Review Article

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Cutting-edge metal-organic frameworks: revolutionizing the adsorptive removal of pharmaceutical contaminants from water

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Abstract: Water is a basic unit for survival of living creature and over the past few years, increased industrialization and urbanization caused a huge contamination of natural water resources. Major water contaminants are pharmacological-wastes, especially antibiotics from hospitals and pharmaceutical industries which causes water pollution. Pharmacological contaminants elimination from ecosystem is very critical environmental challenge because they are persistent and cause potential health hazards. Owing to high surface area, tunable-porosity, and versatile functionality of Metal-Organic Frameworks (MOFs), and their composites have emerged as promising materials for water purification. Various antibiotics including amoxicillin, doxycycline, levofloxacin, and ciprofloxacin are successfully removed from wastewater using MOFs and composites, which purifies the water by adsorption-mechanism. This study reviews the advanced progressions in the application of MOF-based composites and MOFs for the adsorption of pharmaceutical pollutants. Additionally, plant-based MOFs have been explored for their eco-friendly and cost-effective potential in pharmaceutical pollutant removal. Despite these advancements, challenges such as the scalability of MOF synthesis, stability under operational conditions, and potential toxicity need to be addressed for their commercial application. Future research should focus on optimizing the synthesis processes, enhancing the recyclability of MOFs, and conducting long-term environmental-impact assessments to ensure sustainable and effective water treatment solutions.

Keywords: MOFs; composites; pharmaceutical pollutants; water purification; adsorption

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Abbreviation Table

MOF	Metal organic frameworks
DNA	Deoxyribose nucleic acid
AC	Activated carbon
UiO	University of Oslo
GO	Graphene oxide
rGO	Reduced graphene oxide
ZIF	Zeolitic imidazolate frameworks
Rh B	Rhodamine B
HQ	Hydroquinone
CIP	Ciprofloxacin
OCD	Obsessive compulsive disorder
CBZ	Carbamazepine
NFX	Norfloxacin
IBP	Ibuprofen
KTF	Ketoflurbrufen
ATNL	Atenolol
OFX	Ofloxacin
COPD	Chronic obstructive pulmonary disease
ATZ	Atrazine
MTZ	Metronidazole
DFN	Diclofenac
MIL	Material Institutes Lavoisier
HKUST	Hong Kong University of Science and Technology

DOX	Doxycycline
CA	Clofibric acid
WWT	Wastewater treatment
NSAID	nonsteroidal anti-inflammatory drugs
TC	Tetracycline
CNT	Carbon nanotube
UV light	Ultraviolet light
BTC	Benzene tricarboxylic acid
UTI	Urinary tract infection
RTI	Respiratory tract infection
SSTI	Skin and soft tissue infections
GTI	Gastrointestinal tract infection
STI	Sexually transmitted infection
FQ	Flouroquinone
CNS	Central nervous system
PSO	Pseudo second order
PFO	Pseudo first order
LM	Langmuir model
FM	Freundlich model
EDTA	Ethylene diamine tetra acetic acid
CD	Cyclodextrin
LOFX	Levofloxacin
HPLC	High pressure liquid chromatography
AMX	Amoxicillin
RO	Reverse osmosis
RE	Removal efficiency
PCM	Paracetamol
CBZ	Carbamazepine

1 Introduction

Water is crucial for the survival of all living organisms, with the human body comprising approximately two-thirds water, essential for its existence.[1] Water is a fundamental necessity for all life forms. However, rapid industrial advancement has led to the discharge of contaminants into water bodies at high concentrations, significantly degrading water quality. Clean and pure water is vital for living beings. Although water covers a minimum of 1 % and a maximum of 71 % of the Earth's surface, its poor quality often renders it undrinkable according to global standards due to various pollutants.[2] Water pollution is a growing worldwide problem, disturbing both developing and developed countries, and directly impacting life sustainability on Earth. Poor water quality is responsible for approximately 14,000 deaths per day.[3] Pollutants, which cause undesirable and harmful effects, come in various forms, including atmospheric pollutants, chemical pollutants, herbicides and pesticides, pathogens, and antibiotics. These pollutants degrade water quality, directly and indirectly affecting the lives of living organisms.[4] This pollution, including heavy metals, pharmaceutical waste, and non-biodegradable plastics, leads to habitat degradation.[5] Pharmaceutical contamination, originating from pharmaceutical industries, hospitals, and other medical facilities, is often improperly disposed of into water reservoirs, exacerbating the problem (Figure 1).

A survey was conducted in 2001, which showed that 86 tons of acetyl-salicylic acid, 62 tons of paracetamol, 517 tons of antidiabetic drugs made inGermany and Britain, respectively.[6] Pharmaceutical compounds in waster caused indirect effects such as lowering agricultural land productivity and land infrastructure and killing large numbers of aquatic lives. Direct effects include respiratory disorders, reproductive issues, cancer and congenital problems.[7,8] The steroid estrogen sample uses in the female tablet, ethylene

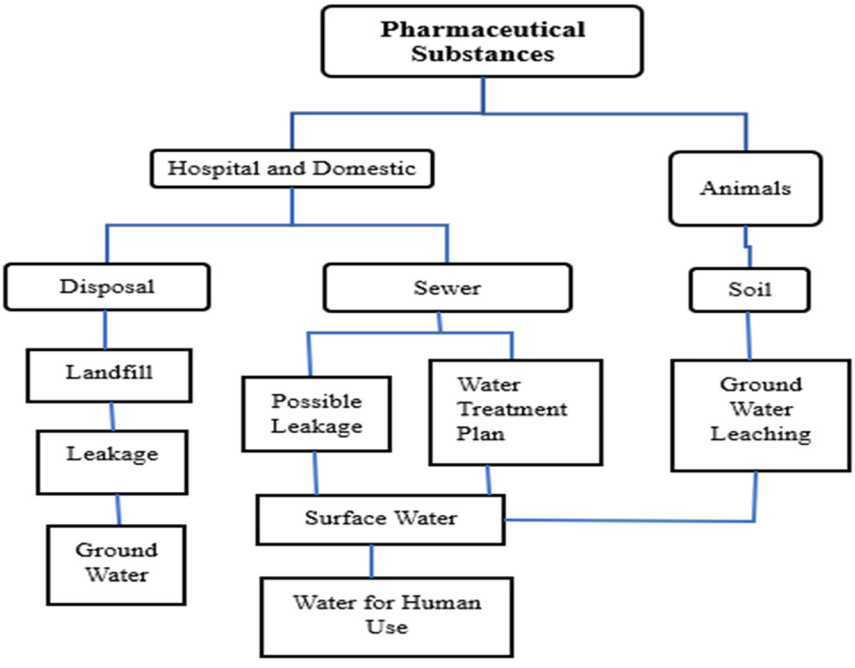


Figure 1: Sources of pharmaceutical waste contamination to clean water.

estradiol amalgams were finally discharged into the environment causing polluted wastewater. The safe modulating agents and antineoplastic were cautious about genotoxic consequences e.g. damage DNA and caused cancer.[9,10]

Pharmaceutical waste is removed using different techniques including membrane technology using ultrafiltration membrane bioreactor,[11] anaerobic treatment,[12] electrochemical treatment, activated sludge method, advance oxidation method, microalgae treatment, adsorption method.[13] Membrane fouling is a significant issue, leading to reduced efficiency and increased maintenance costs.[14] Anaerobic treatment processes are generally slow and require long retention times, making them less efficient for rapid waste removal.[15] In electro-chemical treatment high energy consumption is a major drawback, making this method expensive and less sustainable for large-scale applications.[16] Activated sludge method produces a significant amount of sludge that requires further treatment and disposal, adding to the overall cost and environmental burden. In advanced oxidation method the formation of potentially detrimental by-products through the oxidation method can pose additional environmental and health risks. Microalgae treatment procedure is extremely relied on environmental circumstances like as light and heat, which can be difficult to control consistently. Among these techniques adsorption is often preferred for elimination of pharmacological waste. Adsorption techniques efficiently eradicate extensive variety of pharmaceutical chemicals from water, as well as those present at low concentrations.[16] The adsorption process is relatively simple to implement and can be profitable related to other dealing methods. It can be used for a variety of purposes because it doesn't require a complicated infrastructure or large energy inputs.[14] Adsorbents in adsorption can be made to target particular pollutants by altering their surface characteristics. This adaptability makes it possible to remove a variety of medicinal substances effectively.[16] Since many adsorbents may be recycled and used again, the treatment procedure is low-cost and less of an impact on the environment.[15] Adsorption methods often use environmentally friendly materials, such as activated carbon, biochar, and other natural adsorbents, which minimize secondary pollution and are safer for the environment.[17] Adsorption systems is easy to operate to meet the needs of different dealing capacities, from small-scale applications to large industrial processes.[14] These advantages make adsorption a preferred choice for elimination of pharmacological pollutants from water-bodies, offering an effective, economical, and environmental friendly solution.

