

Metal-organic frameworks for the adsorptive removal of pharmaceutically active compounds (PhACs): Comparison to activated carbon

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A B S T R A C T

During the past few years, there has been growing concern about the presence of various pharmaceutically active compounds (PhACs) in water systems. Although their concentrations could be considered relatively low, their long-term negative impacts on the aquatic ecosystem and human beings cannot be neglected. Therefore, significant efforts have been directed towards finding an effective water treatment method that can completely remove PhACs from water systems. Among the available strategies, adsorption could be considered the most feasible because of a number of advantages, such as high effectiveness and low cost. Until now, activated carbon (AC) has been widely used as the main adsorbent to accomplish this task. However, over the last two decades, there has been growing interest in the development of metal-organic frameworks (MOFs). As a relatively new class of porous material, MOFs could be deployed as an effective adsorbent to remove PhACs from water. However, after more than 20 years of research and development of MOFs, the main question remains: could MOF outperform AC as the most-widely used adsorbent to accomplish this task? This article then tries to answer this question by conducting an extensive comparative study of the recent adsorption performances of MOF and AC towards various PhACs. Through this comparison, a clear difference in adsorption performance between the two adsorbents could be established. In addition, this article also discusses the adsorption mechanisms and various factors that could affect the adsorption performance in each adsorbent. Lastly, some future perspectives are also given which could be used as a guideline in the future studies. This comprehensive analysis could then be expected to guide the selection of either AC or MOF as an effective adsorbent to remove PhACs from water systems.

Keywords:

Activated carbon

Metal-organic framework

Adsorption

Pharmaceutical active compounds

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1. Introduction

The presence of contaminants of emerging concern (CECs) in water systems has recently been a matter of growing concern. Various activities, including household, agricultural, and industrial, can be the main source of CECs. In the past, monitoring of these particular compounds was often neglected because of the various challenges related to their relatively low concentrations and the analytical methods [1]. However, the presence of CECs and their negative impacts to the aquatic ecosystem and human beings can no longer be ignored.

CECs can usually be grouped based on the purpose of the compound, resulting in at least five common CEC groups: pharmaceuticals, lifestyle compounds, endocrine-disrupting compounds and hormones, flame retardants, and pesticides [2]. Among these groups, one of the most prominent classes that has growing concerns about their removal from the environment is pharmaceutically active compounds (PhACs) because of the growing pharmaceutical industry since the beginning of the industrial age and the continuous consumption of such products by human beings. This has led to the massive production of various PhACs, with some now easily obtainable as over-the-counter medicine, which creates difficulties in limiting their consumption. These conditions contribute to the discharge of PhACs into the surrounding environment worldwide, and some PhACs have been detected as far as Antarctica [3,4]. Although the concentration of PhACs in water systems are usually very low (in the range of nanogram to microgram per liter), their continuous release and accumulation can have negative impacts on the aquatic ecosystem [3]. Furthermore, it is also possible that, at some point, such negative impacts will be borne by human beings. This is backed by the fact that PhACs are bioactive compounds, which could cause various toxicological and hazardous effects to both the environments and living things [5].

In addition to the above causes, the ineffectiveness of the process for removing PhACs from the environment is also a contributing factor exacerbating the PhAC pollution [6]. The efficacy of the PhAC removal from water systems depends heavily on the technology or method that is used for the water treatment [1]. When the applied method is not very effective, the pharmaceutical compounds can still be present in drinking water [7]. Therefore, highly effective water treatment strategies that can completely remove these compounds has become an emerging topic in the field of environmental science and engineering during the last few years [8]. There are several strategies that can be employed to address the issue, such as electrochemical treatment [9], photodegradation [10], ozonation [11], biodegradation [12], and adsorption [13].

Among these strategies, adsorption could be considered one of the best approaches because it offers numerous advantages, such as process simplicity, high effectiveness, fast removal rate, avoidance of toxic byproducts, and low cost.

Until now, most adsorption processes have used activated carbon (AC) in either granular or powdered form. However, recent investigations have shown the possibility of employing various new materials, such as graphene oxide (GO) [14], mesoporous silica [15], covalent organic frameworks (COFs) [16], and metal-organic frameworks (MOFs) [17]. Among all of these possibilities, MOFs could be considered the most promising alternative to AC. In addition to the relatively mature development of MOF synthesis, its pore tailorability and functionalization render this particular material with the potential to increase its effectiveness and efficiency in removing PhACs from water systems. Of course, a critical attention has to be paid regarding the water stability of MOFs before they can be deployed in a real application for PhACs removal [18]. However, the number of water-stable MOFs is sufficiently large to still offer a vast amount of suitable materials.

