. Additionally, pesticides have negative effect on the environment. Soil, water and air have been contaminated with pesticides to toxic levels. Water contaminated with pesticides poses a threat to aquatic life and ecosystems. Pesticides are toxic to natural plants, neutral animals and aquatic life. Bioaccumulation occurs due to prolonged use of pesticides. Pesticides have serious effects on plant

and animal biodiversity [9]. Pesticide poisoning cases are recorded every year. DDT (dichlorodiphenyltrichloroethan) was used as a chemical in agriculture but was banned in 1962 due to its harmful effect. Also, the Environmental Protection Agency (EPA) banned the use of EDB (ethylene dibromide) in 1983 due to its carcinogenic and mutagenic effects [25]. The effect of pesticides may be acute or chronic on human health. Immediate effect of pesticide exposure involve dizziness, headache, nausea, diarrhoea, abdominal pain, stinging of the skin and eyes, vomiting, irritation of the throat and nose, blurred vision, skin itching, blindness, blisters on the skin, appearance of the rash and rarely death. long exposure to pesticides causes serious diseases including brain cancer, asthma, allergies, leukaemia, hypersensitivity, lymphoma, etc. Fetuses and children are especially vulnerable to pesticide exposure [9]. Neurological and neuropsychiatric effects have been on adults who exposed to high rates of pesticides. Behavioural problems of children related to organophosphates [26].

2.2. Classification of pesticides

Pesticides are classified into the mode of entry, target pest species, and their chemical composition. Based on the mode of entry, the pesticides are classified into fumigants, repellents, stomach poisons, systemic and contact pesticides. Based on target pest species, pesticides are classified into insecticides, herbicides, fungicides, Bactericides, Acaricides, Larvicides, etc. The class names of these pesticides consist of the Latin word *cide* (meaning killer) after the name of the target pest species. The physical and chemical properties of pesticides differ from one category to another. Therefore, pesticides are classified based on their chemical structure and active ingredients nature. This common classification gives information about the chemical and physical properties and efficacy of the respective pesticide. pesticides are classified based on their chemical composition into main classes, organochlorine, carbamate, organicphosphorous, pyrethrin, and pyrethroid (Figure 1) [27].

Organochlorine acts as an obstruction of the nervous system, leading to paralysis, convulsions, and death. It has a long-term residual impact in the environment and resists most degradation processes. Lindane, DDT (dichlorodiphenyltrichloroethan), and endosulfan are exmples on organochlorine pesticides.

Carbamate (carbofuran, carbaryl, and propoxur) acts as inhibitor of cholinesterase. It is not persistent in the environment and is subject to biodegradation. Organophosphorous, such as malathion, parathion, and diazinon, act as inhibitors of cholinesterase causing a perpetual overlay of the neurotransmitter acetylcholine across the synapse resulting in paralysis and death. Pyrethrins (natural), Pyrethroids (synthetic) work by disrupting the nervous system of an insect, resulting in a weak condition followed by death. It is not persistent in the environment, and is subject to biodegradation. Pyrethroids are such as cpermethrin, deltamethrin, and permethrin [28].

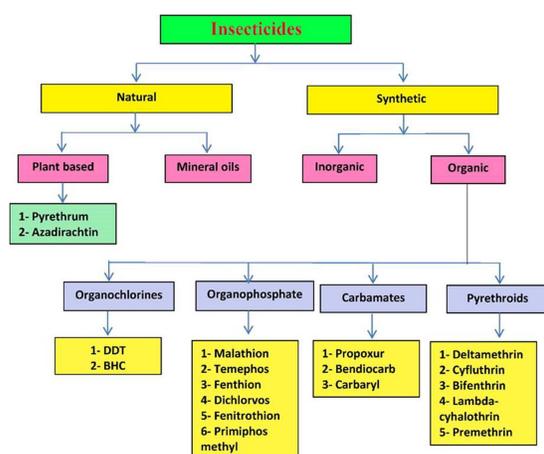


Figure 1: Classification of insecticides [27]

2.3. Removal techniques of pesticides

Pesticides have a lethal nature, and it is difficult to reduce them because pesticides have qualities such as water solubility, heat stability, and polarity. The pesticide residues remain in water and the environment for a long time. The ecological balance is disturbed by killing harmless insects, animals and fish and pests modify their genes for pesticide resistance [9,10]. Methods of removing pesticides from water are one of the necessary research projects to get rid of their harmful effects. Methods of treating water from pesticides such as chemical, physical and biological treatment techniques. Chemical methods such as oxidation, precipitation, coagulation, flocculation and hydrolysis are used to remove pesticides from wastewater. Physical methods such as distillation, filtration, and sedimentation are used to remove pesticides from wastewater. Biological

methods such as activated sludge, extended aeration, anaerobic process, and rotating biological contractors are used to remove pesticides from wastewater (Figure 2). Each treatment method has its benefits and drawbacks in terms of reliability, pre-treatment requirements, environmental impact, operational and capital costs, efficiency, the production of sludge, operability, and production of toxic by-products [11].

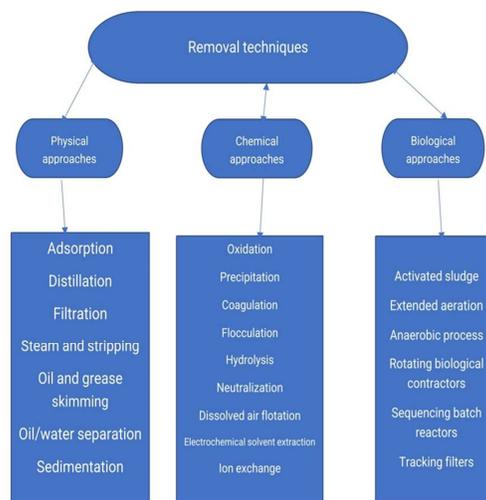


Figure 2: Different biological, chemical, and physical treatment methods

2.3.1. Biological treatment

Biological treatment is another technique used to remove pesticides from water and wastewater. The biological process is characterized by biodegradation. This process converts organic pollutants into less harmful substances such as CO_2 , and H_2O . Basically, there are three types of biological treatment with microorganisms: bioaugmentation, natural attenuation, and biostimulation. Bioremediation can use strains of fungi and bacteria that degrade the pesticide [12]. Biological treatment is classified into aerobic and anaerobic treatment. The combination of aerobic and anaerobic condition increases the uptake efficiency. A combination of aerobic and anaerobic conditions is an effective strategy for the removal of pesticides [11]. Aerobic processes including rotating biological, lagoons, activated sludge, trickling filter, and contactor are able to remove organics. Anaerobic processes including anaerobic fluidized bed (AFB) reactor, anaerobic filter (AF), and up flow anaerobic

sludge blanket (UASB) reactor can remove organics at high rate (80–90%) and produce biogas [29].

The biodegradation of methyl parathion using *P. Decaturense* CBMAI 1234 and *A. Sydowii* CBMAI 935 was studied. *A. Sydowii* CBMAI 935 and *P. Decaturense* CBMAI 1234 were able to degrade pesticides in 20 day and 30 day, respectively [13]. In another study, Atrazine was removed from aqueous solutions by submerged biological aerated filter. Microbial consortium was able to degrade atrazine in the aquatic environment. The results indicated that and soluble chemical oxygen demand (SCOD) and the highest efficiencies removal for atrazine were 98.9% and 97.9%, respectively [30]. A membrane bioreactor (MBR) was used to remove Ametryn, a moderately persistent s-triazine herbicide. Within 15 h (hydraulic retention time (HRT)), MBR showed 65% removal of Ametryn from its influent at the concentration of 1–2 mg/L. The biodegradation process achieved 99%, 92% and 83% removal of Ametryn if the MBR maintained a HRT of 7.5, 2.5 and 1.5 days respectively [31]. Furthermore, the cooperative degradation capacities of *Variovorax* sp. Strain SRS16 as mineralizing organism for linuron and *Arthrobacter globiformis* strain D47 as degrading organism for diuron were combined to construct two-member consortium that could mineralize linuron and diuron (Figure 3). The results indicated that the consortium composed of strains D47 and SRS16 could remediate water and soil contaminated with lenuron and diuron [32].

Although the bioremediation process is most widely used for low cost and efficiency, it depends on various factors, such as temperature, soil moisture content, nutrient availability, oxygen level, and pH [12]. It is noteworthy that microorganisms cannot always get rid of pesticides because of their low water solubility, recalcitrance, or toxicity [33]. Sometimes, pre-treatments are required as the breakdown of some pesticides by enzymatic reactions or photochemical degradation might ease their biological digestion [11]. Coupling of heterogeneous photocatalysis and aerobic biological process was used to treat wastewater containing chlorpyrifos. The degradation values, mineralization for the biological process after the photocatalysis treatment increased to 88.24%, 67.78%, respectively [34].

Biosorption is the adhesion of pollutants to the cell wall without the need for oxidation of aerobic or anaerobic metabolism. Both live and dead biomass

can be used as bio-sorbents in pesticides removal. Bio-sorbents are microbial biomass such as bacteria, fungi, yeast, algae, seaweed, and wastes from agriculture wastes, industries wastes and by-products such as fermentation residues, activated sludge and food waste. However, it is difficult to keep the live biomass viable during the process because it needs nutrients constantly and pesticides are toxic to it. Using dead biomass is more cost-effective because it does not require a nutrient supply. The use of dead biomass in the column faces problems such as the difficulty of separating the biomass after adsorption and mass loss after regeneration. These problems can be solved by immobilizing of biomass, but this leads to an increase in cost and immobilization negatively affects transfer kinetics of mass and pollutants removal [35].

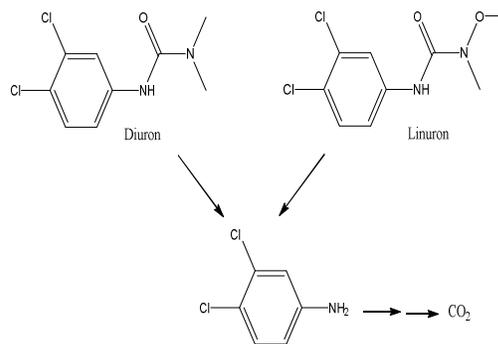


Figure 3: diuron and linuron -mineralizing two-member consortium [32]

Lièvrement et al. used fungal mycelia to remove pentachloronitrobenzene (PCNB) from aqueous solutions. Dead biomass and cell walls of *Sporothrix cyanescens*, *Rhizopus arrhizus*, and *Mucor racemosus* were used for PCNB adsorption. The amount of PCNB adsorbed on dead biomass of *S. cyanescens*, *R. arrhizus*, and *M. racemosus* were 2.56, 4.62, and 5.10, respectively, at the PCNB concentration of 250 mg/L. Whereas, the amount of PCNB adsorbed on isolated cell-walls of *S. Cyanescens*, *R. Arrhizus*, and *M. Racemosus*, were 1.87, 3.49, and 4.17, respectively, at the PCNB concentration of 250 mg/L [36].

2.3.2. Chemical treatment

Unfortunately, most pollutants are chemically stable and difficult to degrade by biotic or/and abiotic processes. Hence, conventional wastewater treatment plants (WWTP) are not effectively able to remove them to the required level. Therefore, alternative methods of wastewater treatment were needed.

Chemical methods such as oxidation, precipitation, coagulation, and etc., are used to treat water and wastewater [11, 37].

An advanced oxidation process (AOPs) oxidizes organic pollutants based on the in situ production of highly reactive and oxidizing radical agents, such as OH \cdot . Hydroxyl radical, SO $_4^{\cdot-}$ sulphate radical [11, 37]. In AOPs, pollutant degradation occurs due to the reaction of radicals with organic pollutant molecules. Where the oxidation of organic pollutants led to the degradation of parent compounds into more benign and biodegradable intermediate products, or to complete mineralization into safe compounds such as carbon dioxide, H $_2$ O, and mineral acids under optimal conditions [37]. AOPs has benefits such as smaller processing space needed to process the system's required flow rate, environmentally friendly technique, and rapid reaction rates that result in lower retention time compared to other traditional treatment methods. However, various disadvantages can be mentioned, including maintenance costs, and high operating [11].

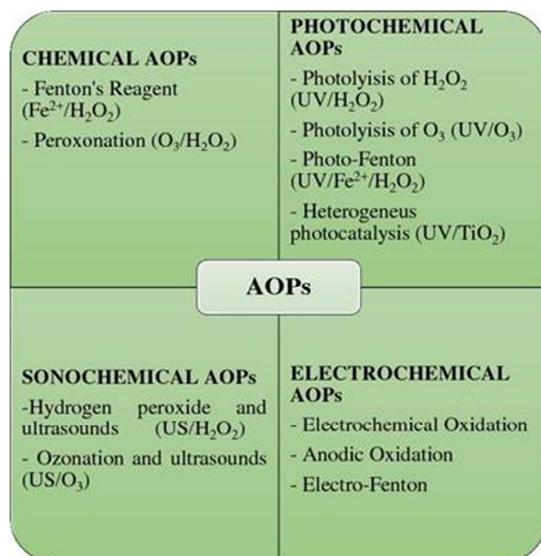


Figure 4: Classification of advanced oxidation processes (AOPs) [37]

Hydroxyl radicals are produced from various pathways using ultraviolet irradiation, catalysts, combination of oxidants. Thus, the classification of AOPs depends on the source production of hydroxyl radicals (OH) [38]. Figure 4 shows different types of electrochemical, chemical, sonochemical, and

photochemical reactions of destruction and degradation have been performed for organic pollutants in water treatment. AOPs can be categorized as photochemical (such as direct photolysis by UV light, UV/ TiO $_2$, UV/ H $_2$ O $_2$, photo-Fenton and photo-Fenton-like processes) or non-photochemical (such as ozonation, Fenton process, hydrodynamic/ultrasonic cavitation, electrochemical oxidation, and sub/super critical) processes. AOPs can also be classified as homogeneous or heterogeneous [37].