Metal organic frameworks (MOFs), activated carbon (AC) and AC-based adsorbents, zeolites, silica, sludge-derived adsorbents, and biopolymer–supported metal composites etc. are different adsorbents which are extensively applied for adsorption of water pollutants.[18] Among these adsorbents MOFs are considered superior adsorbents as compared to activated carbon, zeolites, silica, sludge-derived adsorbents, and biopolymer-supported metal composites because of their exceptionally greater surface to area ratio, high porosity, as well as versatile functionalization, which made them highly effective for adsorption of various water contaminants.[18–24] Examples of simple MOFs include Zr metal MOF (UiO-66) known for its high stability and large surface area, which is effective in adsorbing various organic pollutants.[25] Another example is ZIF-8 MOF having excellent chemical stability as well as high surface area, commonly used for elimination of variety of water contaminants including pharmaceutical and organic waste as well as toxic metals.[26] In addition to simple MOFs, MOF composites have been developed to improve adsorption and degradation performance. For instance, the Bi_2WO_6/UiO-66 composite combines bismuth tungstate with UiO-66, enhancing Vis-light photocatalysis for organic dyes like Rhodamine B.[25] Another example is the GO/MOFs composites, where graphene oxide is combined with MOFs such as Zr/Fe-MOFs, showing high efficacy in removing organic pollutants like tetracycline hydrochloride and orange II from wastewater.[27] Additionally, HBP@MOF composites, which incorporate hybrid bromide perovskites within ZIF-8, demonstrate high stability and efficiency in degrading toxic organic pollutants under various conditions.[28] Furthermore, cellulose-MOF composites, where MOFs are incorporated into cellulose materials such as aerogels and membranes, with enhanced adsorption and photocatalytic degradation of metals, dyes, drugs, and antibiotics.[29]

The purpose of this study is to analyze different methodologies for the removal of pharmaceutical waste from contaminated water using metal organic frameworks and their adsorption mechanism.

1.1 Classification & environmental hazards of pharmaceuticals

Pharmaceuticals are classified based on their therapeutic use, chemical composition, and the way they act in the body. These categories cover medications for treating infections, reducing pain and inflammation, managing mental health, and combating viral diseases. Pharmaceutical materials classified as antibiotics, analgesics, antidepressants, anti-inflammatory, lipid Regulator, anti-convulsant, sunscreens, antimicrobial, steroids, herbicides, antipyretics, and antivirals, pesticide and other pharmaceutical compounds

Table 1: Classification of Pharmaceutical and their major medicinal role.

Classes	Role	Examples	Ref.
Antibiotics	Inhibit microbial growth	CIP, NFX	30
Antidepressants	Treat (OCD) obsessive- compulsive disorder	CBZ, antipyrine	31
Anti-inflammatories	Reduce inflammation and pain, control fever	IBP, KTF	32
Lipid regulator	Treat cholesterol levels	Feno fibric acid, ATNL	33
Anti-convulsant	Treat bipolar disorder and anxiety	CBZ	34
Sunscreens	Prevent sunburn	Octyl methoxycinnamate, oxy benzene	35
Antimicrobial	Treat infections	OFX	36
Steroids	Cure COPD (chronic pulmonary disease)	Dexamethasone	37
Herbicides	Control undesired plants in fields	Atrazine, simazine	38
Pesticides	Control pets and disease carriers	DZN	39

(hydroquinone, fluoxetine, etc.). Table 1 also gives classification and their applications of pharmaceutical medicines.

The pharmacological pollutants in water may have two origins: (i) engineering procedure in industries (ii) usage of pharmaceutics[40] and pharmaceuticals are classified into various categories based on their therapeutic uses, including antibiotics, antineoplastic, cardiovascular drugs, and sex hormones. These classifications help in understanding their specific environmental hazards. For instance, antibiotics can lead to the development of antibiotic resistant bacteria, while antineoplastic, used in cancer treatment, can disrupt DNA replication and cell division in non-target organisms.[41]

Cardiovascular drugs and sex hormones can also have significant ecological impacts, affecting aquatic life and potentially leading to endocrine disruption.[42] The environmental hazards of pharmaceuticals are a growing concern due to their persistence and bioaccumulation in aquatic environments. Pharmaceuticals such as paracetamol, methotrexate, salicylic acid, and clofibrinic acid have been shown to exhibit varying degrees of toxicity towards algae, daphnia, fish embryos, and other aquatic organisms.[43] These substances can enter water bodies through excretion, improper disposal, and industrial waste, leading to contamination of water.[44]

The occurrence of pharmaceuticals in ecosystem poses significant hazards, including the potential for chronic exposure to low concentrations of these compounds, which can lead to adverse effects on wildlife and human health. For example, anticancer drugs have been identified as particularly hazardous due to their potent biological activity and potential to induce cell apoptosis in non-target species.[45] Additionally, the mixture of pharmaceuticals in water bodies can result in complex interactions and cumulative effects that are difficult to predict and manage.[46] To mitigate these risks, it is essential to develop and implement effective environmental risk assessments and treatment methods tailored to the specific properties and behaviors of pharmaceutical pollutants. This includes advanced treatment technologies and strategies for reducing pharmaceutical discharge into the environment.[47] Overall, we can conclude that pharmaceuticals can pose significant environmental hazards when they enter into the ecosystems. These substances often reach water bodies through improper disposal, excretion from humans and animals, or manufacturing runoff. Antibiotics, for instance, can disrupt microbial communities in soil and water, leading to antibiotic resistance. Hormonal drugs, such as birth control pills, can affect aquatic life by altering reproductive systems. Painkillers and anti-inflammatory drugs may cause harm to fish and other wildlife, disrupting natural processes and leading to ecosystem imbalances. In the environment, pharmaceuticals can persist, degrade into harmful byproducts, or bioaccumulate in organisms, leading to long-term ecological and health risks. Antibiotics were known as chemical actuality and were commonly applied in medical treatment. Animals and human beings absorbed 30 % of the antibiotic.[48] When antibiotics were not used properly which caused the severe health problems and could be released to marine environment. This was needed to remove pharmaceutical wastes, especially medication like antibiotics, from contaminated and the wastewater.[49] Antibiotics such as ciprofloxacin can lead to significant changes in the gut microbiome of fish and other aquatic species and human beings, which may affect their immune response. High concentrations of acetaminophen can cause liver damage in fish and humans, disrupting their ability to detoxify their environment. Diclofenac has been linked to the near-extinction of vulture populations in South Asia due to kidney failure.[50] Ethinylestradiol, found in birth control pills, can cause intersex conditions in fish, where males develop female characteristics, leading to population declines.[51] Cyclophosphamide and other chemotherapy

Table 2: Expanded comparison chart: classification of pharmaceuticals & their environmental hazards.