This trend in the use of MOF for PhACs removal can then be clearly depicted in Fig. 1, which shows the number of published studies using AC and MOFs for PhACs adsorption. As can be seen, the number of studies using MOFs has increased consistently over the last 10 years. Though it has not yet surpassed the number of studies using AC, this trend clearly shows an increasing interest in the use of MOFs for PhACs removal. However, the extent to which MOFs compete with AC in adsorbing PhACs is not yet known.

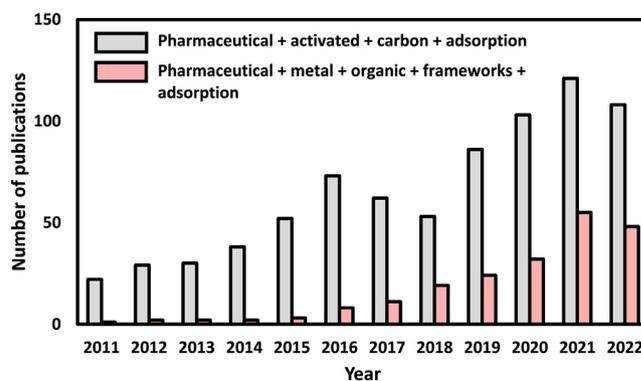


Fig. 1. Number of publications in Scopus based on different keywords for activated carbon (gray) and metal-organic frameworks (rose). The data was obtained until early October 2022.

This review article intends to answer this question. Some previous reviews also discussed the performance of AC [19–21] or MOFs [17,22–25] towards various CECs or PhACs regarding adsorption capability. Differing from the published literature, in this review article, we intend to give a fresh perspective by comparing the performance of AC and MOFs side by side. By thoroughly investigating and comparing the performance of both adsorbents, a clear comparison of the two materials could be obtained and aid in deciding which adsorbents are best to be used and which areas need to be further developed.

2. Adsorbent synthesis

2.1. Activated carbon

AC is an amorphous carbon-containing porous material that has been widely investigated as a commercially available adsorbent to remove various contaminants in water and wastewater. Despite its commerciality, various research is still conducted in which AC is produced using various biomass sources, such as algae [26], apple tree branches [27], bamboo waste [28], cocoa shells [29], coconut shells [30–32], corn straw [33], olive stones [34–36], tea waste [37,38], sugarcane bagasse [39,40], pine tree [32], or potato peel [41], and also from the combination of various sources [42]. In addition, AC can also be produced from the biological sludge from wastewater treatment plants [43]. The production of AC using various types of waste is attractive because it could increase the economical aspect and contribute to the sustainability of AC production.

AC production usually consists of two main steps: carbonization and physical or chemical activation. The carbonization process is performed through pyrolysis in an oxygen-limited environment. The presence of oxygen must be limited to avoid the full oxidation of carbon, which produces char. Afterwards, the carbon can be physically or chemically activated. Physical activation of carbon usually involves an oxidizing agent, such as O₂, steam, or gaseous mixtures, and is performed at high temperature. Various chemicals, such as K₂CO₃ and KOH, can be used as chemical activating agents. AC can then be produced in a granular or powder form. Although differing in particle size, both forms of AC can be effectively used for water treatment.

The pore structure of AC can be influenced by different treatments during the production process. For example, activation using KOH can yield AC with higher Brunauer-Emmett-Teller (BET) surface area and slightly smaller pore size than K₂CO₃-activated AC [27]. Increasing the amount of KOH during the activation process is also beneficial in increasing the surface area of the resulting AC and creating more uniform pores because it can eliminate ash and tar from the surface [44]. During the activation process, temperature also plays an important role. In this regard, an increase in the mesoporous region in KOH-activated and K₂CO₃-activated AC could be obtained by increasing the activation temperature, though an optimum point exists, above which no further gain in porosity could be obtained [45,46]. This may then be beneficial in enhancing the diffusional process of PhACs during the adsorption process. Furthermore, the particle morphology of AC could be influenced by the activation process. For example, the particle morphology has been observed to be retained more in KOH-activated AC than K₂CO₃-activated AC because the latter has been observed to be more destructive [27].

The different activation process for AC also contributes to producing different amounts of acidic and basic functional groups on the surface. For example, activation with KOH leads to a more neutral and slightly acidic surface, whereas a more acidic AC can be obtained by activation using K₂CO₃ [27]. The presence of these

functional groups could usually be quantified by using the Boehm method. This method could then give both qualitative and quantitative information regarding the existing functional groups in AC.