Homogeneous AOPs can be divided into the energy-using and non energy-using processes. Homogeneous AOPs processes use energy such as UV radiations, electrical energy or ultrasonic energy to remove pesticides from water and wastewater [37]. Ultraviolet radiations are the electromagnetic radiations used in the photodegradation of pesticides in water and wastewater, but ultraviolet radiations alone are not enough to degrade organic pollutants, so the combination of ultraviolet radiation and other techniques to improve the performance of photodegradation in removing pesticides [11]. UV radiations have been applied in the presence of oxidants such as UV/O $_3$, UV/H $_2$ O $_2$, UV/O $_3$ / H $_2$ O $_2$, and UV/ Fe $^{2+}$ / H $_2$ O $_2$ (photo-Fenton) [37]. UV/O $_3$ treatment was used to degrade carbamate insecticide, Carbofuran, which achieved higher efficiency compared to the direct UV photolysis and ozonation process. Where 0.2 mM carbofuran was completely removed and 24% mineralization was achieved in 30 minutes [39].

In the field of AOPs, Fenton reaction (Fe $^{2+}$ / H $_2$ O $_2$), and Fenton-like reactions (Fe $^{3+}$ / H $_2$ O $_2$) have been used to treat non biodegradable wastewater. The Fenton method is considered one of the most effective oxidation techniques for removing organic contaminants. Due to their ability to completely mineralize a wide range of organic compounds and rapid rate of pollutant removal, Fenton reactions have been widely used to treat the water contaminated with pesticides. However, two limitations of Fenton systems are the slow reduction of Fe $^{3+}$ by H $_2$ O $_2$ and the significant increase in iron sludge production in their applications. To overcome these limitations, the system was illuminated with UV irradiation, which is termed as the photo-Fenton process. The combination of Fenton reagent with UV visible irradiation enhances the efficiency of process because of the

photoreduction of Fe^{3+} to Fe^{2+} and the ability to produce another source of hydroxyl radicals via photolysis of hydrogen peroxide. Consequently, hydroxyl radicals yields increase and the required amount of Fe^{2+} reduces in Fenton reaction. The photo-assisted Fenton method as an oxidative pre-treatment step has advantages, such as economics, efficiency, less energy demand, harmless process products, and low investment, over the dark Fenton method. However, the Fenton Photo process has drawbacks including the employ of UV light sources and the periodic addition of OH^- that raise the operational cost. [11,38,40].

Different AOPs including UV, $\text{H}_2\text{O}_2/\text{Fe(II)}$, UV/ H_2O_2 , UV/ $\text{H}_2\text{O}_2/\text{Fe(II)}$ and UV/ $\text{H}_2\text{O}_2/\text{Fe(III)}$ were used to degrade profenofos, fenitrothion, and diazinon. Compared to other AOPs, the photo-Fenton method, which uses either Fe(II) or Fe(III), reported the best percentage of total organic carbon (TOC) removal. After a 90-min reaction time, the Fenton method achieved 46.2%, 54.2%, and 12.9% of TOC reduction of profenofos, fenitrothion, and diazinon, respectively. While the photo-Fenton treatment achieved a maximum TOC degradation of 89.7%, 86.9%, and 56.7% and for profenofos, fenitrothion, and diazinon, respectively, within 30 min at pH 3 [40]. Ma et al. used an ultrasonic process and a combination of Fenton and ultrasonic process to degrade carbofuran. The ultrasonic method oxidised more than 40% of the carbofuran in 120 min. The mineralization of carbofuran was less than 15% which was observed by the decrease in TOC. This indicated to the oxidation of part of carbofuran to intermediates. While the combination of Fenton reagents with the ultrasonic process improved the degradation efficiency of carbofuran to over 99% with 40% mineralization within 30 min [41]. Whereas homogeneous AOPs that do not use energy include ozonation with hydrogen peroxid and ozonation in alkaline medium. Ozonation is the process of removing pollutants using ozone. Ozone is generated on-site due to its short life which leads to an increase in treatment cost [11,37]. Ormad et al. used various technique treatments to degrade 44 pesticides. The results indicated that the oxidation by ozone removed 70% of the pesticides. However, the combination of ozonation treatment with activated carbon increased pesticides removal to 90% [42].

Heterogeneous AOPs involve the addition of catalysts to occur the degradation reactions.

Organometal or metal oxides of Ti, Al, Zn, V, Mn, Cr, etc. have been used as catalysts in heterogeneous AOPs. Heterogeneous AOPs include catalytic ozonation ($\text{Fe}^{+2}/\text{O}_3$, TiO_2/O_3), photocatalytic ozonation ($\text{UV}/\text{TiO}_2/\text{O}_3$) and heterogeneous photocatalysis (UV/TiO_2) [37]. In another study by Ormad, The influence of titanium dioxide and hydrogen peroxide in the ozon-based treatment was used to degrade 44 pesticides found in natural water. The ozonation treatment removed about 23% of pesticides. While the average degradation yields from $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/TiO_2 treatments was less than that from ozonation. However, using the $\text{O}_3/\text{H}_2\text{O}_2/\text{TiO}_2$ method significantly improved pesticide degradation, yielding an average degradation rate of 36% [43].

Recently, heterogeneous photocatalysis has been widely used especially in the case of organic pollutants resistant to oxidation by other traditional AOPs [37]. Heterogeneous photocatalysis involves the direct or indirect absorption of UV or visible radiant energy by a solid which, in its excited state, acts as a catalyst for the organic pollutants degradation. Photocatalysis on the semiconductor surface provides an alternative to the production of free radicals. According to the literature, studies of photocatalysts including TiO_2 , SnO_2 , ZnO , CeO_2 , WO_3 , CdS , ZrO_2 and Fe oxides have all demonstrated a good performance in removing a variety of pollutants [44]. This process gradually degrades the pollutants, avoiding the production of sludge and residue, which reduces the probability of secondary pollution. Additionally, there is no need for consumable chemicals due to remaining catalyst unchanged during operation. Furthermore, the pollutant is strongly adsorbed to the surface of catalyst, enabling the photocatalytic process to efficiently remove pollutants even at very low concentrations of pollutants in solution, which saves the cost of water production [38]. Titanium dioxide (TiO_2) has been most widely established material among the semiconductor photocatalysts due to its high stability, cost-effectiveness, abundance, non-toxicity, and unique photocatalytic efficiency in many degradation reactions [38,45]. Unfortunately, the high charge carrier recombination rate of TiO_2 generally limited the photocatalytic performance. Therefore, TiO_{Fig} has been modified to reduce these recombinations [45].

Utrilla et al. used a $\text{UV}/\text{TiO}_2/\text{activated carbon}$ system for the photocatalytic degradation of 2,4-

dichlorophenoxyacetic acid (2,4-D). The results showed that the percentage of 2,4-D removal increased when the activated carbon was present during the photocatalytic degradation (UV/TiO₂). In the presence of activated carbon, the maximum percentage of 2,4-D degradation was obtained with the highest content of carboxyl groups after 60 min of treatment. 40% of the organic matter was mineralized by UV/TiO₂/AC-ozonated system. The degradation by-products were less toxic compared to 2,4-D [44]. In another study, Fe₂O₃/TiO₂ was used to degrade 2,4-D under UV light irradiation. The results indicated that the activity of Fe₂O₃/TiO₂ was higher than that of TiO₂. After 1 h of reaction, Fe₂O₃ (0.5)/TiO₂ achieved 18% degradation of 2,4-D which corresponded to an activity three times higher than that of TiO₂. The Fe₂O₃ (0.5)/TiO₂ material showed reusability and excellent stability for 2,4-D removal [45]. Based on prior studies, AOPs are suggested as pre-treatment stages to degrade the pesticide into more biodegradable intermediates, then a biological treatment procedure is followed to convert them into biogas, biomass, hydrochloric acid, carbon dioxide, and water. This is mainly because AOPs do not effectively remove the bulk chemical oxygen demand (COD) to a level below the regulatory standard for some refractory pesticide compounds [38].

2.3.3. Physical treatment (Adsorption)

Adsorption is the most widely used method of physical treatment. Adsorption is a widely applied rapid technology, used to remove soluble, insoluble pollutants and biological pollutants, the removal efficiency can reach 90-99% [14]. Adsorption has advantages such as low cost, ease of operation, simplicity, high efficiency, versatility, and no harmful by-products. The adsorption effectiveness depends on the surface area, porosity, number of sites available and possible interactions with the pollutant [11,15]. There are many adsorbents used in the process of removing pesticides from water and wastewater such as activated carbon, natural materials, nanomaterials, agricultural wastes, industrial waste, miscellaneous, composite, noncomposite, and bio-adsorbents [11]. Table (1) shows removal of pesticides by different adsorbents. Among the adsorbents, for a long time, carbonaceous materials have occupied a special place as adsorbent materials [46]. Activated carbon (AC) has been

successfully used as an effective adsorbent because of its high surface area and high porosity [11]. The waste rubber tire was used to prepare activated carbon, which was used to remove methyl parathion, methoxychlor, and atrazine. The results exhibited that the highest absorption was 88.9 mg g⁻¹, 104.9 mg g⁻¹, and 112.0 mg g⁻¹ for methyl parathion, atrazine and, methoxychlor, respectively [47]. Picabiol AC was used to remove Atrazine, Atrazine-desethyl, and Triflurosulfuron-methyl pesticides with adsorption capacities of 22.6, 23.1, 19.7 mg g⁻¹, respectively [48]. Although active carbon is effective in removing pesticides, its production cost is high. Therefore, the trend has been to low-cost adsorbents from agricultural and industrial wastes [11].

Table 1
Pesticides removal by different adsorbents

Adsorbent	Pesticide	Adsorption capacity mg/g	Reference
Picabiol AC	Atrazine	22.6	48
Picabiol AC	Atrazine-desethyl	23.1	48
Picabiol AC	Triflurosulfuron-methyl	19.7	48
Fly ash	atrazine, metolachlor, metribuzin,	0.38 0.28 0.20	49
Carbon slurry	2,4-D Carbofuran	152.9 – 212.1 150.2-208.3	51
Blast furnace slag	2,4-D Carbofuran	Negligible Negligible	51
Blast furnace dust	2,4-D Carbofuran	21.0 13.0	51
Blast furnace sludge	2,4-D Carbofuran	30.0 23.0	51
Animal bone meal	Carbofuran	18.5	52
Orange peel	Carbofuran	84.49	54

Fly ash is a cost effective adsorbent and has shown significant ability to adsorb organic pollutants. Fly ash had a maximum adsorption capacity of 0.38, 0.28, and 0.20 mg g⁻¹ for atrazine, metolachlor, and metribuzin, respectively [49]. Date stone, banana peels, and orange were used to remove parathion and diazinon. The reduction of parathion by date stones, orange peels, and banana peels was 39.52%, 45.28%, and 50.34%, respectively. Whereas the reduction of diazinon by orange peels, banana, and date stones was 43.42%, 63.86%, 81.18%, respectively [50]. Gupta et al. used steel industry wastes (blast furnace slag, dust, and sludge) and fertilizer industry waste (carbon slurry) as adsorbents to remove carbofuran and 2,4-D from aqueous solution. The highest

adsorption capacities of Blast furnace dust and Blast furnace slag for removing carbofuran were 13 mg/g, and negligible, respectively. The 2,4-D and carbofuran were removed using carbon slurry with adsorption capacities of 152.9–212.1, 150.2–208.3 mg g⁻¹, respectively [51]. Animal bone meal (ABM) was used as an alternative low-cost adsorbent for the adsorption of Carbofuran from an aqueous solution. The method for preparing the ABM adsorbent. It was found that 25 mg of ABM removed a maximum of 98.3% of Carbofuran. ABM had the highest adsorption capacity of 18.5 mg g⁻¹ [52]. Two agro-industrial wastes, peanut shell and sugarcane bagasse, were used as support of magnetite nanoparticles to prepare magnetic bio-composites: magnetic peanut shell (MPSo) and magnetic sugarcane bagasse (MBO). These magnetic bio-composites were used as low-cost adsorbents for adsorptive removal of carbofuran and iprodione. MBo and MPSo had the highest adsorption capacities of 175 and 89.3 mg/g for carbofuran, and 119 and 2.76 mg/g for iprodione, respectively [53]. In another study, orange peel was employed as low-cost adsorbent for adsorptive removal of carbofuran from aqueous solution. At 30°C, the maximum adsorption capacity of orange peel for carbofuran was found to be 84.49 mg/g [54].

3. Metal-organic frameworks (MOFs)

3.1. Definition of metal-organic frameworks (MOFs)

MOFs are hybrid materials consisting of organic and inorganic units, which are characterized by their porosity and crystallinity [17,55]. The organic units (bridging ligands/linkers) are composed of carboxylates, or anions, including sulfonate, phosphonate, and heterocyclic compounds. The inorganic units are called secondary-building units (SBUs), which are metal ions or clusters. MOFs are obtained through a coordination bond between organic linkers/ bridging ligands and metal ions or clusters, resulting in open frameworks (Figure 5). The diversity of organic linkers and metal ions leads to a variety of MOFs [17]. Wherever most metals can be used to construct MOFs. Organic linkers, such as benzenedicarboxylates (BDCs), benzenetricarboxylates (BTCs), Imidazoles, etc., are used to form MOFs. Furthermore, the use of linkers of various sizes can vary the pore size of MOFs such as 1,4-benzenedicarboxylic acid (BDC),

biphenyldicarboxylate and terphenyldicarboxylate for UiO-66, UiO-67 and UiO-68, respectively [56].

The geometry of MOFs depends on the nature of the functional groups, coordination number, and geometric coordination of metal ions [17]. Therefore, MOFs have various geometries such as linear, tetrahedral, T- or Y-shaped, square-pyramidal, square-planar, octahedral, trigonal-bipyramidal, pentagonal-bipyramidal, trigonalprismatic, and the corresponding distorted forms [57]. Different nodes and linear terephthalic acid linkers compose various geometries of MOFs with their available surface area and characteristic pore size (Figure 6) [55].