Pharmaceuticals	Examples	Pathway to ecosystem	Environmental impact	Affected ecosystem/ species	References
Antibiotics	Penicillin, tetracycline, ciprofloxacin	Improper disposal, excretion, manufacturing runoff	Development of antibiotic-resistant bacteria, disruption of microbial communities	Soil, water, microbial communities, living organism	52,53
Analgesics (painkillers)	Aspirin, ibuprofen, acetaminophen	Excretion, improper disposal	Toxic to aquatic organisms, bioaccumulation in fish leading to health issues	Fish, aquatic invertebrates, humans, animals	54–56
Anti-inflammatory drugs	Diclofenac, naproxen, ketoprofen	Excretion, manufacturing runoff	Liver toxicity in fish, kidney damage, affects the health of vultures and birds that feed on exposed carcasses	Fish, vultures, aquatic mammals, humans	57–59
Antidepressants	Fluoxetine (prozac), sertraline, venlafaxine	Improper disposal, excretion	Alters behavior and reproduction in aquatic species, affects the predator-prey relationship in fish	Humans, fish, amphibians	60–62
Antivirals	Oseltamivir (tamiflu), acyclovir, zidovudine	Improper disposal, excretion	Can disrupt non-target species, potential for bioaccumulation	Aquatic organisms, birds, living organism	63–65
Hormonal drugs	Ethinylestradiol (birth control), testosterone	Excretion, improper disposal	Endocrine disruption, feminization of male fish, reduced fertility in aquatic species	Fish, amphibians, aquatic mammals, humans	66,67
Antihypertensives	Atenolol, enalapril, losartan	Excretion, improper disposal	Cardiovascular effects on fish, altered behavior and survival rates	Fish, aquatic mammals, humans	68–70
Chemotherapy drugs	Cyclophosphamide, methotrexate, doxorubicin	Improper disposal, excretion, hospital waste	Genotoxic effects, potential harm to aquatic organisms, carcinogenic risks	Aquatic life, water systems, humans	71–73
Antidiabetics	Metformin, glibenclamide	Excretion, improper disposal	Potential to affect metabolism in aquatic species, disruption of glucose regulation, sex problems	Fish, amphibians, humans	74,75
Antipsychotics	Risperidone, clozapine, haloperidol	Excretion, improper disposal	Behavioral changes in aquatic life, potential toxicity to non-target species	Fish, amphibians, humans, animals	76–78

agents are cytotoxic, meaning they can kill cells, leading to harmful effects on living organisms that are exposed to them in the environment.[51] Some expanded comparison of medicines with their environmental impact are given in Table 2.

1.1.1 Fabrication of metal organic complex and their composites

Material Institutes Lavoisier (MILs) based MOFs used for removal of pharmaceuticals.[79] Different MOF based composites, for example Zn-MOF-177, ZnMOF-5, Cu-UMCM-150, Zn-ZIF-8, Cu-HKUST-1, Cr-MIL-100 Cu-MOF-55 were used for best stability. Many composites such as Cr-MIL-101 and Fe-MIL-100 are utilized for removal of the naproxen and clofibric acid.[80] For the removal of ciprofloxacin from water, Fe_3O_4 @MIL-100 and Fe_3O_4@MOF-235 are used.[81] The composite of Al-MIL-53 showed maximum adsorption capacity of triclosan on the mesoporous and microporous surfaces.[82] MILs based amalgams and composites such as (ZIF)-8-Cube, (ZIF)-67-Cl, (ZIF)-67-NO_2, (ZIF)-67-OAc, (ZIF)-8-Octahedron, (ZIF)-67-SO_4, (ZIF)-8-Leaf, and (ZIF)-8-Cubic in shape showed maximum strength for removal of pharmaceuticals.[83] Pharmaceutical waste was removed from (ZIFs)-based composites such as MOF based resin, ZIF-8, and CS-ZIF-8 were used as adsorbents.[84] Many composites like ZIF-8-@-SiO_2-@-Fe_3O_4 resulting from ZIF-8, and SiO_2-@-Fe_3O_4 and they formed from acetyl-trimethyl-ammonium bromide was used with sodium-laurate (Figure 2). Ceftazidime showed maximum absorptive capacity 74.25 mg/g and ZIF-8 showed absorptive capacity 39.1 mg/g.[85] Self-propelled nanocomposites (ZIF-8) MOFs showed excellent adsorption towards Congo-red and doxycycline. ZIF-8 which is a derivative from carbons used for ciprofloxacin and sulfamethoxazole removal.[86] ZIF-8-derived carbon showed good result as compared to ZIF-derived-carbons. ZIF-8 carbon derives with higher nitrogen forms hydrogen bonding with pollutant. Hollow structure-based MOF showed maximum adsorption capacity against various pharmaceutical waste.[87] The aquatic removal of tetracycline, N-doped hollow-porous carbon was excellently worked.[88] Some other composites like (N) doped porous-carbons, NHPC1 and NHPC2 were prepared by MOFs such as (ZIF)-8, resorcinol, and tannic-

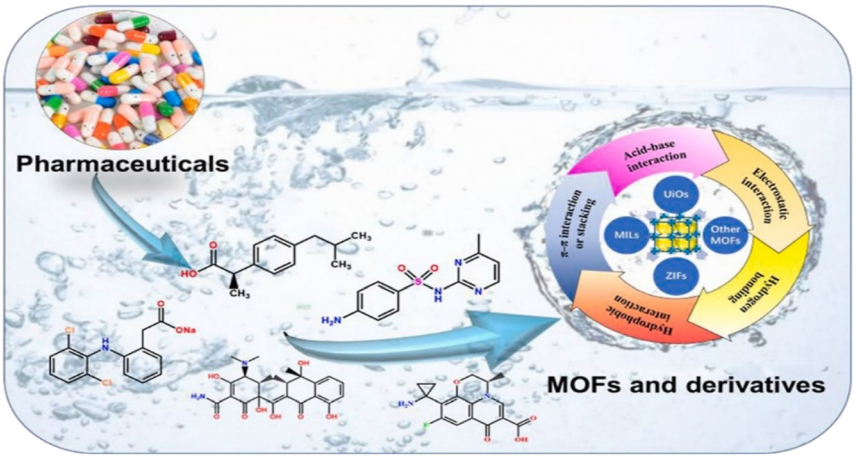


Figure 2: Pharmaceuticals removal from water using MOFs.[93]

acid. ciprofloxacin was removed from water by using N-doped carbon.[89] Zr-MOF (Fe_3O_4@MOF-525) used for pharmaceuticals like tetracycline and diclofenac removal.[90] UiO (a prototype, abbreviating University of Oslo) MOFs are the porous substances showing three diamensional configuration.[91] UiOs are the archetypal MOF like (UiOs)-66, UiOs-67, UiOs-68 were used for removal of pharmaceuticals. UiO-66 prepared through functional groups like SO_3H, NH_2–, and COOH used for purification of wastewater from pharmaceuticals.[89] The SO_3H group showed adsorption capacity of 39.1 % and $-NH_2$ showed adsorption capacity of 43.9 %. They are associated together with electrostatic, π–π linkage and hydrogen interaction. Chloroform impaled UiO-66 displayed sulfachloro-pyradazine adsorption dimension was 417 mg/g,[49] adsorption equilibrium at 30 min and adsorption dimensions from 197 mg/g and 730 mg/g. Cerium, cobalt, and manganese were utilized to work out bi-metallic MOFs.[92] The adsorption of tetracycline through cobalt-doped UiO-66 showed remarkable results. The manganese-doped UiO-66 showed good adsorption capacity against tetracycline. MOFs act as adsorbent, burgeoning and functional MOFs were used in unsaturated site coordination, hydrogen bonding, (π–π) stacking and electrostatic interactions.[13]

1.1.2 Removal of pharmaceutical waste by MOFs and composites

Metal-organic frameworks (MOFs) have emerged as highly effective materials for the removal of pharmaceutical waste from water due to their unique structural properties, including high porosity, large surface area, and tunable functionalities. These characteristics make MOFs particularly suitable for adsorbing a wide range of pharmaceutical pollutants, including antibiotics, nonsteroidal anti-inflammatory drugs (NSAIDs), and other persistent organic compounds.