2.2. Metal-organic frameworks

During the last two decades, there has been strong interest in the development of MOFs as a new class of adsorbent material because they can offer numerous advantages, including high surface area, high thermal stability, tailorability, and the possibility of being functionalized with various functional groups. Regarding the removal of various PhACs, the use of MOFs could actually be beneficial. Various functionalities could enhance the interaction between MOFs and PhACs, enhancing adsorption [47].

As the name indicates, MOFs are constructed from two main elements: metal cluster and organic ligand. An MOF is usually synthesized using a solvothermal method in which the metal source and organic ligand are dissolved in a solvent (mostly dimethylformamide) in an autogenous pressure reactor, followed by a reaction at an elevated temperature. The reaction can also proceed through a hydrothermal reaction when water is used as the reaction medium. The resulting product can be separated by filtrating it out from the mother solution or through centrifugation. Afterwards, the synthesized MOFs can undergo a solvent exchange process to replace the solvent that is trapped inside the pores with a more volatile solvent. Before being used, the MOF is usually activated under vacuum and slightly high temperature to free the pores from the solvents or other molecules. However, in some cases, heating the MOF at a high temperature (~200 °C) is necessary when there is a ligand molecule trapped inside the pore that can only be removed through heating.

Some new methods have also been proposed to improve the conventional synthesis method. For example, MOF synthesis using an electrochemical method has been investigated to synthesize a [Zn(1,3-bdc)_{0.5}(bzim)] MOF [48]. Compared to the conventional solvothermal method, this synthesis strategy offers a faster reaction time, higher yield, and the possibility of controlling the particle size. Recent progress in this field has also shown the possibility of improving the reaction condition in order to make it more environmentally friendly. For example, the solvothermal method can be replaced with a more benign approach, such as ultrasonication [49]. Furthermore, it is possible to synthesize robust MOFs at room temperature using a more environmentally friendly solvent, such as water, and using a sodium salt as the linker source [50,51]. MOFs could also be synthesized through a mechanochemical approach in the absence or minimal amount of solvent [52,53].

Despite their numerous advantages over AC, as has already been mentioned above, most of the MOFs studied are not stable in a humid atmosphere or when exposed to water because of the weak metal–ligand coordination bonding. This may limit their applicability for PhACs removal from water systems. Therefore, the most essential requirement of applying MOF in this particular context is to carefully select or synthesize a water-stable MOF, which could be realized through several strategies [54]. This could be firstly done by choosing the MOFs that are built from high valence ions, such as zirconium and aluminum. These particular MOFs usually have a robust structure because they have a strong coordination bonding and thus are suitable to be applied for PhACs removal from water streams. In addition, modifying the MOFs to have hydrophobic property is another promising way to obtain a water-stable MOF because the contact between water molecules and the MOF will be greatly reduced. This strategy has been proven to improve the framework stability of the notoriously unstable MOF-5 under humid condition [55]. Lastly, a water-stable MOF could also be obtained when it is built from a rigid ligand, which has been proven in the case of UiO-67 [56]. Although UiO-67 is a