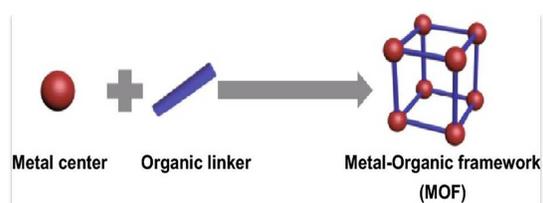


Figure 5: Metal-organic frameworks (MOFs) structure [16]

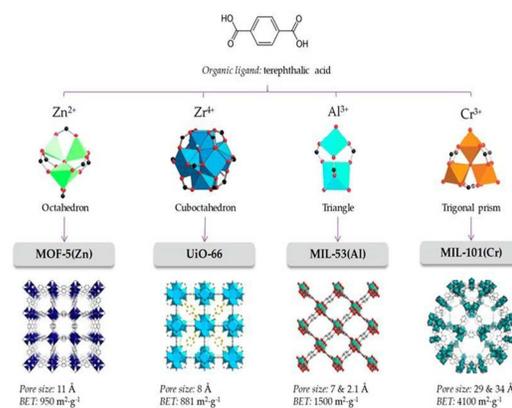


Figure 6: Various metal-organic framework with their geometry [55]

3.2. Most common stable MOFs

Many MOFs are unstable in water or other hard conditions, which has significantly impeded their potential application and commercialization [58]. The hydrothermal, chemical, and thermal stabilities of MOFs are crucial for practical industrial applications because the majority of chemical processes take place at high temperatures (for gas-phase or vapour reactions) or under basic or acidic conditions (for

liquid-phase reactions) [59]. Multiple factors such as organic ligands, metal ions, ligand–metal coordination geometry, the operating environment, the pore surface hydrophobicity can influence the stability of MOFs [58]. When the inertness of metal ions increases, the chemical stabilities in water, bases, and acids increase [59]. Stable MOFs are generally formed from soft Lewis bases (azolate-based ligands) and soft Lewis acids (low valence state transition metal ions) or hard Lewis acids (high valence state metal ions), hard Lewis bases (carboxylate-based ligands), according to the hard and soft acids and bases (HSAB) principle. Stable MOFs were constructed by metal ions (as Ag^+ , Ni^{2+} , Cu^{2+} , Mn^{2+} , and Zn^{2+}) and azolate ligands (as tetrazolates imidazolates, triazolates, and pyrazolates). The highly valent ions (Al^{3+} , Fe^{3+} , Ti^{4+} , Cr^{3+} , and Zr^{4+}) aggregate with carboxylate ligands to form the stable MOFs. [58]. Stable MOFs (such as ZIF, UIO, and MIL series materials) were successfully prepared [60]. However, many so-called “stable MOFs” have not yet achieved the same degree of stability as other organic or inorganic porous materials including porous carbons, mesoporous silica, and zeolites [58].

3.3. The most common synthetic procedures of MOFs

MOFs have been frequently synthesized by the hydro/ solvothermal method. Where metal salt and organic linker are dissolved in a solvent. Then the reaction mixture was heated to obtain MOFs. Crystals obtained by this method are suitable for single crystal X-ray diffraction (XRD) analysis [61]. MOF-5 was prepared by solvothermal method with high quality and high yield of MOF-5 [62]. Bhattacharjee et al. synthesized Fe-MOF-74 by solvothermal processes [63]. However, MOF synthesis using the solvothermal method is slow (hours to weeks) [61]. Therefore, alternative methods for preparing MOFs have been adopted.

Microwave (MW) irradiation can be used for the synthesis of organic or inorganic solids. This synthesis method has advantages such as mitigation in crystallization times, particle size distribution, and control of morphology and phase. MIL100 was successfully prepared by MW irradiation. The synthesis time for MIL-100 was reduced from 96 h by the hydrothermal method to 4 h by microwave method [64]. Microwave-assisted hydrothermal

synthesis has been used to effectively and rapidly prepare MIL-101(Cr) that showed a large surface area and huge giant pores [65]

Sonochemical/ultrasonic synthesis is another method for preparing MOFs that is efficient, friendly environment, facile, and low cost. [64]. MOF-5 was prepared using a sonochemical method with high quality .Sonochemical synthesis took a shorter synthesis time (~30 min) than traditional solvothermal synthesis (24h) [66]. A sonochemical method was used to successfully prepared high-quality MOF-177 crystals in the 5–20 μm size range in the presence of NMP (1-methyl-2-pyrrolidone) as a solvent with 40 min. MOF-177 was also prepared by microwave heating in NMP under similar conditions (35 min, 5–50 μM) with inferior crystallinity. In contrast, a conventional solvothermal method in DEF (diethylformamide) required 48 h to yield MOF-177 crystals of 0.5 and 1.5 mm in size. The sonochemical route produced MOF-177 with product yield of 95.6% , which significantly higher than these of other methods. [67].

Electrochemical synthesis (EC) is an alternative method used to prepare MOFs. This method has advantages such as viable, speed, simple, and precise process controlled. The purity of EC synthesis is high because of the absence of counter ions including chloride, perchlorate, or nitrate from metal salts [64]. For the first time, MIL-100(Fe) was synthesized through electrodeposition [68]. MIL-53 (Al) and NH_2 -MIL-53 (Al) were successfully prepared by electrochemical synthesis. Compared to Solvothermal synthesized MIL-53 and NH_2 -MIL-53 samples, the electrochemical synthesized samples showed suppressed framework flexibility. Electrochemical synthesis offers advantages including easy synthesis of MOF nanoparticles, shorter synthesis time, milder conditions, higher Faraday efficiencies and morphology tuning [69].

Volatile organic solvents used in the synthesis of MOFs have several effects as environmental pollutants. A mechanochemical synthesis for the preparation of MOFs has been proposed to overcome problems related to solvents. The mechanochemical synthesis provides a solvent-free preparation and a short reaction time of about 10-60 min with high quantitative yields [64]. Mechanochemical method was used to obtain HKUST-1 and MOF-14 with high surface areas [70]. Without any applied heating,

isonicotinic acid and copper acetate were grinded together for 10 min to obtain microporous MOFs [Cu(INA)₂] [71]. The mechanochemical method was effective in the MOF-5 synthesis within minutes [72].

3.4. Advantages and disadvantages of MOFs

Recently, MOFs attract the attention due to their excellent properties such as ultra-low densities, discrete ordered structure, ease of synthesis, and large internal surface area exceeding 6000 m²/g [64]. MOFs also have several properties such as luminescence, high surface area, excellent mechanical and thermal stability, porosity, flexible architecture, tunable chemical structure, and magnetism [73,74]. The properties of MOFs can be improved by using the post-synthetic modification (PSM) technique. PSM approaches have been used to improve the properties such as exchange/ adsorption of guest species, modification of metal node or/and ligand (linker) [73]. Methods can be used to introduce functional groups onto MOFs such as post-synthetic modification (PSM), using functional linkers, linker replacement after synthesis, and easily incorporating MOFs with other functional materials [56]. Figure 7 shows various approaches of PSM such as ligand exchange, metal exchange, and/or guest replacement, etc. [73].

MOFs have drawbacks that should be mentioned. The use of MOFs has been limited due to their drawbacks such as low capacity, high fabrication costs, difficulties in regeneration/recycling, and poor selectivity [74]. Also, many MOFs suffer from irreversible structural degradation during the charge/discharge operations, low tap density, poor electrical conductivity, which could restrict their practical applications [75]. Additionally, the chemical or thermal stability of MOFs is lower than that of inorganic parts such as zeolite and carbon. Therefore, operating conditions must be considered in terms of recycling, toxicity (after degradation of MOFs), and longevity, especially under hydrothermal conditions, in a basic or acidic medium, or under high temperature. Moreover, metals and linkers are not cheap, especially when they are complex or complex in structure [56].

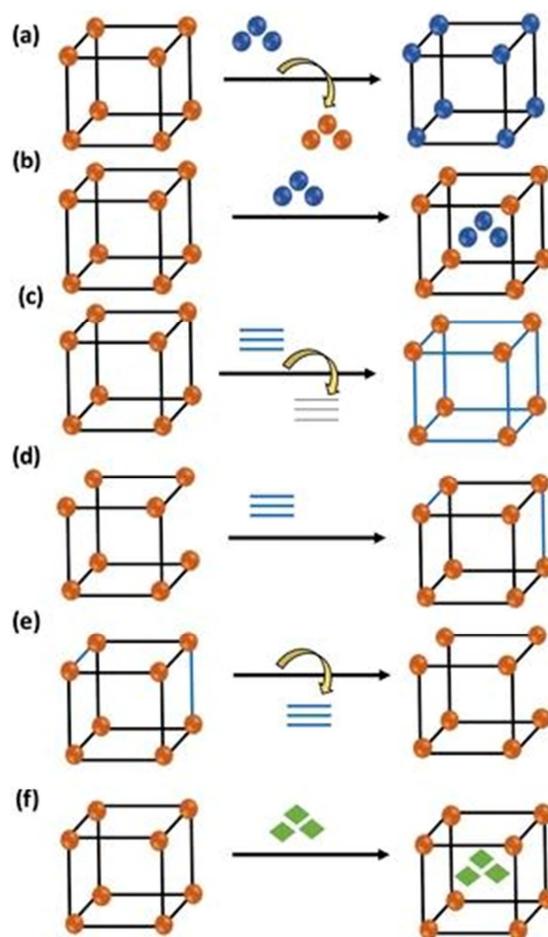


Figure 7: Possible routs of PSM in MOFs: a) metal exchange, b) metal incorporation, c) ligand exchange, d) ligand installation, e) ligand removal, and f) guest incorporation inside the pores [73]

3.5. Applications of MOFs

There are wide applications for MOFs including optics, adsorption/ separation of gases, storage, catalysis, drug delivery, sensing, microelectronics, and bioreactors. etc [17]. MOFs have been applied as heterogeneous catalysts in condensation reactions, Friedel–Crafts reactions, coupling reactions, oxidations, etc. because of their mentioned properties [76]. Stable MOFs have wide applications in redox catalysis, Lewis/Brønsted acid catalysis, electrocatalysis photocatalysis, and gas storage. MOFs have demonstrated remarkable porosity and a potential ability to store H₂ and CH₄ [58]. MOFs have been used to design advanced electrode materials for diverse battery systems. The porous structure of MOFs allows for an ion transportation and easy electrolyte penetration [75]. In analytical

chemistry, MOFs have been applied as sorbent materials in microextraction and extraction methods, as sensors. Additionally, MOFs have been used as sorbent in the procedures of analytical sample preparation, which act as stationary phases in chromatographic systems [55]. MOFs can be used in biomedical applications due to their high biocompatibility, cytotoxicity, and high biodegradability. MOFs can be usefully used in cosmetics including caffeine storage and release, control of fragrance release, skin disease treatments, and parabens determination in cosmetic creams [77]. Nontoxic nano-MOFs with tailored surfaces and cores can be used as anti-HIV drugs and nanodrug carriers for antitumor [17].

3.6. Aluminium-based MOF [MIL-53]

3.6.1. Structure and importance

MIL-53 (Materials Institute of Lavoisier) is a well-known MOF, which first synthesized and named by Gérard Férey in 2002 [78]. To form MIL-53, corner-sharing octahedral chains $\text{MO}_4(\text{OH})_2$ ($\text{M} = \text{Al}, \text{Fe}, \text{Cr}, \text{Ga}, \text{In}, \text{Sc}$) are connected to an organic linker, benzene-1,4-dicarboxylate (terephthalate or BDC) [Figure 9]. The $\text{MO}_4(\text{OH})_2$ octahedral chains and terephthalate linkers are linked to form a three-dimensional framework [79]. Aluminium-based MOFs include MIL-53(Al), MIL-68(Al), MIL-100(Al), and MIL-101(Al), in which MIL-53(Al) is constructed of terephthalate ligands and trivalent cation Al [80,81]. Compared to other MOFs, MIL-53 (Al) has distinctive features such as high thermal stability, remarkable hydrothermal stability, available and cheap raw materials, and distinct framework flexibility [79,81]. It was found that the phenomenon known as the breathing effect of MIL-53, which can expand and contract the size of the pore to accommodate different particle sizes with maintaining its crystallinity [80]. Due to excellent properties of MIL-53(Al), it has been used in diverse applications such as gas storage, CO_2 capture, sensing, catalysis, separation, and wastewater remediation [80]. MIL-53 has shown sufficient ability to withstand soaking in water for extended periods of time up to a week in 100 °C aqueous solution and wide pH ranges (2-12). Therefore, MIL-53(Al) can be used in the purification of water [81]. Moreover, MIL-53(Al) is an effective option for the adsorption of toxic compounds

from aqueous solutions due to its high surface area, moisture resistance, and flexibility framework [20,79].

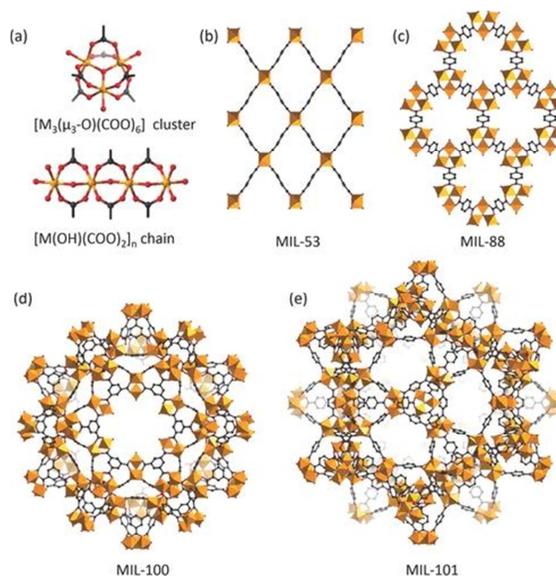


Figure 8: Structure of various MIL-MOFs [58]

3.6.2. Post-synthetic modification of MIL-53- NH_2

Enormous efforts have been dedicated to the functionalization of MOFs to improve the performance of adsorption. In order to design MOFs with demand properties, diverse functional groups are introduced into MOFs. MOF structures are chemically modified using a variety of means that are provided by post-synthetic modification. The functional groups are directly grafted on organic linkers of the MOFs. Which are considered effective and widely used. The post-synthetic modification of amine-contained MOFs attracted attention, in which amine groups provide linking sites to accept functional groups. Consequently, a variety of chemical moieties such as halo-functional groups, photo-switchable functional groups, and azo dye-functional groups have been successfully integrated into MOFs through amine groups [82].

The Al-MIL-53- RSO_3H was synthesized from the incorporation of 1,3-propane sulphonate in Al-MIL-53- NH_2 by post-synthetic modification in chloroform solution. Al-MIL-53- ArSO_3H was synthesized from the incorporation of an aromatic sulfonic acid group into Al-MIL-53- NH_2 by post-synthetic modification

in chloroform solution. Al-MIL-53-RSO₃H and Al-MIL-53-ArSO₃H were applied as catalysts in [4 + 2] cycloaddition with high selectivity, high activity, and loading of only 1 mol% of the catalyst [83]. Amidoxime groups were incorporated into MIL-53(Al)-NH₂ to prepare MIL-53(Al)-AO. The prepared MIL-53(Al)-AO was used to adsorb uranium [U(VI)] from an aqueous solution. The results showed that the adsorption capacity of MIL-53(Al)-AO for U(VI) was 2.36 times more than that of MIL-53(Al)-NH₂ at pH 6.0 [84].