One of the most studied MOFs is UiO-66, a zirconium-based framework known for its robustness and high adsorption capacity. UiO-66 has been effectively used to remove various pharmaceuticals, including antibiotics and NSAIDs, from aqueous solutions. The functionalization of UiO-66 with different groups has been shown to significantly enhance its adsorption performance.[94] Another notable example is ZIF-8, a zeolitic imidazolate framework, which has demonstrated excellent chemical stability and high efficiency in adsorbing heavy metals and organic pollutants from water.[26] ZIF-8 MOF is a type of metal-organic framework composed of zinc ions (Zn^{2+}) connected by imidazolate linkers. Its crystalline, porous structure gives it unique properties that make it highly effective in adsorbing heavy metals and organic pollutants from water. ZIF-8's application in water purification, particularly in removing antibiotics and pharmaceutical contaminants, has gained significant attention due to its excellent chemical stability, large surface area, and high adsorption capacity. ZIF-8 is characterized by a sodalite topology, where each zinc ion is tetrahedrally coordinated with four imidazolate linkers, forming a cage-like structure. This arrangement creates a highly porous material with a large surface area (typically over 1,000 m^2/g) and pore sizes around 11.6 Å. The porosity and surface area are crucial for trapping contaminants within the framework. ZIF-8 exhibits remarkable chemical stability, even in harsh conditions. It can withstand a wide range of pH values, making it suitable for various water treatment applications. Unlike other materials that may degrade in acidic or basic environments, ZIF-8 maintains its structural integrity, ensuring long-term effectiveness.[95]

The adsorption mechanism of ZIF-8 involves multiple interactions that contribute to its high efficiency in removing contaminants. The large surface area of ZIF-8 allowed it to adsorb a significant amount of pollutants. Organic pollutants, such as antibiotics, are attracted to the surface

of ZIF-8 through van der Waals forces, hydrogen bonding, and π-π interactions with the imidazolate linkers. These interactions are particularly strong for pharmaceutical compounds with aromatic rings, which can stack onto the aromatic imidazolate linkers. The pores within ZIF-8 act as traps for small molecules. Once pollutants enter the pores, they are physically confined within the structure. This is especially effective for small pharmaceutical contaminants, which can be encapsulated within the pores, preventing their release back into the water.[95] ZIF-8 can also remove heavy metals through ion exchange. In this process, the zinc ions in the framework can be replaced by heavy metal ions (such as Pb^{2+}, Cd^{2+}, and Hg^{2+}) from the water. This ion exchange mechanism is highly efficient, as the strong binding affinity between the framework and the heavy metals ensures their removal from the water (Figures 3 and 4). ZIF-8 is particularly effective in removing antibiotics and pharmaceutical contaminants, which are challenging to eliminate through conventional water treatment methods. Antibiotics, such as tetracycline and ciprofloxacin, are often resistant to degradation and can persist in the environment, leading to the development of antibiotic-resistant bacteria. ZIF-8's ability to adsorb these compounds is attributed to the synergistic effects of surface adsorption and pore trapping. In addition to antibiotics, ZIF-8 can also remove other pharmaceutical compounds, such as analgesics, anti-inflammatory drugs, and hormones, from water.[96] These compounds can disrupt aquatic ecosystems and pose risks to human health if they enter the drinking water supply. ZIF-8's high adsorption capacity and stability make it a promising material for addressing these challenges. ZIF-8 is a powerful adsorbent for water purification, particularly in removing persistent contaminants like antibiotics and pharmaceuticals. Its unique combination of high surface area, chemical stability, and effective adsorption mechanisms enables it to tackle pollutants that are difficult to remove with traditional methods. As water pollution continues to be a global concern, materials like ZIF-8 offer promising solutions for ensuring clean and safe water.[97]

MIL-101, a chromium-based MOF, has a large surface area and high porosity, making it suitable for the adsorption of various pharmaceutical pollutants. It has been used to remove drugs like ibuprofen and diclofenac from water.[98] Hong Kong University of Science and Technology (HKUST-1), a copper-based MOF, is known for its high surface area and strong adsorption capabilities. It has been utilized to remove pharmaceutical compounds such as tetracycline and

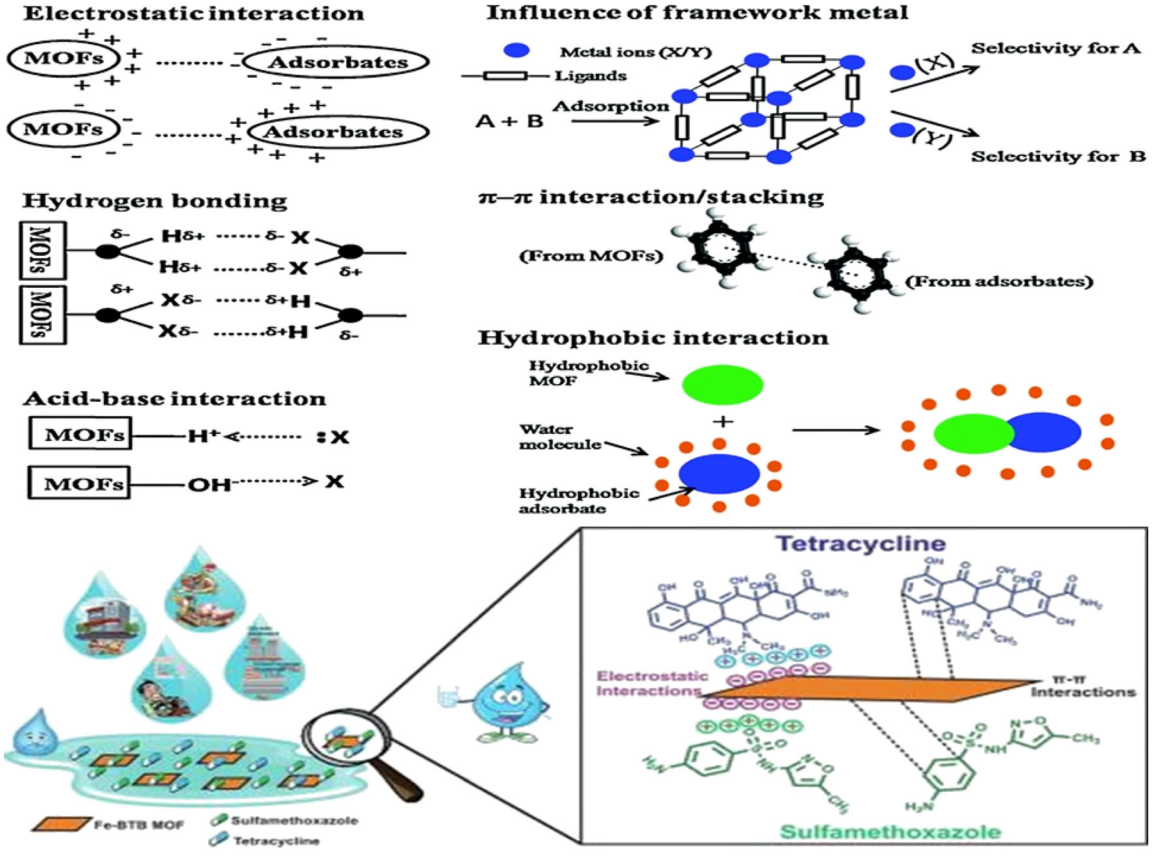


Figure 3: MOFs showing removal of antibiotics from water.[103]

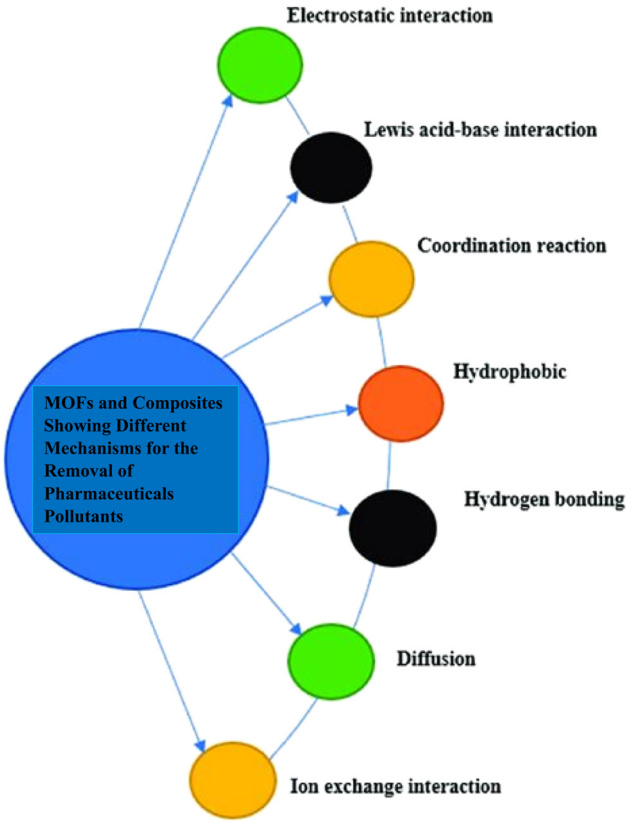


Figure 4: MOFs and composites showing different interaction with pharmaceutical waste.[103]

sulfamethoxazole from aqueous environments.[14] MOF-5, a zinc-based framework, is effective in adsorbing a range of pharmaceutical pollutants due to its high porosity and large surface area. It has been applied in the removal of drugs like naproxen and carbamazepine from water.[99] MIL-53(Al), an aluminum-based MOF, has shown high efficiency in removing pharmaceutical pollutants such as diclofenac and ibuprofen from water due to its flexible framework and high adsorption capacity.[100] MIL-100(Fe), an iron-based MOF, is effective in adsorbing various pharmaceuticals, including antibiotics and anti-inflammatory drugs, due to its large surface area and high porosity.[101] UiO-67, another zirconium-based MOF, has been used for the removal of pharmaceutical pollutants like sulfamethoxazole and trimethoprim from water, benefiting from its high stability and large surface area.[102]

1.1.3 MOFs and composites showing different mechanisms for the removal of pharmaceuticals pollutants

These examples illustrate the versatility and effectiveness of simple MOFs in addressing various pharmaceutical pollutants through adsorption, providing promising solutions for water purification and environmental remediation.