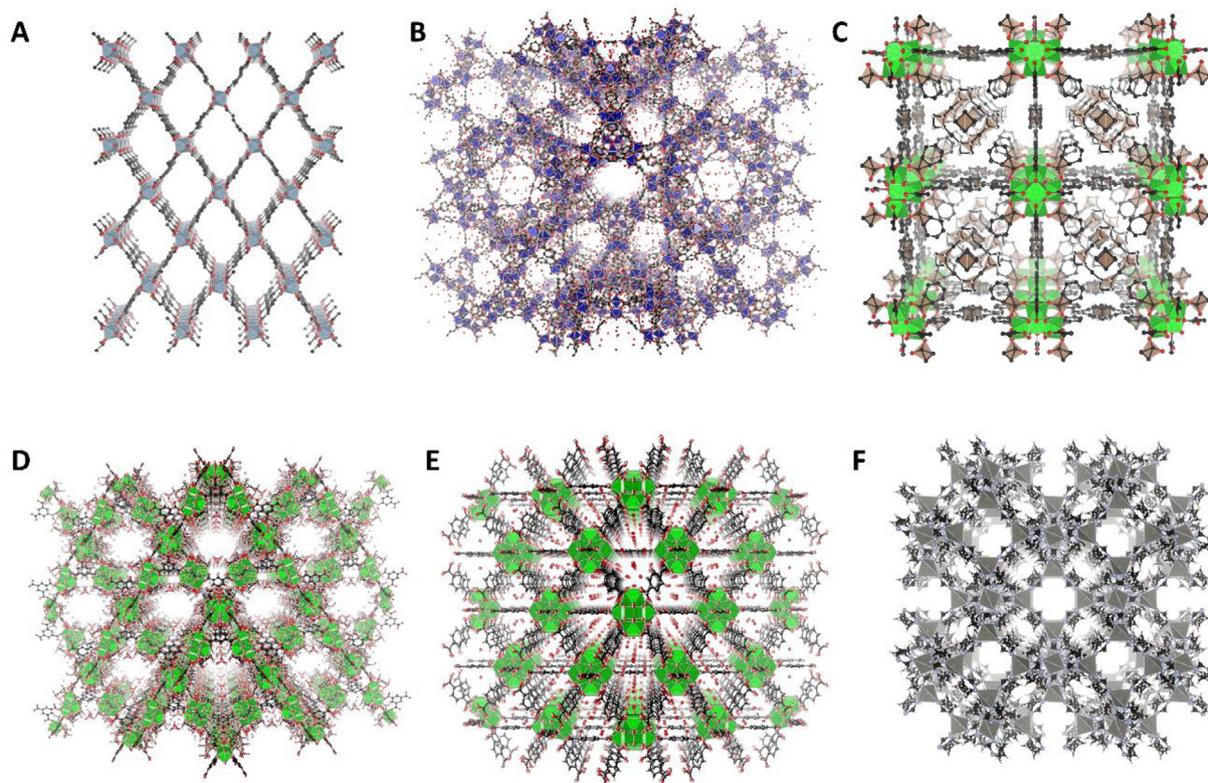


Fig. 2. Various MOF candidates for PhAC removal from water. (A) MIL-53(Al), (B) MIL-101(Cr), (C) MOF-525(Zr), (D) MOF-808(Zr), (E) UiO-66(Zr), and (F) ZIF-8 (Zn).

Zr-based MOF, its framework is not stable in a humid condition or when exposed to water, which might be caused by the rotational freedom of the biphenyl cores. Therefore, synthesizing a new ligand that is rigid and could minimize such a rotational freedom is necessary to obtain a robust and water-stable MOF. Some of the most commonly used MOF candidates are then shown in Fig. 2. These particular MOFs could also be further modified or functionalized to improve their adsorption performance towards various PhACs.

3. Factors affecting PhACs removal in AC and MOF

Before comparing the PhACs adsorption between AC and MOF, various factors that could significantly affect this performance is worth to be discussed. Such a discussion is important to give an insight regarding the existence of optimum conditions that have to be fulfilled in order to achieve an excellent performance in both adsorbents. At a glance, the surface area of an adsorbent could be hypothesized to be the greatest determinant because the higher the surface area, the greater the adsorption capacity. However, this is only true to some extent because an opposite trend has been observed in which AC or MOF with higher surface area exhibits a lower adsorption capacity [57–59]. In addition, an adsorbent with a surface area comprised mainly of ultramicropores could have a low adsorption capacity because some PhACs may not be able to diffuse through the pores to reach the adsorption sites, rendering the ultramicropores inaccessible [41]. Therefore, other factors will be further discussed below.

3.1. Pore size

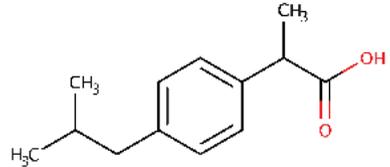
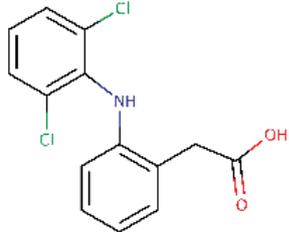
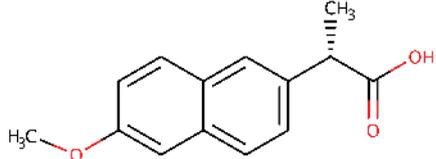
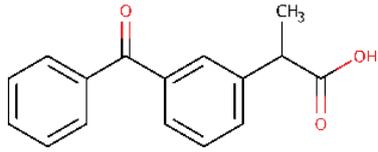
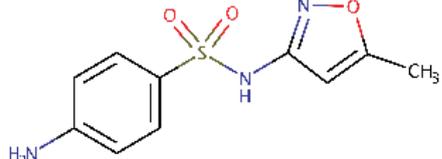
As has been previously stated, the surface area of either AC or MOF barely affect the adsorption performance of both materials.