MIL-53-NH₂ was functionalized with amino acids, such as L-glutamic acid (L-Glu) and L-histidine (L-His) to prepare MIL-53-NH-L-Glu and MIL-53-NH-L-His nanocrystals, respectively. Then, MIL-53-NH-L-Glu and MIL-53NH-L-His nanocrystals were embedded in a polyethersulfone (PES) matrix to create homochiral mixed matrix membranes (MMMs). MMMs showed excellent selectivity for racemic 1-phenylethanol with the highest value up to 100% [85]. Kalthor et al. synthesized MIL-53-NH₂ based on anodic electrosynthesis, which was then functionalized with phosphorus acid tags via the post-synthetic modification process. MIL-53(Al)-N(CH₂PO₃H₂)₂ as an effective catalyst was applied to prepare the novel (N-methyl-pyrrol)-pyrazolo[3,4-b] pyridines. This catalyst was recyclable and reusable with a minimum degree of catalytic activity [86]. Huang et al. used NH₂-MIL-53 (Al), pyridine-2-formaldehyde, and transition metal Cu⁺² to synthesis Cu@ Al-MIL-53-P21. Cu@Al-MIL-53-P21 was applied as a catalyst for the oxidation of styrene with the improved formation of yield [87].

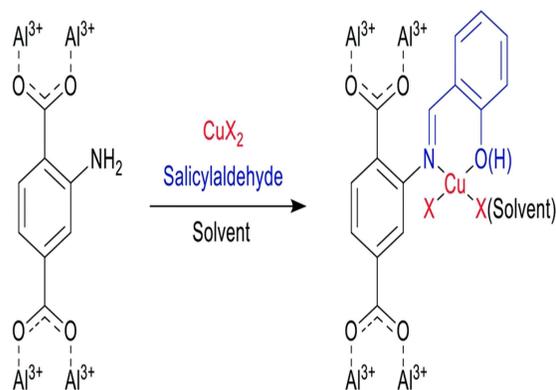


Figure 9: modification of MIL-53(Al)-NH₂ with salicylaldehyde and Cu (II) ions [88]

In another study, MIL-53(Al)-NH₂ was functionalized with copper (II) Schiff-base complexes by one-pot post-synthetic modification. MIL-Sal-OAc, MIL-Sal-Cl, and MIL-Sal-OTf were prepared from functionalization of MIL-53(Al)-NH₂ with salicylaldehyde and copper (II) acetate, copper (II) chloride and copper (II) triflate, respectively (Figure 9). The Schiff base reaction between the amino group in MIL-53(Al)-NH₂ and salicylate aldehyde provided coordination sites for copper (II) by microwave irradiation. An imine bond was formed between the copper complexes and the amino group of the MOF. The functionalized materials were applied in catalysis. MIL-Sal-OAc served as an effective catalyst, which was used to oxidize cyclohexene and styrene with values of TOF of 73 and 88 h⁻¹, respectively [88]. Gotthardt et al. used maleic anhydride and palladium (II) acetate to modify MIL-53- NH₂ (Al) by post synthesis reaction in two steps. The modified material as a catalyst showed high selectivity and conversion in Heck-type C-C coupling reactions [89].

4. Metal-organic frameworks and pesticides

4.1. MOFs as sensors for the pesticides

Human health is negatively affected by food risk factors such as pesticide residues, mycotoxins, veterinary drugs, heavy metals, pathogens, etc. Recently, foodborne illnesses have increased. So food safety has attracted attention all over the world [18]. The analytical methods, such as high performance liquid chromatography (HPLC), gas chromatography (GC), and mass spectrometry (MS), have been used to detect pesticides due to their sensitivity and reliability. However, these methods have some limitations such as requirements of large set-ups, highly skilled manpower and expensive equipment [90]. The selectivity, sensitivity, cost, and stability of the sensor depend on the selection and design of the sensor materials used in the sensor. Recently, to improve the performance of the sensors, new materials such as quantum dots, carbon-based materials, magnetic nanoparticles, metal-organic framework, etc. have been used (Figure 10) [18].

The primary drivers promoting the use of MOFs in chemical and bio-sensing are a number of their excellent features such as biodegradability, luminescence, non-toxicity, and availability of redundant functional groups. The applications of MOFs can be expanded to include detection of

pesticides, small molecules, gases, explosives, solvents, biological markers, aromatic compounds [91]. MOFs are applied as sensing materials to produce sensing methods such as surface enhanced Raman scattering, colorimetric, electrochemical, luminescent, and electrochemiluminescence. These methods provide advantages such as fast, accurate, and sensitive, easy of use to monitor harmful compounds in food online [18]. Table 2 shows MOF-based different sensors for the detection of pesticides.

Luminescence-based sensing technique has been used in various applications due to its simple operation, quick response, and high sensitivity. Luminescent MOFs have been applied as ideal sensing material in the fabrication of fluorescent sensors due to their excellent properties such as the intrinsic luminescence, desirable adsorption capacity, easy-to-functionalize surface, and tunable pore size. Sensor-analyte interactions result in a change in fluorescence, which is exploited in luminescence-based sensing. The mechanisms for fluorescence quenching of the MOF-based sensors are photoinduced electron transfer (PET), Förster resonance energy transfer (FRET), the excitation light competition between analyte and MOF and inner filter effect (IFE) [18].

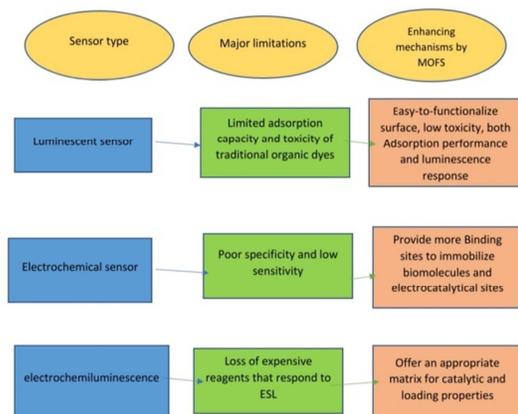


Figure 10: Limitations of various sensors and the potential for using MOFs to solve these problems

Among the 15 different types of organophosphates (OPPs), the Zn-MOF demonstrated a selective response to parathion by quenching the fluorescence intensity. Zn-MOF was used as luminescent sensor to

detect parathion with wide linear range from $5 \mu\text{gL}^{-1}$ to 1 mg L^{-1} and low limit of detection (LOD) of $1.950 \mu\text{gL}^{-1}$. The luminescent Zn-MOF has selective and rapid detection of parathion and a sensor repeatability of 97.23% [92]. Rhodamine B (RhB), luminescent dye molecule, and Zr-MOF were used to construct a RhB@Zr-MOF composite through the encapsulation method. RhB@Zr-MOF as built-in self-calibrating luminescence sensor was used to detect nitenpyram with LOD of $0.2 \mu\text{M}$ and stability after 5 detection cycles [93]. Lanthanide metal-organic frameworks (Ln-MOFs) have excellent fluorescence properties with long lifetime, visible light emission and pure color, so they are used as effective sensing materials. Eu-MOF was used for rapid detection of 2,6-dichloro-4-nitroaniline (DCN) pesticide in water by a fluorescence quenching fashion with low detection limit and good recyclability [94].

Electrochemical method is an alternative technique for food safety sensing due to its advantages including short response time, low cost, easy miniaturization, and convenient operation. However, the specificity and sensitivity of electrochemical sensors are usually limited. Improving conductivity by modifying the electrode surface, introducing more electrocatalytic sites, or providing more binding sites to immobilize biomolecules is required to improve the specificity and sensitivity of the electrochemical sensor. MOFs have large surface that facilitates nanoparticles loading, which helps to improve amplify the electrical signals and improve conductivity [18]. However, the insulating property of organic ligand leads to poor electrical conductivity of MOFs. Modification of MOF with certain materials, such as nanotubes, nanoparticles, and ionic species, induce the electronic properties in MOFs [91].

CO_3O_4 @MOF-74 nanocomposite was used as an electrochemical electrode to detect the Phenamiphos insecticide with high sensitivity and selectivity. The results showed that this sensor exhibited the LOD ($3.0 \times 10^{-12} \text{ M}$), and quantification limit (LOQ) $1.0 \times 10^{-11} \text{ M}$. It has a high sensing property due to the synergistic effect between MOF-74 and CO_3O_4 nanowire and the large surface area [95]. The electrochemical sensor Zr-BDC-rGO achieved rapid and sensitive detection of methyl parathion with the low detection limit 0.5 ng mL^{-1} and wide linear range

from 0.001 to 3.0 $\mu\text{g mL}^{-1}$ [96]. The electrochemical sensor based on Cu-BTC MOF material was used to determine glyphosate in soybean. Cu-BTC MOF sensor exhibited ultralow detection limit (1.4×10^{-13} mol L^{-1}) and wide detection range (1.0×10^{-12} to 1.0×10^{-9} mol L^{-1} and 1.0×10^{-9} to 1.0×10^{-5} mol L^{-1}

¹). Cu-BTC MOF material has a large surface area that can enhance adsorption capacity, improve detection performance, improve detection limit, and increase electrode reaction site. Moreover, this sensor showed stability, good selectivity, and acceptable reproducibility [97].

Table 2
MOF- based various sensors for pesticides detection

Sensing materials	Sensor type	Target analytes	Application	Analytical performance	Advantages	Reference
Zn-MOF	luminescent sensor	Parathion	Irrigation water	Linear range from 5 $\mu\text{g L}^{-1}$ to 1 mg L^{-1} LOD of 1.950 $\mu\text{g L}^{-1}$	Selective rapid repeatability, and wide linear response	92
RhB@Zr-MOF	Luminescent sensor	Nitenpyram	Water source	LOD of 0.2 μM	Recyclability	93
Eu-MOF	Fluorescence sensor	2,6-dichloro-4-nitroaniline (DCN)	Water	-	Good recyclability, low detection limit, and sensitivity detection	94
UiO-66-NH ₂ (Zr)	Luminescent sensor	Methyl parathion	Tomato and orange	Wide range of 10–10 ⁶ ng/mL	Reusable up to at least eight times, and stable on long-term storage (at least 60 days).	99
CO ₃ O ₄ @MOF-74	Electrochemical sensors	Phenamiphos	Orange juice	LOD (3.0 $\times 10^{-12}$ M)	High sensitivity, and high selectivity	95
Zr-BDC-rGO	Electrochemical sensors	Methyl parathion	Chinese cabbage	LOD 0.5 ng mL^{-1} , wide linear range from 0.001 to 3.0 $\mu\text{g mL}^{-1}$	Rapid detection, sensitivity, and wide linear range	96
Cu-BTC MOF	Electrochemical sensors	Glyphosate	Soybean	LOD 1.4×10^{-13} mol L^{-1} , wide detection range (1.0×10^{-12} to 1.0×10^{-9} mol L^{-1} and 1.0×10^{-9} to 1.0×10^{-5} mol L^{-1})	Stability, ultralow detection limit, good selectivity, wide linear range, and acceptable reproducibility	97
BCL@MOF nanofibers/chitosan	Electrochemical sensor	Methyl parathion	Vegetables	Linear range: 0.1–38 μM LOD: 0.067 μM	low limit of detection, wide linear range, high sensitivity, excellent stability, good recovery rates and good reusability	100
Cu/Co-MOF	Electrochemiluminescence	Acetamiprid and malathion	Apple and tomato	linear range of 0.1 μM to 0.1 pM, LOD of 0.015 pM, and 0.018 pM	Stability, reasonable specificity, good sensitivity, and repeatability	98

Electrochemiluminescence (ECL) is chemiluminescence resulting from electrochemical techniques. The combination of electrochemistry and chemiluminescence endows electroluminescence (ECL) with various advantages including wide linear range, low detection limit, and high sensitivity [18]. Due to their advantages such as low background signal, simple equipment, low detection cost, and fast detection speed, ECL sensors have been used in the detection of pesticide residues. Lui et al. constructed a dual-signal ECL aptasensor based on graphite-like carbon nitride nanosheet (g-C₃N₄) and the ECL

4.2. MOFs as stationary phase extraction

Purification and extraction of pesticides from food and water samples require several stages due to their complex matrices. The analyses of component depend on several factors such as the nature of the samples and their matrix, instrumental detection process, and sample preparation procedures [101]. Various instrumental techniques, such as gas chromatography (GC), spectrophotometry, and high-performance liquid chromatography (HPLC), have been applied in the determination of pesticides. These techniques provide a precision and high sensitivity. However, these techniques suffer from limitations, such as expensive equipment, matrix interference, complicated operating, and relatively high detection limits. The purification and extraction of sample have been applied to solve these limitations. Common analyte extraction methods involve dispersive liquid-liquid microextraction, solid-phase extraction, etc. [101,102].

Recently, MOFs have been used as a novel and reliable sorbent material in the sample preparations, including contaminants, heavy metals, large molecules, and others. Several MOF materials have been employed in various extraction modes, such as solid-phase extraction (SPE), solid-phase microextraction (SPME), dispersive-micro solid phase extraction (D- μ SPE), stir-bar solid-phase microextraction (sb-SPME), in-tube solid-phase

signal of luminol. To load the luminol, a hollow Cu/Co-MOF, containing cobalt and copper metal sites was used to stimulate the luminescence performance of the luminol resulting in the enhancement of the ECL signal of the luminol. The dual-signal ECL aptasensor was used to simultaneously detect acetamiprid and malathion with a linear range of 0.1 μ M to 0.1 pM, LOD of 0.015 pM, and 0.018 pM, respectively. Furthermore, the aptasensor showed stability, reasonable specificity, good sensitivity, and repeatability [98].

microextraction (it-SPME), thin-film solid-phase microextraction (tfSPME), and needle trap device. Different types of MOFs, such as MOF family, isorecticular metal-organic framework (IRMOF), University of Oslo (UiO), MIL, and zeolite imidazolate frameworks (ZIF), have been employed in diverse sample preparation strategies [103]. Table 3 shows the determination and extraction methods of pesticides in the environmental.