MOF composites have been developed to enhance the adsorption capabilities for pharmaceuticals by combining MOFs with other materials to improve properties such as surface area, stability, and functionalization. Below are some examples of MOF composites that have shown improved performance in pharmaceutical adsorption. For instance, the Bi_2WO_6/UiO-66 composite combines bismuth tungstate with UiO-66, enhancing its visible-light photocatalytic performance for the degradation of organic dyes like Rhodamine B.[25] Similarly, GO/MOF composites, where graphene oxide is combined with MOFs such as Zr/Fe-MOFs, have shown high efficacy in removing organic pollutants like tetracycline hydrochloride and orange II from wastewater.[27] Magnetic MOF composites such as $Fe_3O_4/Zn_3(BTC)_2$ have also been developed, offering the advantage of easy separation from water after adsorption. These composites have demonstrated high efficiency in removing antibiotics like ciprofloxacin from pharmaceutical wastewaters.[104] Combining ZIF-8 with graphene oxide (GO) enhances the surface area and adsorption capacity due to GO's excellent conductivity and large surface area. This composite has shown improved adsorption of antibiotics like tetracycline and ciprofloxacin due to increased π-π interactions between the pharmaceuticals and the GO layers. Effective in removing pharmaceutical contaminants from water, particularly in cases where high adsorption capacity is required. MIL-101(Cr), a chromium-based MOF, is combined with carbon nanotubes to create a composite with enhanced adsorption capacity and structural stability. The addition of CNTs enhanced the composite's ability to adsorb pharmaceuticals such as ibuprofen and diclofenac through hydrophobic interactions and π-π stacking. Used in water treatment for the removal of non-steroidal anti-inflammatory drugs (NSAIDs) and other pharmaceuticals.[105,106]

UiO-66, a zirconium-based MOF, is combined with TiO_2 nanoparticles, which enhance the composite's photocatalytic activity and stability. This composite can adsorb and degrade pharmaceuticals like acetaminophen and sulfamethoxazole under UV light, making it effective in advanced oxidation processes. Suitable for water purification systems where simultaneous adsorption and degradation of pharmaceuticals are needed.[107] HKUST-1, a copper-based MOF, is integrated with magnetic nanoparticles, allowing for easy recovery and reuse of the adsorbent. This composite effectively adsorbs pharmaceuticals such as carbamazepine and diclofenac, and can be magnetically separated from the water after adsorption. Ideal for repeated use in water treatment systems, especially in

scenarios where easy recovery of the adsorbent is necessary.[108] MOF-199 (Cu-based) is combined with chitosan, a biopolymer known for its adsorption capabilities and biocompatibility. The composite exhibited enhanced adsorption of antibiotics like amoxicillin due to the presence of functional groups in chitosan that interact with pharmaceutical molecules. Used for the removal of pharmaceutical residues from aqueous solutions, especially in environmentally friendly water treatment applications.[109] NH_2-MIL-53(Al), an amino-functionalized MOF, is combined with reduced graphene oxide (rGO) to enhance adsorption efficiency. This composite showed a high affinity for removing pharmaceutical contaminants like naproxen due to enhanced interactions between the amino groups and the pharmaceuticals. Effective in adsorbing a range of pharmaceuticals from wastewater, particularly where strong chemical interactions are needed. A composite of Cu-BTC (also known as HKUST-1) and cellulose, which adds biocompatibility and mechanical strength to the MOF. The composite showed enhanced removal of antibiotics like sulfadiazine and cephalexin, thanks to the synergy between Cu-BTC's high surface area and cellulose's adsorption sites used in environmental friendly and sustainable water treatment processes.

These MOF composites demonstrate how combining MOFs with other materials can significantly enhance their adsorption capabilities for pharmaceutical contaminants, making them more effective in various water treatment and environmental remediation applications. The adsorption mechanisms of MOFs involve various interactions, including hydrogen bonding, electrostatic interactions, and π-π interactions between the MOF structures and pharmaceutical molecules. These interactions significantly influence the adsorption efficiency and capacity of MOFs.[16]

1.1.4 Removal of different pharmaceutical medicines using MOFs and composites

1.1.4.1 Ciprofloxacin

Ciprofloxacin is an broad spectrum antibiotic used to treat bacterial infections such as urinary tract infections (UTI), respiratory tract infections (RTI) like bronchitis, pneumonia and chronic obstructive pulmonary disease (COPD), skin and soft tissue infections (SSTI), gastrointestinal infections (GIT), bone and joint infections, sexually transmitted infections (STI) anthrax and plague etc.[110] Ciprofloxacin, like other fluoroquinolones, is generally effective but can cause several side effects and toxicities. While most patients tolerate it well, certain adverse effects can be significant. Here are some key aspects of ciprofloxacin toxicity are gastrointestinal toxicity which includes nausea, vomiting, diarrhea, abdominal pain, musculoskeletal toxicity, tendinitis and tendon rupture, muscle weakness, central nervous system (CNS) toxicity, neurological effects such as headaches, dizziness, confusion, and seizures may occur, particularly in the elderly or those with pre-existing CNS conditions. Ciprofloxacin is an effective antibiotic but comes with significant potential toxicities, particularly related to tendons, the central nervous system, and the heart. Its use should be carefully monitored, particularly in high-risk populations, and it should be avoided when safer alternatives are available. Always consult with a healthcare provider before starting or continuing ciprofloxacin therapy.[111]

For this reason, the removal of ciprofloxacin (CIP) using MOFs and composites by adsorption methods has been extensively studied. The MOF (Fe/Ni) was used to remove CIP from aqueous solution by chemical adsorption. Took (Fe/Ni)-MOF in 250 mL beaker at room temperature. Then 30 mg, 40 mg, 50 mg, and 100 mg of the (Fe/Ni)-MOFs were added to CIP solutions at the concentration of 5 mg/L, 10 mg/L, 20 mg/L, and 30 mg/L with constant stirring using magnetic stirrer. After every 30 min, 2 mL of sample was taken, and observed under UV-spectrophotometer at λ_{max} = 277 nm. For added 100 mg of (Fe/Ni)-MOFs to 10 ppm CIP solution removal efficiency was 94.1 %. When 100 mg of Fe/Ni-MOFs were added to 20 ppm CIP solution, the removal rate was showed 61 % after 5 h.[92] The concentration can be calculated having absorbance by using this these equations.[112]

$$\mathrm{C}\ (\%) = \frac{Co - Ct}{C0} \times 100\ \%$$

$$qe = \frac{(C0 - Ce)V}{m}$$

For this MOF-5 were mixed (50 mg) to 100 mg with CIP at 30 °C. The samples were separated and filtered through 0.2 µm filter and was analyzed by HPLC after definite time. The pH range was maintained from 3 to 9 using buffer solution. The removal efficiency of CIP was 71 % and the kinetics study showed that pseudo second order (PSO) were best applied.[113] Beiranvand et al. added 30 mg HAP/MIL-101(Fe)/Fe_3O_4 into 50 mL of CIP and then stirred for 30 min constantly. HAP/MIL-101(Fe)/Fe_3O_4 was separated from the CIP solution. This experiment showed 93 % removal of CIP from aqueous solution at pH 7 and this was endothermic and spontaneous process.[114] Binbin Yu prepared (1,000 mgL^{-1}) stock solution of CIP at different concentrations and by diluting from (2,000 mgL^{-1}) distilled water. The 40 mg of MOFs were added to 50 mL of the CIP solution. Then for 180 min solution was put on orbital shaker for shaking. At fix intervals 5 min, 10 min, 30 min, 60 min, 90 min, 120 min, and 180 min 1.0 mL of floatable was sucked

with a describing needle syringe then filtered the solution. Next, after equilibrium the concentrations of CIP was determined in the solution by UV spectrophotometer which showed concentration of CIP at 275 nm and kinetics showed pseudo second order equation.[104]