However, this does not necessarily mean that the whole physical properties of both adsorbents could be fully neglected. In this respect, the size of the adsorbents' pores plays a critical role in influencing their adsorption performance. However, this situation might be different as usually encountered in a typical gas and liquid adsorption process, where the presence of ultramicropores is essential since they are considered as active sites where the adsorption process occurs. This is because the size of these compounds is considerably larger than gas molecules (Table 1).

In a study involving various AC, the highest ibuprofen adsorption capacity was obtained by AC that has the largest average pore width around 1.2 nm [60]. In contrast, the AC with narrow microporosity distribution around 0.7 nm exhibited the lowest adsorption capacity, which indicates the size exclusion of ibuprofen to access the adsorption sites in the AC. AC with larger pore size could then normally be obtained by adjusting their synthesis condition such as by adjusting the pyrolysis temperature and increasing the mass ratio of KOH (as the activating agent) and AC precursor [44,61]. In some cases, it may also be necessary to optimize the ratio of activating agent and the precursor. In the case of H_3PO_4 -activated AC, for example, an optimum ratio exists where further increasing the amount of H_3PO_4 during activation process leads to the destruction of the AC morphology and also its porosity [62]. The use of a mineral-rich precursor with a combination of a two-step process could also be effective to obtain AC with mesoporous structure, as illustrated in Fig. 3(A) [63]. The first step involves the chemical activation process of the precursor with $ZnCl_2$ to develop micropores. This is then followed by physical activation with CO_2 at 950 °C to develop mesopores, where a reaction between CO_2 and the pore framework occurs and is catalyzed by the inherent minerals in the precursor.

The importance of employing an adsorbent with sufficient pore size could render MOF a slight edge in comparison with AC because of the tailorability of MOF. Therefore, rationally selecting MOF with

Table 1
The molecular structure, pKa, and molecular dimension of selected PhACs.

Class	Compound	Molecular structure	pKa	Log K _{ow}	Molecular size (nm)	Ref
Non-steroidal anti-inflammatory drugs (NSAIDs)	Ibuprofen		4.91	3.97	1.03 × 0.52 × 0.43	[128,129]
	Diclofenac		4.15	4.51	0.96 × 0.71 × 0.47	[113]
	Naproxen		4.15	3.22	1.03 × 6.07 × 4.59	[129,130]
	Ketoprofen		4.45	3.2	0.39 × 0.61 × 0.77	[129,131]
Antibiotics	Sulfamethoxazole		1.7; 5.8	0.89	1.03 × 0.59 × 0.53 0.89 × 0.80 × 0.72	[132,133]

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Table 1 (continued)

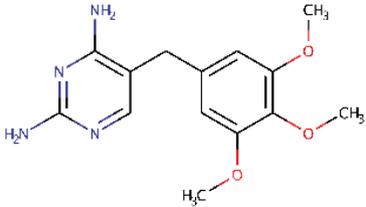
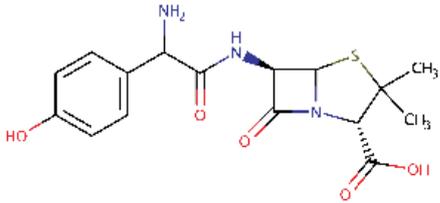
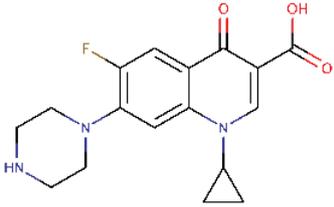
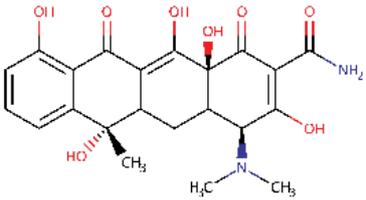
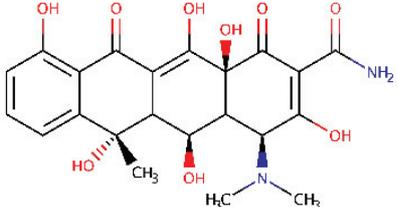
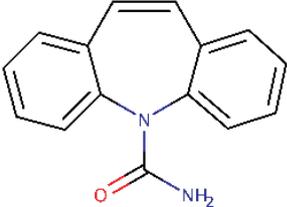
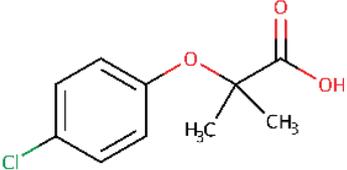
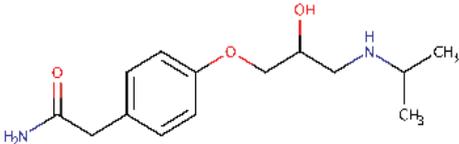
Class	Compound	Molecular structure	P_{Ka}	Log K_{ow}	Molecular size (nm)	Ref
	Trimethoprim		7.12	0.91	1.12 × 0.92 × 0.81	[133]
	Amoxicillin		3.23; 7.22	0.87	1.24 × 0.56 × 0.46	[128]
	Ciprofloxacin		6.27; 8.87	0.28	1.28 × 0.78 × 0.4	[134]
	Tetracycline		3.3; 7.7; 9.5	-1.37	1.29 × 0.62 × 0.75	[135,136]
	Oxytetracycline		3.3; 7.3; 9.1	-0.9	1.26 × 0.82 × 0.53	[282,323]