The solid phase extraction (SPE) procedure has been widely used for extraction and concentration of pesticide residues due to its advantages, such as high extraction efficiency, low organic waste, simplicity, solvent consumption and sensitivity [103,104]. Pipette tip solid phase extraction (PT-SPE) was coupled to HPLC for the detection of phenoxy herbicides in tap water, cucumber and soil samples. Cotton@UiO-66 was packed as an absorbent into the pipette tip for the fabrication of the extraction device. Cotton@UiO-66 showed excellent properties in the phenoxy herbicides extraction. Linear ranges of 2-(2,4-dichlorophenoxy) propionic acid, dicamba, 4-chlorophenoxyacetic acid, and 2,4-dichlorophenoxyacetic acid were 3.2–160 μ g/L, 5.6–280 μ g/L, 1.4–72 μ g/L, and 2.8–140 μ g/L, respectively. The results showed the detection limit range (0.1 μ g L⁻¹ to 0.3 μ g L⁻¹), recovery between (83.3 and 100.8 %) with relative standard deviations RSDs < 6.7 % [104].

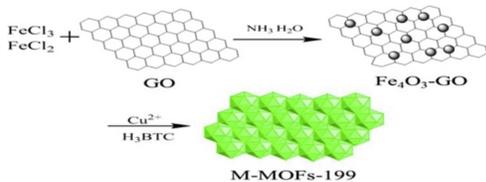


Figure 11: Synthesis of M-MOF-199 [106]

Magnetic SPE (MSPE) is a relatively new form of SPE, in which a small amount of magnetic nanoparticles are dispersed to absorb and release target analytes. The typical SPE technique is not suitable for many MOFs because of high column resistance caused by the fine particle of MOFs. MSPE and MOFs are combined to solve this problem [105]. Magnetic Solid Phase Extraction (MSPE) is environmentally friendly, filter/centrifugal free, rapid, and simple method for the pre-treatment of pesticides by the mechanical separation. A magnetic sorbent is added to the solution for fast adsorption of the analyte and then extracted from the magnetic sorbent for more analysis [106].

Fe₃O₄@SiO₂-MIL-101 was used as MSPE sorbents and coupled with high performance liquid chromatography-diode-array detector (HPLC-DAD) to determine four pyrazole/pyrrole pesticides (fenpyroximate, chlorfenapyr flusilazole, and fipronil) in environmental water samples. The results exhibited excellent linearity in the range of 2.0–200.0 µg/L for chlorfenapyr and fenpyroximate, and 5.0–200.0 µg/L for flusilazole and fipronil, with correlation coefficients $r > 0.9911$. Quantification and limits of detection were 1.0–5.0 µg/L, and 0.3–1.5 µg/L respectively. Since the Fe₃O₄@SiO₂-MIL-101 could be quickly extracted from solutions using an external magnet, there was no need for complicated devices for the analysis [105]. In another study, a magnetic Copper-based metal-organic framework (M-MOF-199) has been synthesized using Nanocomposite (Fe₃O₄-graphene oxide) (Figure 11) that was used for magnetic solid-phase extraction (MSPE) of flusilazole, fenbuconazole, myclobutanil, penconazole, and epoxiconazole (five triazole) pesticides from water samples. The benefits of combining MOFs and M-GO are the highly selective adsorption and rapid separation of triazole pesticides. High performance liquid chromatography (HPLC) coupled with tandem mass spectrometry was applied for sample determination and quantification. The limit of detection was 0.05–0.1 µg L⁻¹, the recovery range was 72.3%–91.53% with the relative standard deviations (RSD) ranging from 1.5% to 9.1 %. The mechanism may be the hydrogen bonding, π - π stacking/interactions, hydrophobic interactions, electrostatic interactions between the five membered heterocycles and the benzene rings in the triazole pesticides with GO-MOFs. Researchers have established technique of the combining HPLC/MS with M-MOF-199 that is a sensitive detection, simple, and rapid method for triazole pesticides [106].

Dispersive solid-phase extraction (DSPE) is another sample preparation method, which is considered as safe, quick, effective, easy, cheap, and rugged. This technique involves dispersing the adsorbent into a

sample solution, then collecting it by centrifugation to extract the analytes. The primary advantage of DSPE method is the promotion of the contact area between the analytes and sorbent [107]. Amiri et al. Prepared Zn-based MOF from histamine as an organic linker and zinc as the metal ion under solvothermal conditions. Zinc-based MOF was used as sorbent for DSPE of organophosphorous pesticides (OPPs) in water and fruit juice samples. The instrument detection was used the gas chromatography-flame ionization detector (GC-FID). Good linearity exhibited in the range of 0.1–100 ng mL⁻¹ for the target analytes. The DSPE-GC-FID procedure indicated the detection limit (0.03–0.21 ng mL⁻¹) and the recovery range (91.9–99.5%) [107].

MIL-101 was used in dispersed solid micro-phase extraction (DMSPE) to extract phenylurea and triazine herbicides in vegetable oils. Herbicides were determined and separated using HPLC. The results showed that limits of detection were in the range of 0.585 - 1.04 µg/L for the herbicides and the recoveries were of the herbicides in the range of 87.3 - 107% [108]. A 100 Al-based MOF was applied as adsorbent for pre-concentration and extraction of carbaryl from fruit, vegetables, and water samples. DSPME was coupled with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-TMS) for high sensitive detection of carbaryl. The limit of quantification (LOQ), LOD, RSD was 0.03 mg L⁻¹, 0.01 mg L⁻¹, and 0.8–1.9 %, respectively [101].

Solid phase microextraction (SPME) is another mode of sample preparation, which can be combined with HPLC, and GC. SPME has been widely used in food, biological and environmental analysis, which has the advantages of low cost, time and labor-saving, simplicity, environmental friendly, and high extraction efficiency [103,109]. In a study, templated MOF composite, C₃N₄@MOF, was prepared by introducing g-C₃N₄ as a template during the synthesis process of NH₂-MIL-125. Then, C-(C₃N₄@MOF) was synthesized by the carbonization of the C₃N₄@MOF [Figure 12]. The C-(C₃N₄@MOF) showed high mechanical stability, large surface area, good thermal stability and high adsorption capacity. A sol-gel technique was used to coat C-(C₃N₄@MOF) on a stainless steel wire, that serve as SPME fiber coating. The coated fiber was used to extract fourteen organophosphorous pesticides, phorate, diazinon, dimethoate, disulfoton, iprobenfos, malathion, parathion methyl, chlorpyrifos, isocarbophos, parathion, phenthoate, profenofos, triazophos, and ethion, from different vegetable (baby cabbage, chinese cabbage, oilseed rape, pakchoi and lettuce) and fruit (apple, plum, peach, nectarine and pear) samples. Gas chromatography-mass spectrometric (GC-MS) was

used for the detection of pesticides. The linear response was in the range from 0.69 to 3000 ng g⁻¹ for the fourteen OPPs. LODs and coefficients of determination (r²) ranged from 0.23 to 7.5 ng g⁻¹ and from 0.9981 to 0.9998, respectively. The method

recoveries (R) ranged from 82.6% to 118%, with RSDs in the range of 2.8% - 11.7%. The coated fiber can be recycled more than 100 times without greatly reducing the extraction efficiency [109].

Table 3
The determination and extraction methods of pesticides in the environmental samples

Method	Matrix	Adsorbent	Pesticides	Analytical performance	Reference
PT-SPE-HPLC	tap water, cucumber and soil	Cotton@UiO-66	Phenoxy herbicides	LOD: 0.1 µg L ⁻¹ to 0.3 µg L ⁻¹ , recovery : 83.3 - 100.8 %), RSDs < 6.7 %	104
MSPE-HPLC-DAD	Environmental water	Fe ₃ O ₄ @SiO ₂ -MIL-10	Pyrazole/pyrrole	LOD: 0.3-1.5 µg/L r>0.9911	105
MSPE-HPLC	Water	M-MOF-199	Triazole	Recovery 72.3%-91.53%, RSD: 1.5% - 9.1 %, LOD: 0.05-0.1 µg L ⁻¹	106
MSPE-GC-MS/MS	Agricultural irrigation water	M-M-ZIF-67	Nine organochlorine	Recoveries 74.9-116.3% and 75.1-112.7%, LOD : 0.07-1.03 µg L ⁻¹	112
DSPE-GC-FID	water and fruit juice	Zinc-based MOF	Organophosphorous	Recovery (91.9-99.5%), LOD:0.03-0.21 ng ml ⁻¹	107
DSPME-UPLC-TMS	Fruit, vegetables, and water	100 Al-based MOF	Carbaryl	LOQ:0.03 mg L ⁻¹ , RSD :0.8-1.9 %, LOD: 0.01mg L ⁻¹	101
DSPME/GM-FID	Rice, cucumber, tomato, and mice liver	Magnetic NH ₂ -MIL-53(Al)@ Chitosan	Diazinon Ethion	Linear range of 0.23-220 µg L ⁻¹ , LOD: 0.07 µg L ⁻¹ Linear range: 0.13-200 µg L ⁻¹ , LOD:0.04 µg L ⁻¹ , RSD: (≤6.45%), and recovery range: 91.25-104.35 %	113
DMSPE-HPLC	Vegetable oils	MIL-101	Phenylurea and triazine	Recoveries: 87.3 - 107% LOD: 0.585 - 1.04 µg L ⁻¹	108
SPME-GC-MS	Vegetables and fruits	C-(C ₃ N ₄ @MOF)	Fourteen organophosphorous	Recoveries (R): 82.6% - 118%, RSDs : 2.8% - 11.7%. LOD: 0.23 to 7.5 ng g ⁻¹	109
SPME-GC/ECD	water convolvulus, river water, soil and longan	MOF-199/GO	eight organochlorine	LODs: 2.3-6.9 ng/L, RSD: 5.3% - 8.8%	110
TFME-SESI-IMS	Agricultural wastewaters and underground water	ZIF-67	Ethion	Recoveries: 91 - 107%, detection limit : 0.1 µg L ⁻¹	111

In another study, MOF-199/GO were fabricated by combination of graphite oxide (GO) and MOF-199 at room temperature, which was used as SPME coating. MOF-199/GO SPME fibers were used to simultaneously extract eight organochlorine pesticides [hexachlorobenzene (HCB), heptachlor epoxide, aldrin, p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE), dieldrin, p,p'-dichlorodiphenyldichloroethane (p,p'-DDD), trans-chlordane, and α -endosulfan] from water convolvulus, river water, soil and longan followed by gas chromatography/electron capture detector (GC/ECD) analysis. This fiber has high porosity, long lifespan (more than 140 extractions), and good thermal stability (above 300°C). The results exhibited that adsorption affinity of MOF-199/GO to OCPs was much higher than that of MOFs and GO, respectively. The method recoveries of eight organochlorine pesticides for longan, river water, water convolvulus, and soil were in the range of 82.8–94.3%, 90.6–104.4%, 72.2–107.7%, and 82.7–96.8%, respectively. The LODs were 2.3–6.9 ng/L, with RSD ranging from 5.3% to 8.8% [110].

Mohammadi et al. prepared flexible/self-supported ZIF-67 film that was used as a sorbent in the thin-film microextraction ((TFME) method. This film was used to extract ethion from agricultural wastewaters and underground water. Secondary electrospray ionization source with ion mobility spectrometry equipped (SESI-IMS) was used to detect the analyte. The linear dynamic ranged between 0.5 and 100 $\mu\text{g L}^{-1}$. the method recoveries ranged from 91 to 107% for spiked samples, with a detection limit of 0.1 $\mu\text{g L}^{-1}$. This method showed the appropriate reproducibility, the good sensitivity, and the satisfactory recoveries [111].

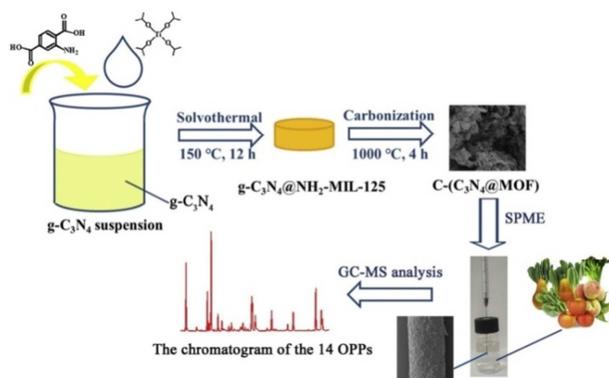


Figure 12: Synthesis of C-(C₃N₄@MOF) and extraction of OPPs [109]

4.3. MOFs as adsorbent for pesticides

Various methods, such as chlorination, oxidation, ion exchange, neutralization, filtration, activated carbon, and membrane filtration, have been reported in literature for removing organic pollutants from environment. However, these methods are limited in their application due to high prices, low effectiveness, the production of harmful by-products, and high concentration requirements of pesticides, which complicate their removal. The adsorption approach has been used as an alternative wastewater treatment method and proposed a solution to the difficult problem of insufficient removal of pollutants during wastewater treatment [21]. Adsorption has been widely used to remove pollutants due to its ease

of operation, no sludge formation, simplicity, versatility, and harmless by-product. The efficiency of adsorption is based on the possible interactions with pollutants, surface area, available sites, and porosity [11,15].

MOFs applications are effective in the removal of toxic compounds due to its surfaces and high porosity, the capability to purposefully control the size and shape of pores in the meso- and micro-ranges, and the chemical features of pore surfaces. The breathing effect, known a phenomenon to MOFs, as an external influence increasing the pore size, facilitates the adsorption [20]. Additionally, the flexibility to form diversity frameworks from organic linkers with many clusters of metal ions, allowing for

the existence of many MOFs with mesoporous or microporous structures. Moreover, the functional groups are varied in the organic linkers and the metal node that act as adsorption centers of various organic pollutants. MOFs are used as adsorbents in

removing contaminants from wastewater such as MIL-53 (Cr), MIL-101(Cr), ZIF-8 (Zn), ZIF-67 (Co), UiO-67 (Zr), Cu-BTC, etc. [21]. Various MOFs were used as adsorbents materials for different pesticides as shown in Table 4.