Naseem Ahmad Khan et al. added 10 mL of CIP solution to 10 mg of Mn-PBA. The removal efficiency of CIP was 98.5 % at pH 7. In next experiment the CIP concentrations were taken from 100 to 250 ppm with contact time 6 h and volume was 240 mL. The concentration of CIP at 321 nm (λ_{max}) was determined by UV visible spectrophotometer.[115] Magnetic mesoporous carbon composite (Fe_3O_4/C) were synthesized via low-temperature hydrothermal methods which exhibits high adsorption capacity and stability, retaining over 85 % capacity after 10 cycles. It was studied that best performance of this composite was under neutral pH conditions.[116] Ethylene diamine tetra acetic acid/β-cyclodextrin composite (EDTA/β-CD) showed rapid adsorption kinetics and fits the Dubinin–Radushkevich isotherm model. It was effective under varying pH and ionic strengths due to electrostatic interactions.[117] Graphene oxide-kaolinite-poly (vinyl alcohol) composite also demonstrated high adsorption capacity (408.16 mg/g) and good recyclability. In this composite adsorption process was driven by hydrogen bonding as well as π-π interactions.[118] Magnetic MOF (Fe_3O_4/$Zn_3(BTC)_2$) composite also achieved a maximum removal rate of 72.15 % with optimal performance at pH 3.84. This composite followed PSO kinetics, indicating chemical adsorption.[104] Fe/Ni-MOF composite was prepared by solvothermal methods, showed a maximum adsorption capacity of 232.1 mg/g. This composite was very effective under various pH conditions and followed the Freundlich isotherm model.[92] In another study chitosan/zeolite composite also achieved a maximum removal efficiency of 97.5 % under optimal conditions and fits the Langmuir isotherm model and followed second-order kinetics.[119]

These studies highlight the effectiveness of various MOFs and composites in removing ciprofloxacin from aqueous solutions through adsorption, with each material offering unique advantages in terms of capacity, stability, and operational conditions. The removal of ciprofloxacin (CIP) using MOFs and composites by adsorption involves several mechanisms, including electrostatic interactions, hydrogen bonding, π-π interactions, and coordination with metal sites. Here is a detailed explanation of the mechanisms including electrostatic interactions. CIP molecules, which are zwitterionic, interact with the charged surfaces of MOFs or composites. The pH of the solution can influence the charge on both the adsorbent and the CIP molecules, affecting the adsorption efficiency.[92] Hydrogen bonds form between the functional groups of CIP (e.g., carboxyl and amino groups) and the oxygen or nitrogen atoms in the MOFs or composites.[119] π-π interactions occur between the aromatic rings of CIP and the aromatic structures in the MOFs or composites, enhancing adsorption.[118] CIP can coordinate with the metal ions in the MOFs, forming stable complexes. This is particularly significant in MOFs with open metal sites.[92] As shown in Figure 5.

1.1.4.2 Levofloxacin

Levofloxacin antibiotic used for treatment of urinary tract infection, pneumonia, skin infection, inhalational exposure.[120] UiO-66/CA was used as adsorbent and the solution of 25 mg of LOFX in 40 mL methanol aqueous was mixed. Then, at room temperature the 500 mg of UiO-66 were shifted into mixed solution. After removal of UiO-66, the sample were purified by filtration and then analyzed by HPLC. The composites beads were prepared by solidification of UiO-66 and sodium alginate in the $CaCl_2$ solution. These composite beads were used to apply to removal of LOFX. The levofloxacin removal was 70 % from aqueous solution at pH 7. The kinetics was showed pseudo second order[121] (Figure 6).

Different concentration solutions were prepared by 0.25 mg/L, 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L solution of levofloxacin in a 250 mL glass beaker reactor with a 100 mL reaction solution which contained 1 mg LEV, 0.035 mM potassium per-sulfate, and 5 mg of catalyst. After every 3 min, 2.5 mL of sample was withdrawn by using describing needle syringe and shifted into a vial through a 0.22 μm filtration membrane. MOFs (PW@ZIF-67) were showed the highest degradation of 80.11 % within 3 min at pH 7. The UV visible spectrophotometer was used for determination of LV degradation.

1.1.4.3 Amoxicillin

Amoxicillin is beta-lactam antibiotic and it is used for *Helicobacter pylori* infections and displays activity against certain spirochetes.[122] Felycia et al. prepared 250 mg/L AMX solution in one liter of RO water. Many Erlenmeyer flasks were filled up with AMX solution of 50 mL then (10 mg–100 mg) HKUST-1 was added to the Erlenmeyer flasks and then Erlenmeyer flasks was placed in the water-bath. The water-bath was at 200 °C for temperature maintenance. When it was reached to equilibrium in 180 min centrifugation was done. The concentration of AMX was determined at 628 nm from UV visible spectrophotometer.[123] The MIL-53(Al) was used as adsorbent and the samples of 2 mg of MIL-53(Al) were added in 20 mL AMX solution with different concentrations. Then, the mixture was shaken for 10–120 min. Eventually, the adsorbent from solution was separated through filtration. The 228 nm concentration of AMX was by UV–visible spectrophotometer.[124] MIL-101,

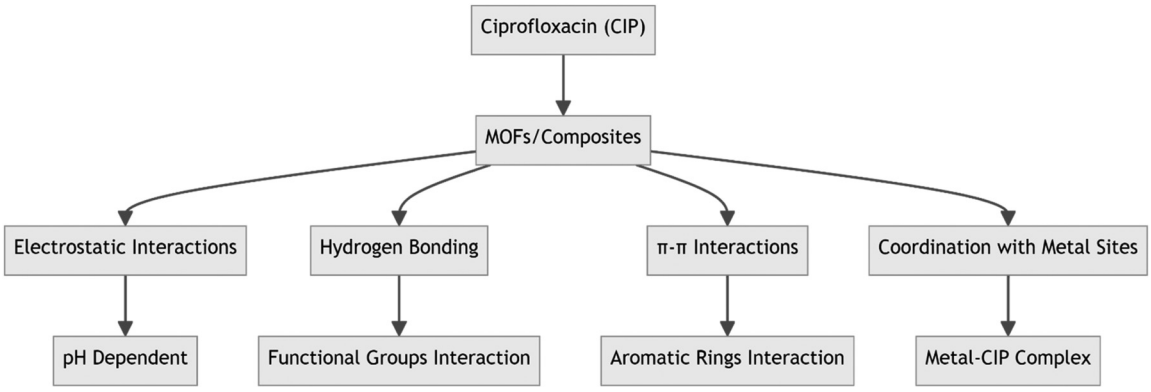


Figure 5: This diagram illustrates the primary mechanisms involved in the adsorption of ciprofloxacin onto MOFs and composites. Each mechanism contributes to the overall adsorption process, making these materials effective for removing CIP from aqueous solutions.

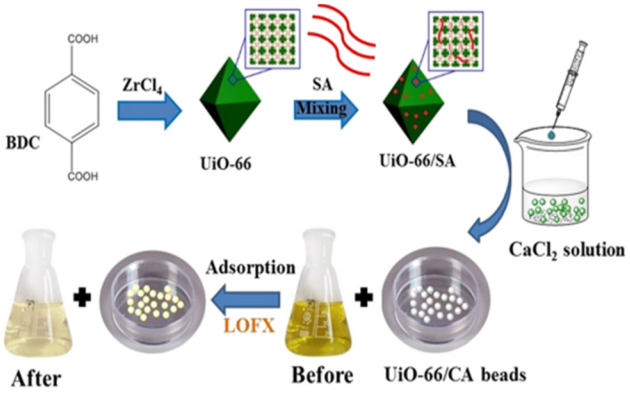


Figure 6: Removal of levofloxacin using UIO-66/CA beads.[121]

NH_2-MIL-101, MOF-235 and NH_2-MOF-235 were used as adsorbent and experiment was performed by 40 mg/L amoxicillin and 100 mg/L MOFs was mixed in thermostat shaker at 120 min. Amoxicillin was removed 65.38 % and 67.13 % using MIL-101 and NH2 -MOF-235 from the solution within 120 min at pH 7.[125]