Table 1 (continued)

Class	Compound	Molecular structure	P_{Ka}	Log K_{ow}	Molecular size (nm)	Ref
Anticonvulsant	Carbamazepine		9.73	2.45	0.89 × 0.53 × 0.51	[132]
Anticholesterolemic drugs	Clofibric acid		3.6	2.57	0.5 × 0.58 × 1.9	[137]
Beta-blockers	Atenolol		9.6	0.16	1.8 × 0.7 × 0.7	[27]

Data for P_{Ka} and Log K_{ow} was obtained from PubChem (pubchem.ncbi.nlm.nih.gov) and Drugbank online (go.drugbank.com)

appropriate pore size is the simplest step to obtain a MOF with good adsorption capability. For instance, in a tetracycline removal investigation involving 3 Zr-based MOFs, MOF-525 performs better than UiO-66 [64]. This is mainly attributed by the fact that the pore size of the former (1.2, 1.6 and 1.9 nm) is larger than the later (0.7 and 1.2 nm) and thus not obstructing the diffusion of tetracycline into the MOF pores. In addition, as can be seen in Fig. 3(B), obtaining a MOF with larger pore size could also be accomplished through a defect engineering. This strategy is based on the possibility to obtain a MOF with larger pore size when its periodical atomic arrangement is obstructed. For example, defective UiO-66 [65] and MOF-801 [66] with a predominance of pore size above 1 nm could be obtained by modifying the reaction condition of their non-defective counterparts. As a result, these defective MOFs are more effective in capturing diclofenac from water streams.

3.2. Surface properties and functional groups

One of the most important properties that has to be considered for the removal of PhACs from water systems is hydrophilicity/hydrophobicity. For PhACs, this property could be estimated from the log K_{OW} (Table 1). The higher the number, the more soluble

the compound in oil phase (more hydrophobic). This value can then be used as a guideline for determining the hydrophobicity or hydrophilicity of a compound. A good adsorbent-adsorbate interaction could then be expected when they have similar properties. Therefore, for example, adsorption of a hydrophobic PhAC could be improved by increasing the hydrophobic property of the adsorbent. Attention to this interaction is particularly important when the PhACs are neutrally charged and cannot establish an electrostatic interaction with the adsorbent [67].

In the case of AC, both the hydrophobic and hydrophilic functional group in AC are responsible in enhancing its adsorption capability towards organic compounds and polar species, respectively [68]. Various strategies could then be employed to engineer the functional groups of AC in order to improve the adsorption capacity towards various PhACs. The first strategy is to selectively choose the precursor of AC. AC that is derived from lignocellulose has been reported to exhibit a more developed pore structure than keratin-based AC. The former also has more oxygen functionalities and a more acidic surface than the latter, which contribute to enhancing the adsorption property of the lignocellulosic-based AC [69]. The second strategy is to select the most appropriate method during the activation or modification of AC without