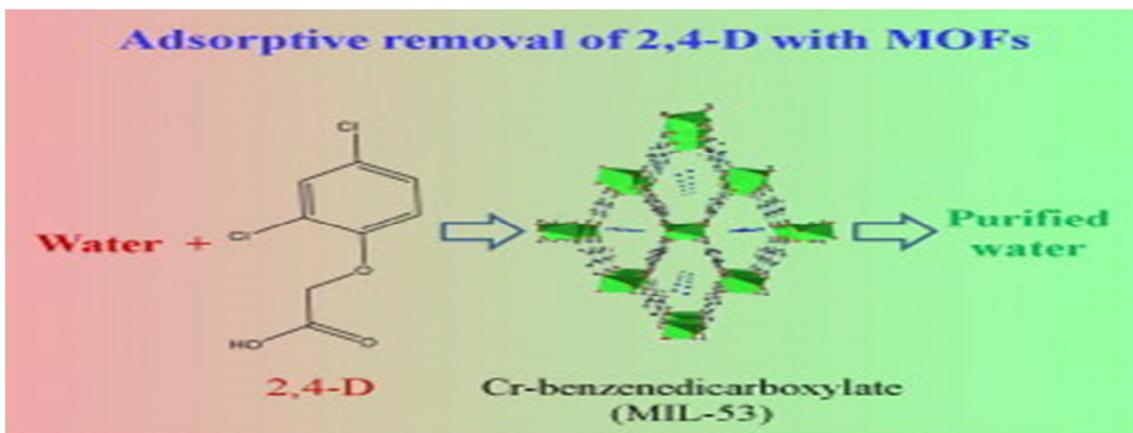


Figure 13: Removal of 2,4-D by MIL-53 (Cr) [114]

Cr-based MIL-53 was first applied for the uptake of 2,4-dichlorophenoxyacetic acid (2,4-D) from contaminated water by Jung et al.(Figure 13). MIL-53 (Cr) showed much higher uptake capacity and much faster uptake within 1 hour, compared with activated carbon (AC) or zeolite (USY). The adsorption of 2,4-D by MIL-53 (Cr) was highly effective, especially at low concentrations of 2,4-D in the solution, with a high adsorption capacity (556 mg/g). The adsorbent was still effective after being used in four cycles. The potential for the adsorption process is due to π - π stacking and electrostatic interactions between 2,4-D and MIL-53 (Cr) [114]. Either MIL-101 (Cr) succeeded in adsorbing diazinon from aqueous

solutions in a fixed-bed system with maximum adsorption efficiency (92.5%). Reports were obtained that the thermal stability was up to 550 °C, the surface area was 2600 m² / g, and the crystallinity was 96% for MIL-101(Cr) [115]. De Smedt et al. used Fe-based MOF-235 to remove isoproturon, clocyralid, and bentazon from water. MOFs performed well due to their rapid adsorption of pesticides in large quantities. However, the reusability of MOF-235 (Fe) was poor due to its unstable[116].

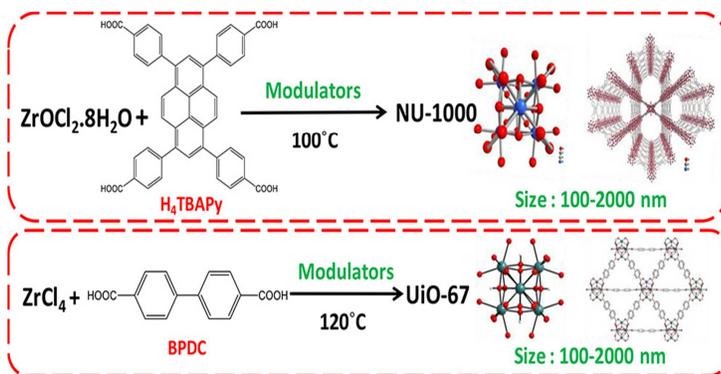


Figure 14: Synthesis of NU-1000 (Zr) and UiO-67 (Zr) [120]

According to the presence of Zr-OH group, high surface area, high water stability, and suitable pore size, Zr-based MOFs have been largely used in the removal of different pesticides by adsorption [21]. The researchers successfully synthesized Zr-based UiO-67 with properties such as appropriate pore size, and strong affinity. UiO-67 (Zr) was applied to remove glyphosate (GP) and glyphosinate (GF) with high adsorption capacity of 537 mg/g and 360 mg/g, respectively [117]. Zr-based UiO-66, Zr-BDC, was studied to uptake methylchlorophenoxypropionic acid (MCP) from contaminated water. The adsorption capacity and the kinetic constant were ~ 7.5 (particularly at low concentrations of MCP) of 1 mg/L and ~ 30 times that of AC, respectively. The adsorption mechanism was attributed to π - π interactions (at high pH) and electrostatic interactions (at low pH). The performance of UiO-66, after washing with water/ethanol for MCP adsorption, did not significantly reduce with 3 recycles [118]. In other study, UiO-66 and UiO-67 were studied in removal, dichlorvos and metrifonate, two organophosphorus (OPPs) insecticides. The adsorption capacities of UiO-67 approached 378.78 mg/g for metrifonate and 571.43 mg/g for dichlorvos. Whereas the adsorption capacities of UiO-66 were 90.49 mg/g and 172.40 mg/g for metrifonate, and dichlorvos, respectively. According to their adsorption capabilities, UiO-67 exhibited greater performance for the efficient removal of dichlorvos and metrifonate, due to abundant Zr-OH groups and larger pore size. The computed removals for the samples are between 97.8 and 99%, which indicated that the UiO-67 can be used to remove of Metrifonate and Dichlorvos in real samples [119]. Pancajakchan prepared two Zr-based MOFs, NU-1000 and UiO-67 in various sizes (100 - 2000 nm) to remove glyphosate from aqueous media (Figure 15). NU-1000 composed of 1,3,6,8 (p-benzoate) pyrene (TBAPy⁴⁻) linkers and $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4$ nodes, whereas UiO-67 composed of 4,4'-biphenyl dicarboxylic acid (BPDC) ligands and $Zr_6O_4(OH)_4$ clusters nodes. Although both MOFs contained the same metal node, the efficiency and reusability of NU-1000 (Zr) were higher than that of UiO-67(Zr). Compared with UiO-67 (Zr), NU-1000 (Zr) had the larger pore diameter, and the interaction energy of metal nodes of NU-1000 with glyphosate was higher (-37.63 KJ mol⁻¹) than that of UiO-67 (-17.37 KJ mol⁻¹), which were the reason of the higher efficiency of NU-1000(Zr) [120].

Three water stable MOFs, ZIF-8 (Zn), UiO-66 (Zr), UiO-67 (Zr), and commercial activated carbon (CAC), F400, were used to adsorb atrazine (ATZ), an agricultural herbicide, from water. Up to 98% of atrazine was removed from water by ZIF-8, UiO-67, and F400, but UiO-66 was found to be ineffective.

UiO-67 removed 98% of atrazine from the contaminated water in just 2 minutes, while ZIF-8 and F400 took more than 40 and 50 minutes, respectively, to remove the same concentration of atrazine [121]. NU-1000 (Zr) among the eight Zr₆-based removed nearly 100% of atrazine within 5 min. This study also showed that the linker structure could remarkably affect the adsorption properties of MOFs. Their performance was developed with the number of aromatic rings and groups of carboxylic acid in the linker. The results showed the adsorption of atrazine by NU-1000(Zr) due to the presence of pyrene-based linker in the structure of MOF providing suitable sites for π - π interactions [122].

Abdelhamid et al. compared the use of ZIF-67 (Co) and ZIF-8 (Zn) in the removal of two greatly used pesticides, ethion and prothiofos. It was found that the high adsorption capacities of ethion over ZIF-67 (Co) and ZIF-8 (Zn) were 210.8 and 279.3 mg/g, respectively, while that of prothiofos were 261.1 and 366.7 mg/g over ZIF-67 (Co) and ZIF-8 (Zn), respectively. The difference in adsorption capabilities occurred due to the coordination of ethion and prothiofos with zinc metal ion, which was stronger than that of with Co metal ion [123]. In another study by Abdelhamed et al., Cu-based MOF, Cu-BTC, was used in the adsorptive removal of toxic and carcinogenic insecticide, ¹⁴C-ethion. The adsorption capacity of Cu-based MOF was approximately 122 mg/g at pH 7, 150 min and 75 mgL⁻¹ of ¹⁴C-ethion concentration. Cu-BTC showed stability for up to six adsorption cycles. The adsorption might occur due to the coordination of ethion molecule to copper (II) atom of MOF via phosphoryl group (P-O) [124]. MILs are very attractive for practical environmental remediation applications due to their physiochemical characteristics and multifunctionality [125]. Al-based MIL-53 was used to remove metolachlor (MET) herbicide from an aqueous solution. Due to high surface area (1104 m²/g) of MIL-53 (Al), the maximum adsorption capacity of MET was 241.62 mg/g with a rapid equilibrium time of about 25 min [126].

4.3.1. Functional MOFs for pesticides removal

The functionalization or post-synthesis modification of MOFs and the synthesis of MOFs with the other active components have increased the adsorption properties of MOFs. Modified MOFs and composites of MOFs were also used in removal of pesticides from water [127]. Yang et al. studied the modified Cr-based MOF, MIL-101 (Cr), with groups of urea (UR₂) and amino (NH₂) for removing glyphosate (GP) and compared them to (CAC). The amino - and urea-functionalized MOFs showed good adsorption performance due to electrostatic interactions (ESI) between MOFs and GP. At pH 3, the highest

adsorption capacity for $\text{NH}_2\text{-MIL-101 (Cr)}$ was 64.25 mg/g. The adsorption performance of urea-modified MIL-101 (Cr) was lower compared to that of $\text{NH}_2\text{-MIL-101 (Cr)}$ due to steric hindrance [128]. UiO-66 was functionalized with cationic sites NMe_3^+ , which applied in removing a common toxic herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). UiO-66(Zr)- NMe_3^+ exhibited a maximum adsorption capacity (279 mg/g), which was the highest compared to both the pristine UiO-66 and aminated UiO-66. The mechanism of adsorption was ascribed to electrostatic interactions (ESI), the ion exchange sites on UiO-66- NMe_3^+ , and $\pi\text{-}\pi$ conjugation between the linkers in

2,4-D molecules and MOFs, which enhanced the adsorption performance of UiO-66- NMe_3^+ . The UiO-66- NMe_3^+ MOFs possessed shorter equilibrium time, higher adsorption capacity, as well as practicality and good reusability compared with resin materials and activated carbon [129]. Cr-MIL-101 (Cr)-C (1–5) samples were obtained from the modification of MIL-101(Cr) with thiophene or furan (Figure 15), which used to remove gramoxone, diuron (DUR), alachlor (ALA), and tebuthiuron. The MOF samples were able to remove up to 96.9% of herbicides from solution even at very low herbicide concentrations of 30 ppm [130].

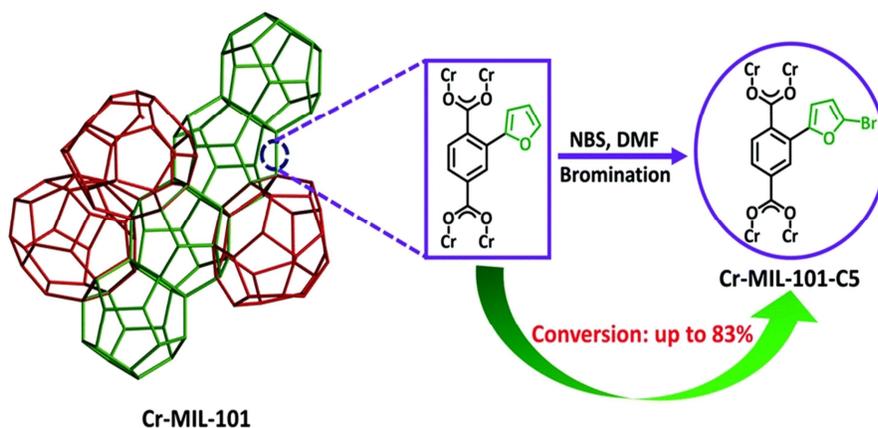


Figure 15: Synthesis of Cr-MIL-101 (Cr)-C5 [130]

MIL-53 (Al) was functionalized with amine group, in which an organic linker was 2-aminobenzene-1,4-dicarboxylic acid ($\text{NH}_2\text{-BDC}$ or aBDC). The formula of $\text{NH}_2\text{-MIL-53 (Al)}$, amino-functionalized MIL-53 (Al), is $\text{Al (OH)[O}_2\text{C-NH}_2(\text{C}_6\text{H}_3\text{)-CO}_2\text{]}$. This material showed noticeable breathing effects with various morphologies. $\text{NH}_2\text{-MIL-53 (Al)}$ had a very high surface area in the range from 180 to 1934 m^2/g . The reports showed that $\text{NH}_2\text{-MIL-53 (Al)}$ had great potential in the field of environmental remediation, which could be used to detect and remove hazardous pollutants including insecticides, herbicides, pharmaceuticals, organic dyes, fluorides, phenols, and heavy metals [131].

Abdelhamed prepared MIL-53(Al) with different ratio amino-group $[\text{Al-(BDC)}_x(\text{BDC-NH}_2)_{1-x}]$, $x = 0.00, 0.25, 0.50, 0.75$ and 1.00. $[\text{Al-(BDC)}_{0.75}(\text{BDC-NH}_2)_{0.25}]$, $[\text{Al-(BDC)}_{0.5}(\text{BDC-NH}_2)_{0.5}]$, $[\text{Al-(BDC)}_{0.25}(\text{BDC-NH}_2)_{0.75}]$ and Al-BDC-NH_2 showed the surface areas (SBET = 866, 1105, 1260, 1100 and 1060 m^2g^{-1}), respectively. These materials were employed to remove dimethoate, organophosphorus insecticides, from an aqueous solution. Al-BDC, [Al-

$(\text{BDC})_{0.75}(\text{BDC-NH}_2)_{0.25}]$, $[\text{Al-(BDC)}_{0.5}(\text{BDC-NH}_2)_{0.5}]$, $[\text{Al-(BDC)}_{0.25}(\text{BDC-NH}_2)_{0.75}]$ and Al-BDC-NH_2 exhibited adsorption capacities of dimethoate insecticide, which were 154.8, 267.2, 513.4, 344.7 and 266.9 mg/g, respectively. The results indicated that the amino group affected the adsorption performance as it improved the ability to adsorb the pesticide. $\text{Al-(BDC)}_{0.5}(\text{BDC-NH}_2)_{0.5}$ showed the highest adsorption capacity, thus it was the best adsorbent Al-MOF ratio for removing the dimethoate pesticide from an aqueous solution. The mechanism of dimethoate uptake was attributed to electrostatic interactions (ESI) and hydrogen bonding (HB) [132]. MIL-53- NH_2 was post-synthetic modified by a diazotization-coupling reaction with anthranilic acid to form MIL-53-AZA. MIL-53-AZA-La and MIL-53-AZA-Ce were synthesized from the incorporation of La^{3+} and Ce^{3+} into the MIL-53-AZA framework. The as-prepared MOFs were used to adsorb and remove carbofuran from aqueous solution. The highest adsorption capacities for MIL-53- NH_2 , MIL-53-AZA, MIL-53-AZA-Ce, and MIL-53-AZA-La were 367.87, 433.50, 610.23, and 635.05

mg g⁻¹, respectively. MIL-53-AZA-La showed excellent reusability and good stability. The adsorption mechanism of carbofuran on MIL-53-MOFs attributed to π - π stacking interaction, hydrogen bonding, and coordination bonding [[133].