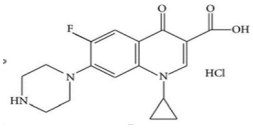
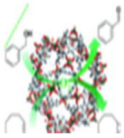
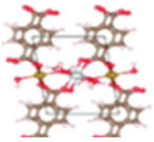
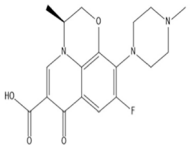
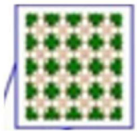
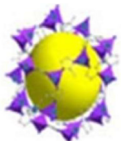
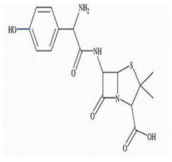
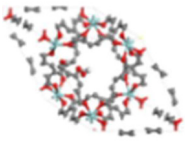
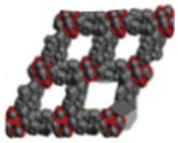
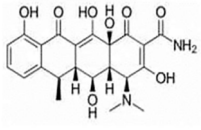
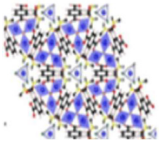
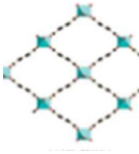
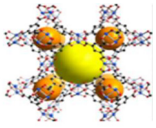
The UiO-66@Cr-MIL-101 was used as adsorbent and the percentage range of Cr-MIL-101 was 10 %–30 %, amoxicillin initial concentration range was 20 mg/L–140 mg/L and the time was 20 min–60 min, and pH range was 20–10. For the 20 % weight, the initial concentration of AMX was 80 mg L^{-1}, contact time was 20 min at pH 6. This was showed 99.5 % removal efficiency of amoxicillin. The kinetics were showed pseudo second order and the concentration the AMX was at 270 nm and this concentration was measured with help of UV visible spectrophotometer. The mechanism of AMX adsorption by UIO-66@Cr-MIL-101 was depend on hydrogen bonding, (π–π) interaction and electrostatics. The π–π interaction mechanism was observed for adsorption of amoxicillin and it was 1,111.11 mg g^{-1}.[112]

1.1.4.4 Doxycycline

Doxycycline (DOX) bacteriostatic drug that is commonly used for treatment of bacterial infections.[126] Removal of DOX could be achieved by different MOFs. For this procedure, mixed 5 mL solution of doxycycline with different concentrations of 5 mg of UiO-66 (250 µM, 500 µM, 750 µM, and 1,000 µM) with constant stirring at room temperature. After an hour, it reached to equilibrium. UiO-66 removed up to 90 % doxycycline in an aqueous solution. The kinetics showed pseudo second order.[127]

The stock solution (150 mg L^{-1}) was prepared for DOX by dissolving 150 mg DOX in water and diluted to different concentrations of solutions (150 mg L^{-1}) and 50 mL conical flasks were contained DOX solution 50 mL. Ni-MIL-53(Fe)-X was used as adsorbent. Ni-MIL-53(Fe)-X was dried for removal of DOX before experiment. The experiment was performed by adding adsorbent (10 mg) in a conical flask to each solution (50 mL) and at speed of 200 rpm with different temperatures the mixture was stirred constantly and then solutions were filtered. The concentration was observed at 346 nm by UV spectrophotometer. The adsorption activities were evaluated in terms of the removal efficiencies of MOF against doxycycline (DOX) in aqueous solution. Ni-doped MIL-53(Fe) showed the adsorption capacity of 397.22 mg/g at about pH 7.[127] Different masses of Zr-MOF (20 mg, 30 mg, 40 mg, and 50 mg) were added to 200 mL of doxycycline solutions, containing different concentrations (20 mg L^{-1}, 30 mg L^{-1}, 40 mg L^{-1}, and 50 mg L^{-1}) and then the solutions were constantly stirred in natural light. The samples were analyzed after 30 min. The concentration of doxycycline was determined at 269 nm using UV visible spectrophotometer. when solution of DOX was 30 ppm and the concentration of Zr-MOF was 50 mg, the removal rate of DOX was approximately 84.4 % after 5 h. When mass of Zr-MOF was taken 30 mg, and concentration of doxycycline was taken 50 mg/L the maximum adsorption was 148.7 mg/g at pH 6–10 and the

Table 3: Removal mechanism of pharmaceutical wastes on metal-organic frameworks.

Antibiotics MOFs					Ref.
					104,112–114
Ciprofloxacin	MOF-5	MIL-101(Fe)	Fe / Ni-MOFs	Mn-PBA	
					121,129
Levofloxacin	UiO-66/ CA	PW@ZIF-67			
					112,123,125
Amoxicillin	Ni-MIL-53(Fe)	UiO-66	Zr-MOFs		
					127,128,130
Doxycycline	NH_2-MOF-235	MIL-53 (Al)	HUKST -1		

kinetics shown pseudo second order.[128] Tables 3 and 4 also showed the removal of pharmaceutical pollutants from water using different MOFs.

1.1.5 Adsorption mechanism

Water contamination with pharmaceutical residues is an emerging concern due to their potential adverse effects on human health and aquatic ecosystems. Pharmaceuticals such as antibiotics, analgesics, and hormones are not fully removed by conventional wastewater treatment processes, necessitating advanced methods for their elimination. MOFs and composites are promising materials for the adsorption-based removal of pharmaceuticals from water due to their high surface areas, tunable porosity, and functionalize surfaces. Adsorptive removal of pharmaceutical used the mechanism of electrostatic attraction, and hydrogen bonding, π–π stacking interaction, coordination interaction and hydrophobic interaction.[167] Cephalexin was removed by electrostatic and coordination interaction by using Zr-based MOFs.[135] Mostly absorption mechanism was due to π–π interactions and hydrophobic interactions on the other hand the effect of pH was showed, and electrostatic interaction also took place.[168] The antibiotics such as Ciprofloxacin, *β*-Lactam, Sulfone-amides Macrolides, Tetracyclines removed by the *π*-π interactions, with maximum

Table 4: Comprehensive list of pharmaceutical pollutants using MOFs, having removal efficiency (RE), absorptive capacity (AC), and kinetics in wastewater treatment.

Medicine	MOFs	Time (mnt)	RE (%)/AC (mg/g)	Kinetics	Ref.
Tetracyclines	UiO-66-NH_2-CA-Cu/MOF-5	30	94/233	PSO	131,132
Azithromycin	MIL/CS@Fe_3O_4NC/ZIF-8	60	73.21/131	PSO	133
Cephalexin	PCN-777	60	90/442.48	PSO	104,134,135
Doxycycline	Zr-MOFs	300	90/148.7	PSO	129
Amoxicillin	Co@Co_3O_4/C	45	91/156	PSO	136,137
Sulfamethoxazole	NH_2-MIL-53(Fe)/MOF-545	30	96/690	PSO	138,139
Trimethoprim	Zr-Bio-MOF	300	95/18.40	PSO	140,141
Levofloxacin	POMS@ZIF-67/MIL-100(Fe)	30	91.46/87.34	PSO	142,143
Ciprofloxacin	Fe/Ni-MOFs/ZIF-8	300	60/270.67	PSO	129,144
Metformin	Art ich Bch/Art ich-Bch-NaOH/MIL-125-NH_2	20	80/164	PSO	145,146
Acetaminophen	Fe_3O_4	480	84.6/68.9	PSO	37,147
Ofloxacin	Cu-dopped ZIF-8s/ZIF-8	–	90/10	PSO	148,149
Norfloxacin	Zr-MOF/MIL-101(Cr)	300	-/450.4	PSO	129,150
Ibuprofen	MIL-53(Fe)	120	80/400	PSO	151,152
Carbamazepine	Fe_3O_4 Zn-MOFs	30	100/663.7	PSO	84,153
Trimethoprim	Bio-MOF/ZIF-8-C	60	95/50.90	PSO	140,154
Metronidazole	Zr-IV-MOF	60	97/200.2	PSO	155,156
Cefazolin	UIO-66-NH_2/Zr-MOFs	3 days	83.31/346.0	PSO	157,158
Chloramphenicol	(Al-MIL)	120	71/96.1	PSO	159,160
Tylosin	UiO-66-NH_2	60	91.30/161.60	PSO	161
Trimethoprim	Zr-Bio-MOF	60	95/-	PSO	162
Diclofenac	Sulphonic-functionalize MIL-100-Fe MOF(MIL-100-Fe-AMSA)/UiO-66	4	80/256.41	PSO	163,164
Metoprolol	TiO_2-@-SnO_2-@-Mn/	60	95.89/349.03	PSO	165
Venlafaxine	ZIF-67/MOF-74 (Ni)/g C_3N_4 (ZNG)	120	91/-	PSO	14
Naproxen	MCNTs–UiOs-66-NH_2 $CuFe_2O_4$/MIL-53 (Al)	60	92.3/297	PSO	110,153
Fluoroquinolone	MIL-101(Cr)SO_3H	30	91/450	PSO	150,166
Paracetamol	MIL-100(Fe)@CP/Ti-MIL-NH_2	167	89.75/519.1	PSO	37,167