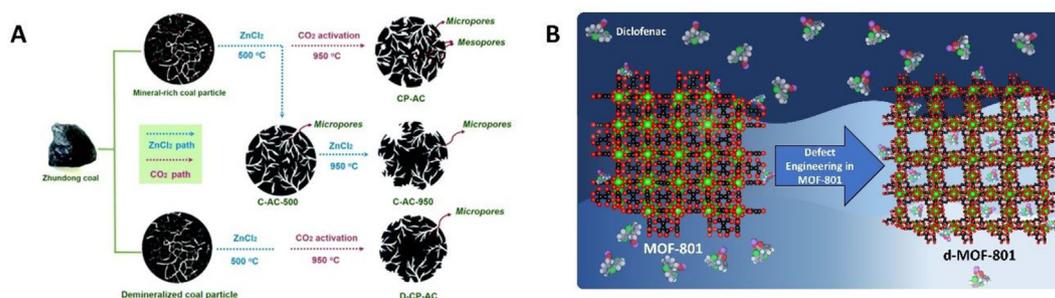


Fig. 3. Strategies to develop mesoporous structure in both AC and MOF: mesoporous structure development in AC using a two-step process employing a mineral-rich precursor [63] (A) and defect engineering in MOF-801 [66] (B). All the figures are reproduced with permission from the rightsholders.

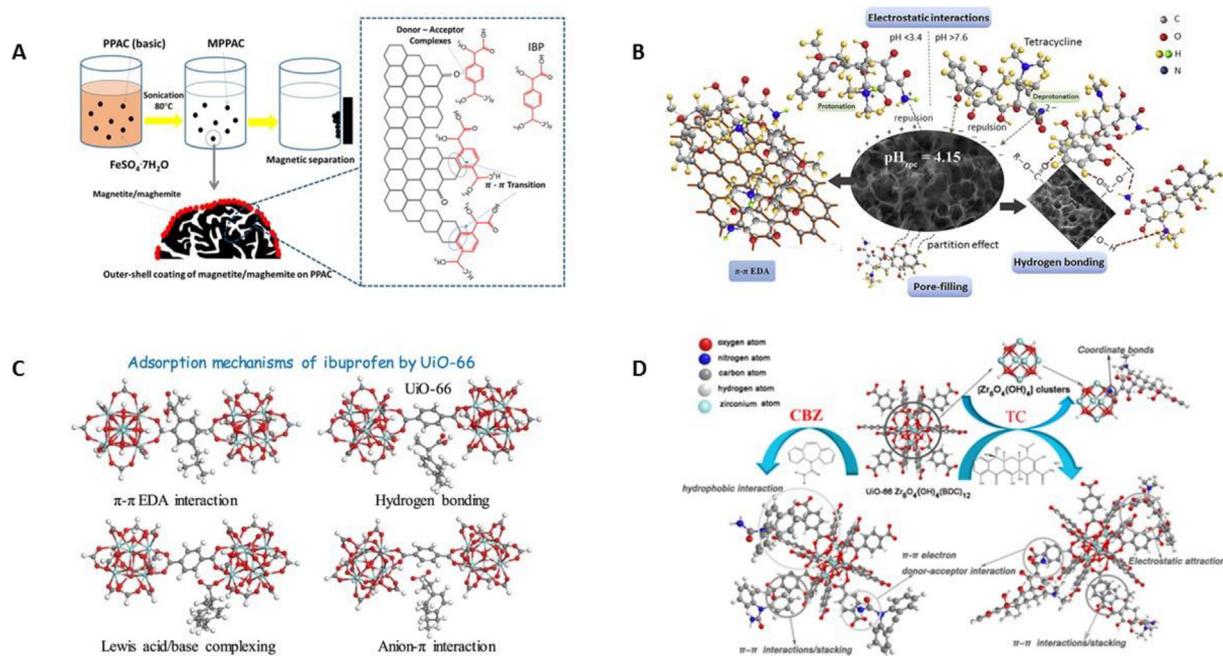


Fig. 4. Various PhAC adsorption mechanisms for AC and MOFs: ibuprofen on AC (A) [71], tetracycline on AC (B) [62], ibuprofen on UiO-66 (C) [83], and tetracycline and carbamazepine on UiO-66 (D) [94]. All the figures are reproduced with permission from the rightsholders.

destroying the integrity of its porous structure. In an investigation of H_3PO_4 -activated AC, for instance, it has been observed that various functional groups such as aromatic carbon, carboxyl and hydroxyl could be generated [62]. The presence of such groups is important to establish a π - π electron donor acceptor interaction and hydrogen bonding with PhACs molecules. Some studies have also shown that surface oxidation could be employed to increase the number of carbonyl and lactonic functional groups in AC, which could improve the interaction with the aromatic rings of the PhACs through the establishment of donor-acceptor complexes, resulting in a higher adsorption capacity towards ibuprofen [70,71]. However, the oxidation process should also be carefully controlled since it could destroy the pore structure of AC because of the erosion and pore blockage by degradation products during the process [72].