4.3.2. Composites based MOFs for pesticides removal

UiO-66(Zr) was deposited on ionic liquid-modified chitosan (ILCS), which obtained a powder material, ILCS/U-X. ILCS/U-X materials were used to remove organic herbicides (2,4-D) from the aqueous solution. The results exhibited that the large adsorption capacity of ILCS/U-10 was 893 mg/g with fast complete adsorption within 60 min due to the existence of O-containing groups in MOF. A powder adsorbent, ILCS/U-10, had good stability and reusability. Adsorption was ascribed to electrostatic interactions (ESI) and hydrogen bonding (HB) [134]. The UiO-67/GO nanocomposite was prepared by combining UiO-67 (Zr) and graphene oxide, which was used for glyphosate (GP) adsorption. At pH 4, the highest adsorption capacity of GP on UiO-67/GO was 482.69 mg/g, which exceeds that of other GO-based adsorbents. UiO-67/GO composites showed improved adsorption capacity for glyphosate due to the large surface of available GO and the abundant Zr single bond OH groups on the GO surface [135].

Various proportions (20-60%) of Cu-BTC were incorporated into cellulose acetate (AC), which obtained Cu-BTC @ cellulose acetate compounds. The authors applied Cu-BTC@Ac in the uptake removal of dimethoate. Cu-BTC@AC showed a higher adsorption capacity (282.3 - 321.9 mg/g) compared to the CA membrane (207.8 mg/g)(Figure 17). 40% Cu-BTCAC accelerated adsorption by a factor of 2.1. After 5 cycles, the efficiency of adsorption was reduced by 22.5, so the composite membrane had a good reusability. Adsorption might occur due to HB, ESI, and coordination bonding between dimethoate molecules and Cu-BTC@AC active sites [136]. Abdelhamed et al. prepared Cu-BTC@cotton composite and applied this composite to adsorb ethion from water with removal 97%. Cu-BTC@cotton composite showed the maximum sorption capacity of 182 mg/g. The adsorption process remained virtually unchanged for up to five cycles of reusability. The adsorption performance of composite was demonstrated by the coordination bond between sulfur atom in ethion and copper atom in MOF and HB by available cellulose functional groups [137]. Su et al. prepared and used cotton@UiO-66 to extract some phenoxy herbicides such as 4-chlorophenoxyacetic acid, dicamba, 2,4-dichlorophenoxyacetic acid (2,4-D), and 2-(2,4-dichlorophenoxy) propionic acid [138].

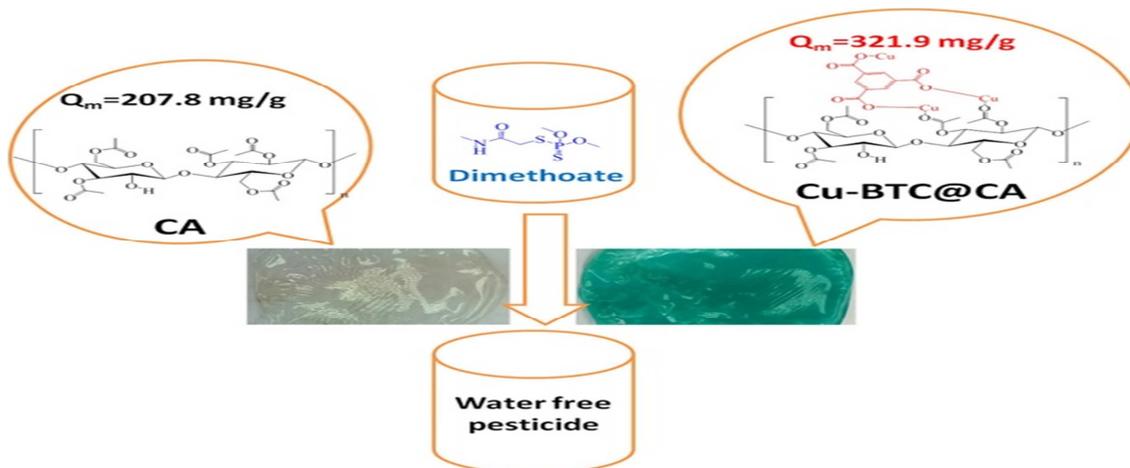


Figure 16: Removal of dimethoate by Cu-BTC@Ac [136]

Recently, magnetic separation approach has been widely used in the fields of separations and adsorptions [139]. The M-MOF magnetic nanocomposite was synthesized from Fe₃O₄-graphene (GO)-cyclodextrin oxide (β -CD) as the magnetic core and support, and copper-based MOF. This nanocomposite had a high Brunauer-Emmett-Teller

(BET) surface area (250.33 m² g⁻¹) and thus enhanced its the adsorption performance. The M-MOF was used to adsorb and remove neonicotinoid insecticide such as clothianidin, thiamethoxam, nitenpyram, acetamiprid, imidacloprid, thiacloprid, and dinotefuran from aqueous solution. M-MOF was able to quickly separate from water samples due to its

large BET surface area and high super-paramagnetism. Additionally, the rate and adsorption capacity of M-MOFs for neonicotinoid insecticides were significantly improved by supramolecular recognition of Fe₄O₃-GO-β-CD and hydrophobic inner cavities. M-MOF exhibited a significant capability for adsorbing neonicotinoid pesticides, according to the adsorption experiments [140]. ZIF-8(Zn) was deposited on magnetic multiwalled carbon nanotubes (MWCNTs) through coordination polymerisation, which produced the functional magnetic composite (M-M-ZIF-8). ZIF-8 particles coated on the surface of the magnetic MWCNTs caused M-M-ZIF-8 to exhibit super-paramagnetism, porous structure, and a high specific surface area. The hybrid composite (M-M-ZIF-8) was effective in the adsorption and removal of eight organophosphorous (OPPs) pesticides (i.e; isazofos, phosalone, triazophos, ethoprop, methidathion, diazinon, profenofos, and sulfotep) from soil and environmental water samples. In particular, the use of M-M-ZIF-8 (15 mg) as an adsorbent achieved a removal efficiency of 96%. M-M-ZIF-8 had large uptake capacity of eight OPPs due to its large surface area and porosity. Moreover, five cycles of absorption-desorption could be performed using M-M-ZIF-8, indicating that it has good performance and stability. The researchers claimed that the potential mechanism of organophosphorous adsorption was valence-electron-driven, where the electrons shared or exchanged between the vacant active sites of the M-M-ZIF-8 composite and the molecules of organophosphorous (OPPs) pesticides [141].

The magnetic hybrid adsorbent [Fe₃O₄@SiO₂@UiO-67 (Zr)] was prepared by applying the method

of layer-by-layer assembly, which was used to recognise, detect and remove glyphosate. This adsorbent showed significant detection and adsorption performance with maximum adsorption capacity (256.54 mg g⁻¹), a LOD (0.093 mg L⁻¹) and good recyclable for glyphosate. The produced adsorbent has Zr-OH groups with strong affinity for phosphate groups, which gave it higher adsorption capacity and selective recognition for glyphosate. Additionally, the use of Fe₃O₄ as the magnetic core of this adsorbent facilitated the removal and separation process using an external magnetic field [142]. Lie et al. prepared double magnetic layer metal-organic framework (M-ZIF-8@ZIF-67) from single layer Fe₃O₄-ZIF-8 as magnetic core and covered by an outer layer of ZIF-67 (Figure 17). M-ZIF-8@ZIF-67 was used as an adsorbent to adsorb and remove fipronil, fipronil sulfide, fipronil desulfiny, and fipronil sulfone from cucumber and environmental water samples. The adsorption experiments showed that the adsorption capacity of M-ZIF-8@ZIF-67 was high for fipronil and its metabolites, while more than 95% of the target was adsorbed and removed in cucumber and water samples. [143]. CaF MOF was prepared and used to remove the highly used pesticide, imidacloprid, by Singh et al. This adsorbent exhibited the high adsorption capacity of imidacloprid (467.23 mg/g) and reusability for 5 cycles without noticeably loss in adsorption capacity. The results indicated that the CaF MOF removal efficiency of imidacloprid reached 98.3% in 70 minutes. CaFu MOFs showed excellent ability for the removal of toxic pollutants due to its properties such as better surface area, stability, high porosity, and easily accessible active functional sites [144].

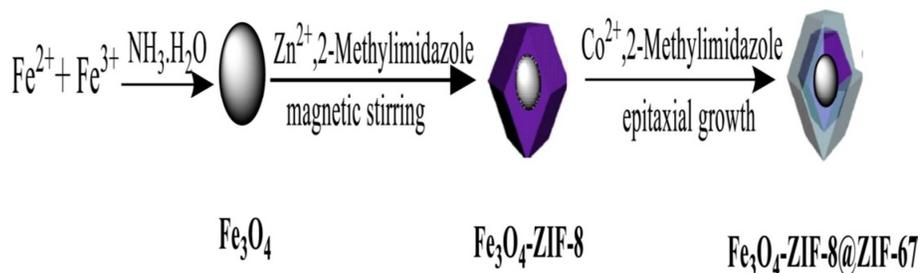


Figure 17: Synthesis of M-ZIF-8@ZIF-67 [143]

MOFs nanoparticles are effective in removing pesticides from the environment. However, the use of MOFs as adsorbents poses environmental risks such

as their leakage into the environment and their accumulation in living organisms. In which, direct exposure to the environment by MOFs nanoparticles may contaminate drinking water. Additionally,

accumulation of MOFs or their dissociated metal ions (Cr^{3+} , Zr^{4+} , etc.) in organisms lead to affect human health, long-term environmental nano-toxicity, and heavy metal pollution problems. Therefore, Liang et al. proposed a novel idea to mitigate the risks of using MOFs, which involved incorporating two MOFs (UiO-66-NH_2 or ZIF-8) with nano-carbon aerogels (MPCA) via in situ nucleation. MOFs@MPCA aerogels were applied in removing herbicides, alachlor and chipton, with stronger adsorption capacity than that of MOF. The UiO-66-NH_2 @MPCA composite exhibited the equilibrium chipton adsorption capacity (227.3 mg/g) and was reusable for five cycles without significant loss of adsorption performance. The adsorption of chipton might be explained by electrostatic interactions (ESI), hydrogen bonding (HB), and π - π stacking, whereas that of alachlor explained by hydrogen bonding (HB), and π - π stacking [145].

Bhadra et al. prepared MOF-74(Zn)-derived carbon (CDM-74) from pyrolysis of Zn-based MOF-74. CDM-74 was used to absorb and remove N, N-diethyl-3-methylbenzamide (DEET) insecticide and the other four contaminants. This adsorbent exhibited the highest adsorption capacity (340 mg/g) of DEET insecticide from water because of its large mesopore volume and density of acidic sites. Furthermore, CDM-74 was reused for 4 cycles without any change in the adsorption performance, which confirmed its efficacy in desorption of pesticides from water [146]. β Liu et al. used β -cyclodextrin MOF (β -CD MOF), that served both as precursor and potassium source, to synthesize a multifunctional porous carbon. The prepared β -CD MOF-NPC was equipped with microporous structure, rich potassium content, and high surface areas, which applied in removing amide herbicides. The results indicated that β -CD MOF-NPC possesses effective ability to remove four amide herbicides from water. The adsorption might occur through hydrogen bonding (HB), electrostatic interaction (ESI), and π - π interactions [147].

The Fe (III) modified-MOF-5 was pyrolyzed to obtain MOF-derived magnetic porous carbon with core-shell structure. The obtained Magnetic porous carbon sorbent (MPCs) was used to remove atrazine (ATZ) from water [148]. Ahmed et al. prepared two porous carbons materials from high temperature pyrolysis of ZIF-8 with or without modification. The MOF-derived carbon (MDC) was synthesized from carbonization of ZIF-8 , whereas the IL@MOF-derived carbon (IMDC) was synthesized from carbonization of IL@MOF, where ZIF-8 was introduced into ionic liquid (IL). The authors used MOF-derived carbons (MDCs), IL@MOF-derived

carbons (IMDCs) and activated carbon to remove atrazine (ATZ). The modification or conversion of metal-organic frameworks (MOFs) to MOF-derived carbons (MDCs) or IL@MOF-derived carbons (IMDCs) enhanced the performance of adsorption for removal atrazine (ATZ) and diuron (DUR). IMDC showed the highest absorption capacity of atrazine (208 mg/g), compared to MDC (173 mg/g) and activated carbon (60 mg/g). Therefore, IL@MOF-derived IMDCs could have different applications based on mesoporosity, high porosity, functional groups, and high nitrogen content [149]. In another study, IL@ ZIF-8 -derived carbon (IMDC) was also used for removing toxic herbicides, 2,4-dichlorophenoxyacetic acid (2,4-D) and diuron [3-(3,4 dichlorophenyl)-1,1-dimethylurea], DUR, from water. The highest adsorption capacities of IMDC for 2,4-D and DUR were 448 and 284 mg/g, respectively. The efficiency of IMDC adsorption might be because of its relatively high porosity and many active sites on its surface due to nitrogen doping. The authors proposed the adsorption mechanism of IMDC attributed to HBI, HB, and π - π interactions [150]. ZIF-67 (Co) was carbonized to obtain magnetic nanoporous carbon (MNPC) with super paramagnetism, large pore volume and high surface area. The cobalt-based magnetic nanoporous carbon (Co-MNPC) was applied to eliminate some neonicotinoid insecticides from water and watermelon samples. The results showed that Co-MNPC has a good adsorption capability [151].