In this table AC, adsorption capacity; RE, removal efficiency; PSO, pseudo second order; PFO, pseudo first order.

adsorption.[169] SMZ and TC were positive and neutral when the pH = 2 and 7, it showed that the TC was removed from electrostatic interaction. The antibiotics would ionize at pH 7–9 shown electrostatic repulsion. While π-π interaction and hydrogen bonding was observed at lower pH.[170] Clofibric acid (CA) and carbamazepine (CBZ) were removed by mechanism of hydrophobicity/hydrophilicity.[171]

The adsorption of pharmaceuticals onto MOFs generally occurs through several interactions. Aromatic rings in both the MOF's organic ligands and the pharmaceutical molecules enable π-π stacking interactions, enhancing adsorption capacity. Pharmaceuticals with functional groups such as hydroxyl (-OH), amine (-NH_2), and carboxyl (-COOH) can form hydrogen bonds with the MOF's ligands, further aiding in adsorption. Depending on the charge of the pharmaceutical molecules and the surface charge of the MOF, electrostatic attraction or repulsion may occur, influencing adsorption efficiency.[172] MOFs with hydrophobic surfaces may adsorb hydrophobic pharmaceuticals more effectively through van der Waals forces (Figure 7). The adsorption process involves the diffusion of pharmaceuticals into the porous structure of the MOF, where they interact with the available adsorption sites. The high surface area and porosity of MOFs allow for the accommodation of large quantities of pharmaceuticals, making them highly efficient adsorbents.

Composites, which combine MOFs with other materials like graphene oxide (GO), carbon nanotubes (CNTs), or polymers, enhance the adsorption properties and stability of MOFs. These materials often exhibit synergistic effects, improving the overall performance for pharmaceutical removal. The incorporation of materials like GO increases the surface area and introduces additional pores, facilitating greater adsorption capacity. The presence of functional groups on composite materials can increase interactions with pharmaceuticals. For example, GO contains oxygen-containing groups that can form hydrogen bonds with pharmaceuticals. Materials like GO and CNTs provide electron-rich sites that can interact with electron-deficient pharmaceutical molecules, promoting adsorption through

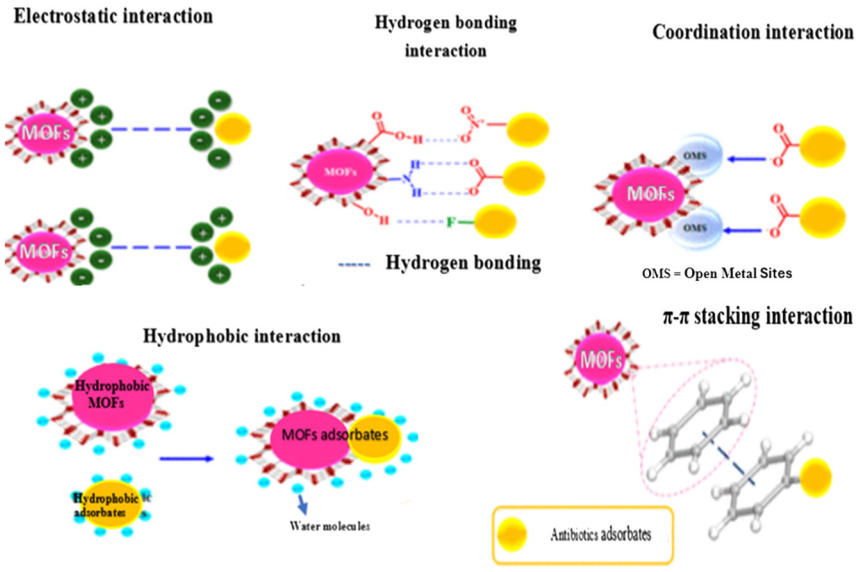


Figure 7: Mechanism of adsorptive removal of pharmaceuticals waste from wastewater using MOFs.[145,147]

π-π interactions. Composites often combine the adsorption properties of MOFs with the mechanical strength, chemical stability, and conductivity of the added materials. This synergy can lead to higher adsorption capacities and faster adsorption kinetics. Several factors influence the adsorption efficiency of pharmaceuticals onto MOFs and composites. The pH affects the surface charge of the MOF/composite and the ionization state of the pharmaceutical, influencing electrostatic interactions and adsorption capacity. Higher initial concentrations may saturate the adsorption sites more quickly, leading to reduced adsorption efficiency. Adsorption is typically an exothermic process; thus, higher temperatures may reduce adsorption capacity. However, temperature also affects the diffusion rate of pharmaceuticals into the pores of the adsorbent. The presence of other ions in the water can compete with pharmaceuticals for adsorption sites, potentially reducing the efficiency. One of the advantages of using MOFs and composites is their potential for regeneration and reuse. The desorption of pharmaceuticals from the adsorbent can be achieved by altering the pH, using solvents, or applying thermal treatment. Effective regeneration ensures the sustainability and cost-effectiveness of the adsorption process.[20,115]

MOFs and composites represent advanced materials for the adsorption-based removal of pharmaceuticals from water. Their high surface area, tunable porosity, and ability to form specific interactions with pharmaceutical molecules make them ideal candidates for this application. The use of MOF-based composites further enhances adsorption performance through synergistic effects. However, optimizing the adsorption process requires careful consideration of factors such as pH, pharmaceutical concentration, and the presence of competing ions. The development of effective regeneration techniques is also crucial for practical applications in water treatment. As research progresses, these materials hold great promise for mitigating the environmental impact of pharmaceutical contaminants.[173,174]

In adsorption mechanism-process, toxic pollutants shift to MOFs surface, and desorption can be shown by result of secondary contamination.[145]

2 Future directions

MOFs and their composites have proved for polluted water reduction, detection, and storage of energy. Biomass-MOFs get famous for great performance and they are highly advance with improved, mechanical strength, reuse of materials and low costs. They synthesized them towards green and sensible development. MOFs are valuable materials for supercapacitors and different batteries because they have large surface area, active sites and huge porosity. MOFs remove many contaminants from Pharmaceuticals wastes, wastewater and heavy metals. Metal-organic frameworks as highly porous structures with the capability of functionalization with various combination with metal oxides, planar materials, and magnetic materials extreme porosity, and superficial-modification used for the wastewater treatment (WWT) for various pollutants.

Thus, chemical research related to metal-based MOFs is required for safety confirmation upon removing of dyes from water with MOFs. During water treatment, MOFs are not considered as viable considering to lower yields and more material costs. In addition, the absence of studies was discovered on the impacts of coexisting ions, agitation speed, and operation mode on the adsorption and degradation of

pharmaceutical wastes from water. Even though MOFs were capable of to remove all pharmaceutical wastes, more research is advised before using these materials for actual water treatment. Despite the promising results, several challenges remain in the application of MOFs for pharmaceutical waste removal. These include the scalability of MOF synthesis, stability under operational conditions, and potential environmental impacts. Future research should focus on optimizing the synthesis processes, enhancing the recyclability of MOFs, and conducting long-term environmental impact assessments to ensure sustainable and effective water treatment solutions.

3 Conclusion

It is understood that water contamination due to pharmaceutical waste is serious issue and this contamination is increasing day by day and needs to have a proper system for decontamination. To conclude, this contamination leads to serious health hazards by increasing the risk of untreatable disease and anti-microbial resistance bacteria. Metal organic frameworks with their improved functionalization, metal doping, large recycling capacity, high porosity and enhanced adsorption kinetics of metal-organic framework make them highly functional for the removal of pharmaceutical debris from waste bodies. Although there is a lot of work in this perspective, the application of metal organic framework for pharmaceutical waste removal is just at the beginning.

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