Fe_2O_3 nanoparticles was added into a reaction solution containing MIL-53 (Al) to obtain MIL-53(Al)/ Fe_2O_3 nanocomposite. This nanocomposite was used to extract six organophosphorus compounds (i.e: disulfoton, diazinon, malathion, parathion, chlorofenvinphos, and phorate) from grape juice, tea, and river water samples. The results indicated that the ability of the MIL-53(Al)/ Fe_2O_3 nanocomposite to extract OPPS was high [152]. Lu et al. synthesized Fe_3O_4 @ZnAl-LDH@MIL-53(Al) composite through three-step process, which was used to adsorb and remove azole fungicides (i.e: triadimefon and epoxiconazole) from environmental water. Fe_3O_4 @ZnAl-LDH@MIL-53(Al) composite showed the maximum adsorption capacity for triadimefon (43.54 mg/g) and epoxiconazole (71.79 mg/g). Furthermore, the adsorption process of azole fungicides reached equilibrium within 5 minutes, which was exothermic and spontaneous. The mechanism of adsorption for azole fungicides ascribed chemisorption, hydrogen bonding interaction, and π - π interaction [153].

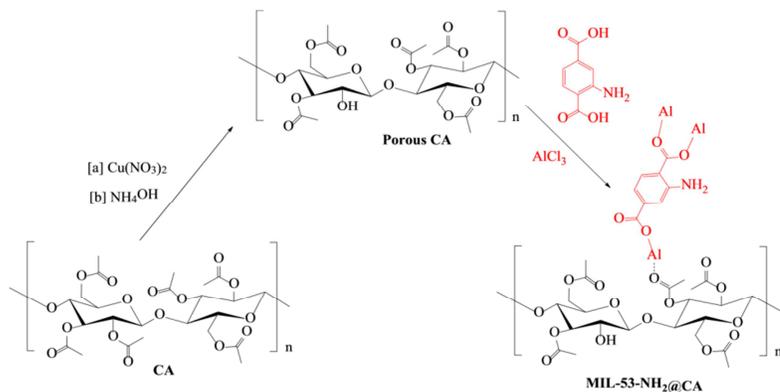


Figure 18: The synthesis of MIL-53-NH₂@CA [154]

To remove Chlorpyrifos organophosphorus pesticide, different ratio of MIL-53-NH₂ (20-60 %) was incorporated with porous cellulose acetate (CA) memberen (Figure 19). The adsorption capabilities of 20% MIL-53-NH₂@CA, 40% MIL-53 NH₂@CA, and 60% MIL-53- NH₂@CA were 207.62, 285.37, and 356.34 mg/g, respectively, which were higher than those of CA (160.36 mg/g) (Figure 20). The results indicated that the adsorptive removal rate of chlorpyrifos fastened by factor of 2.2 in case of Impregnation of 60% MIL-53-NH₂. MIL-53-NH₂@CA showed good recoverability and reusability due to only 27.9% reduced adsorption capacity after 5 cycles. The adsorptive removal of chlorpyrifos pesticides might occur via coordination, hydrogen bonding, and π - π interactions [154]. Isaeva et al. synthesized MIL-53 (Al), NH₂-MIL-53, and three MIL-53 (Al) types of materials under microwave (MW) irradiation. The three MIL-53 (Al) types of materials MixL1, MixL2 and MixL3, were prepared from Al⁺³ ions and mixed linkers (MixLR) of

benzene-1,4-dicarboxylic acid (bdc) and 2-aminobenzene-1,4-dicarboxylic acid (abdc) in three different proportions. The ratios of bdc and abdc linkers used in synthesis of MixL1, MixL2, and MixL3, were 1:1, 1:3, and 3:1, respectively. All MIL-53 (Al) type materials were applied in adsorptive removal of 2,4-D herbicide. Compared with matrix activated carbon (CSAC), the MIL-53(Al)-type materials exhibited much high 2,4-D adsorption rates. NH₂-MIL-53(Al) showed an adsorption capacity (~250-240 mg/g) lower than that of the MIL-53(Al) and MixLR materials (over 300 mg/g) due to differences in the porous structures. In particular, the mesopore fraction in NH₂-MIL-53(Al) sample was order lesser than mesopore content in the samples of MIL-53(Al) and MixLR. The as-prepared MIL-53 (Al) type materials were tested for a long time of up to 225 hours without any loss in adsorption capacity. Moreover, the MIL-53(Al) framework was more flexible than the NH₂-MIL-53(Al) network [155].

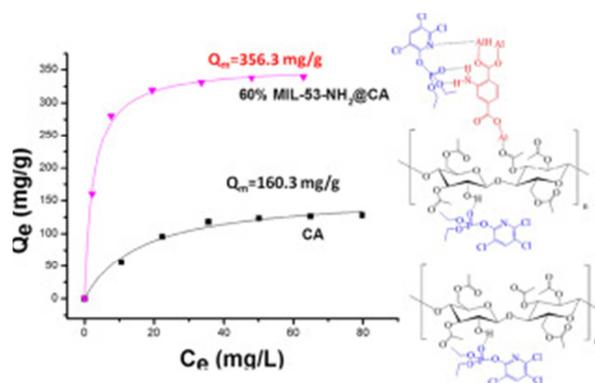


Figure 19: The maximum adsorption capacity of chlorpyrifos onto MIL-53-NH₂@CA [154]

MIL-53- NH₂ was functionalized with phthalic anhydride to form the modified material, MIL-53-NH-ph. Then, MIL-53-NH-ph was reacted with iron,

zinc, and copper salts to form the complexes, MIL-53-NH-ph-Fe, MIL-53-NH-ph-Zn, and MIL-53-NH-ph-Cu, respectively. The modified materials, MIL-

53-MOFs, were used to adsorb and remove carbofuran from wastewater. The adsorption capacities of MIL-53- NH₂, MIL-53-NH-Ph, MIL-53-NH-Ph-Fe, MIL-53-NH-Ph-Zn, and MIL-53-NH-Ph-Cu were 367.8, 462.1, 662.94, 717.6, and 978.6 mg g⁻¹, respectively. The results showed that the ability of the adsorbent to remove the carbofuran increased after the modification (Figure 20). This confirms that the post-synthetic modification improved the adsorption properties. The adsorption mechanism of carbofuran on MIL-53-MOFs might be ascribed to π - π stacking interaction, hydrogen bonding, and coordination bonding [156]. Njaramba et al. prepared MOF-alginate composite beads (CA-MIL-53-AC) from calcium chloride (complexing agent) and sodium alginate (gelling agent). CA-MIL-53-AC was used to remove dichlorodiphenyltrichloroethane (DDT) in aqueous solution. This adsorbent exhibited superior adsorption performance for DDT (5.29 mg/g), compared with pristine CA, granular AC, CA-AC, and CA-MIL-53.

The behaviour of adsorption for DDT was very favorable, exothermic, and spontaneous based on thermodynamics calculations. The mechanisms of DDT removal by CA-MIL-53-AC were attributed to hydrogen bonding, ion exchange, hydrophobic, π - π interactions, and surface complexation [157-158].

In summary, functionalized MOFs and composites of MOFs have effective ability to remove pesticides from water because of their sufficient adsorption sites. Especially, MOFs synthesized with cationic or anionic active sites can be suitable for removing cationic or anionic, respectively, pesticides from water due to electrostatic interactions (ESI). As well, the reports indicated that MOFs composite are effective in the removal non-ionic pesticides due to hydrogen bonding interaction, π - π stacking, and active sites for coordination. Furthermore, MOFs comprising magnetic materials showed good reusability as the adsorbents can be easily separated from the solution using a magnetic field [127].

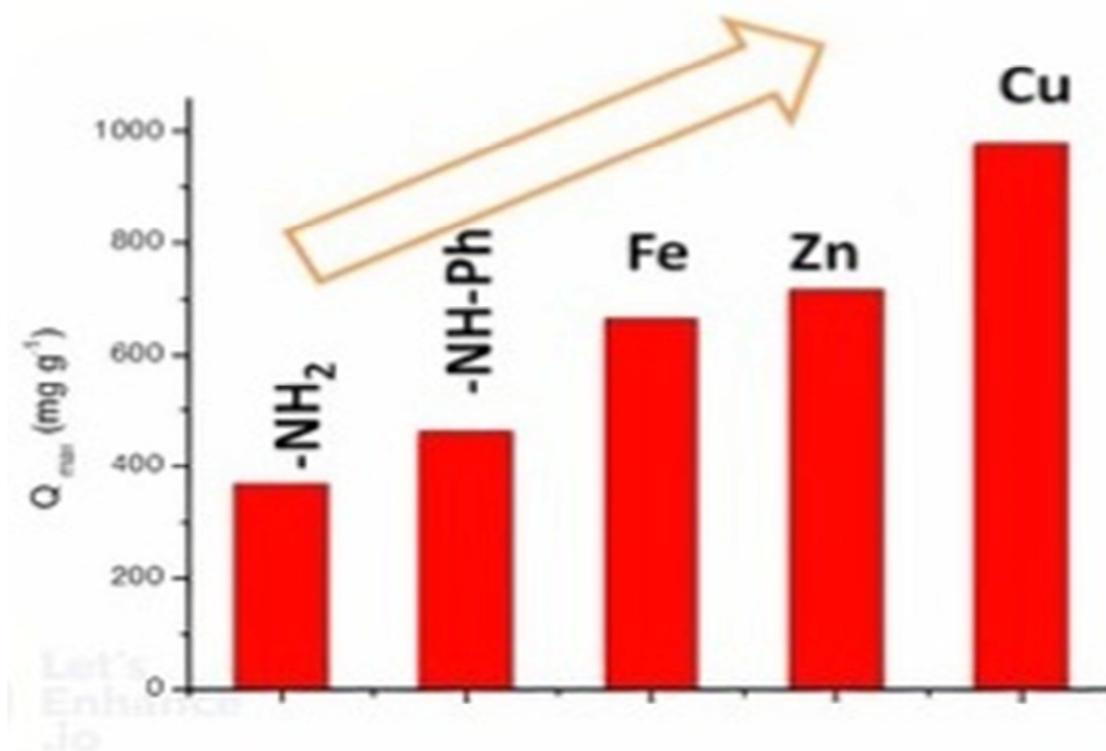


Figure 20: The adsorption capacity increased after the modification [156]

Table 4
Removal of pesticides by MOFs

MOF	Pesticide	Adsorption capacity mg/g	Reference
MIL-53 (Cr)	2,4-D	556	114
UiO-67 (Zr)	Glyphosate Glyphosinate	537 360	117
UIO-67	Metrifonate Dichlorvos	378.78 571.43	119
ZIF-67 (Co)	Ethion Prothiofos	210.8 261.1	123
ZIF-8 (Zn)	Ethion Prothiofos	279.3 366.7	123
Cu-BTC	¹⁴ C-ethion	122	124
MIL-53(Al)	Metolachlor	241.62	126
NH2-MIL-101 (Cr)	Glyphosate	64.25	128
UiO-66(Zr) NMe ³⁺	2,4-D	279	129
UiO-67/GO	Glyphosate	482.69	135
Cu-BTC@Ac	Dimethoate	282.3 - 321.9	136
Cu-BTC@cotton	Ethion	182	137
Fe ₃ O ₄ @ SiO ₂ @ UiO-67 (Zr)	Glyphosate	256.54	142
CaF MOF	Imidacloprid	467.2	144
UiO-66-NH ₂ @MPCA	chipton	227.3	145
IL@ZIF-8-derived carbon	2,4-D Diuron	448 284	150

5. Comparison between MOF- based materials and other adsorbents for the adsorption of pesticides

Various MOFs and activated carbon (AC) were used to remove pesticides. The adsorption capacity of both was compared. The results showed that MOFs have higher adsorption capacity than AC [127]. As shown in Table 5, MOFs performed much better than conventional adsorbents in adsorbing various pesticides. For example, different functional Cr-based MOFs, MIL-101(Cr), NH₂-MIL-101(Cr), UR₂-MIL-101(Cr), were used as adsorbents materials for glyphosate and compared with CAC. All MOFs

exhibited the highest adsorption capacities compared to CAC [128]. Similarly, the 2,4-D adsorption capacity of MIL-53(Cr) was about twice that of AC [114]. The adsorption rate of UiO-66 for MCPP was a very high, in which the kinetic constant was ~30 times that of AC. The adsorption capacity over UiO-66 was 7.5 times that of AC at 1 ppm of MCPP [118]. Moreover, CDM-74 showed good performance to remove DEET from water with adsorption capacity around 4 times that of AC [146]. The photodegradation of pesticides with MOFs was investigated [159-162].

Table 5

Comparison between activated carbon and various MOF-based adsorbents for pesticides removal

MOF based adsorbents	Pesticide	Maximum adsorption capacity mg g ⁻¹ of MOF (Q°)	Maximum adsorption capacity mg g ⁻¹ of AC (Q°)	Ratio of Q°	Reference
MIL-53 (Cr)	2,4-D	556	286	1.9	114
UiO-66 (Zr)	MCPP	370	303	1.2	118
MIL-101(Cr), NH ₂ -MIL101 (Cr), and UR ₂ -MIL-101(Cr)	Glyphosate	33.81 37 25.36 mmol/g	16.91 mmol/g	1.99 2.2 1.5	128
UiO-66(Zr)- NMe ₃ ⁺ , UiO-66(Zr)- NH ₂ , and UiO-66(Zr)	2,4-D	279 222 179	182	1.53 1.2 0.98	129
MDC	Atrazine	173	60	2.88	149
IMDC		208		3.4	

6. Conclusion

Pesticides cause pollution of water, soil and plants, which negatively affects living organisms. Hence, removal of pesticides is essential. Various methods such as biological, chemical and physical treatment are used to remove pesticides. MOFs have excellent properties that allow them to be used in many applications. They are widely used to remove pesticides. The applications of MOFs as sensors and

as stationary phase extraction for the detection and removal of pesticides are described in this review. MOFs have shown improved performance for sensors and extraction modes. Moreover, the use of MOFs as adsorbents in the removal of pesticides. The modification of MOFs improved the adsorptive removal of pesticides. Compared with other adsorbents, MOFs showed superiority in removal.

7. References

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