Although the presence of functional groups in AC are generally beneficial for PhACs removal, not all of them contribute equally to enhance the adsorption capacity. In a study using diclofenac as the adsorbate, the phenolic in the oxidized AC had the most important role in improving the interaction between diclofenac and AC, followed by the acidic and carboxylic groups. Both the phenolic and acidic group then contribute to establishing a hydrogen bond with diclofenac [39,73]. The presence of both particular groups could then be more pronounced when the carbon is produced from an MOF [74]. Moreover, there is also a possibility where the presence of certain functional groups might negatively impact the adsorption process towards certain PhACs. In a study involving chemically-activated (K_2CO_3 and H_3PO_4) and physically-activated (steam) AC, for example, it has been observed that the abundance of oxygen functional groups, particularly the R-COOH and R-OCO, in the former than the later leads to the lower ibuprofen adsorption capacity [75,76]. This is because such groups are responsible in attracting water molecules which eventually form three-dimensional clusters at the pore entrance of AC and thus blocking its access. As a consequence, the ibuprofen could not diffuse through the pores and get adsorbed.

As with AC, the presence of various functional groups in MOF is also beneficial in enhancing the interaction between the MOF and the adsorbate. Firstly, because most MOFs contain benzene or imidazole rings as their ligands, a better interaction with the PhACs and MOF framework could be expected through the establishment of a π - π interaction [77–80]. In addition, the presence of hydrophobic functional groups in MOF, such as fluorine, have also been observed to have a beneficial impact to improve the adsorption capacity of UiO-66 towards carbamazepine [81]. Another functional group that could be beneficial is basic functional groups. For example, MIL-101 with such functional groups is more efficient at adsorbing naproxen and clofibric acid than an acidic functional group because of the possibility of interacting with the -COOH group from the adsorbate [58]. A similar phenomenon was observed when investigating the positive effect of an amino group on the loading of ketoprofen in UiO-66 [82]. The interaction between the basic amine group and the carboxylic acid group of ketoprofen is beneficial in enhancing the drug adsorption capacity compared to UiO-66-NO₂. This was further proven when ketoprofen was released from the MOF, as only a partial release of ketoprofen could be achieved in UiO-66-NH₂ but both UiO-66 and UiO-66-NO₂ could achieve a complete release, indicating a strong amine-ketoprofen interaction. The presence of an amino group could also be beneficial when the MOF is used to remove various PhACs, such as ibuprofen [83], naproxen [83,84], tetracycline [85], and oxytetracycline [86,87], as it contributes to building a hydrogen bond between the PhACs and MOF. The hydrogen bonding between the MOF and PhAC could also be strengthened by increasing the number of hydroxyl groups. This was proven when MIL-101(Cr)-(OH)₃ and MIL-101(Cr)-OH with the most hydroxyl groups had

higher ketoprofen and naproxen adsorption capacities than the non-functionalized MIL-101(Cr) [84,88]. The presence of a hydroxy functional group is also beneficial for enhancing the adsorption of clofibric acid by MIL-101 [89]. However, there is also a possibility of weakening the metal-ligand bonding when the amino group of the ligand interacts with the PhAC. This has been demonstrated in a computational study in which UiO-66-NH₂ was used to adsorb tetracycline [90]. In this case, the hydrogen bonding between the amino group and the adsorbate weakened the metal-ligand coordination bonding, which could destroy the MOF.

Differing from AC, MOFs also have metal clusters within the structure of the framework. This metal cluster could build an interaction with PhACs during the adsorption process. First, a hydrogen bond, such as what could happen between the adsorbate and the functional group in MOFs, could be established between the hydroxyl group in the metal cluster and the PhACs. This has been reported for the adsorption of amoxicillin on MIL-53(Al) [91]. Another possible interaction is a weak metal-adsorbate interaction as observed in the adsorption of tetracycline on UiO-66 and MOF-525 [64] and a metal- π interaction as observed in the adsorption of diclofenac by functionalized UiO-66 [92]. The presence of an oxygen atom in the metal cluster could also contribute to a hydrogen bond with the PhACs because it can also act as a hydrogen acceptor [77]. However, stronger coordination bonding could also occur as observed in the XPS study after the adsorption of tetracycline hydrochloride on MIL-101(Fe), MIL-88A(Fe), and MIL-53(Fe). Such a bond could be established because of the interaction between tetracycline and the open metal sites in the MOF by replacing the water molecule that was previously coordinated with the metal cluster [93]. This phenomenon has also been proposed in the adsorption of tetracycline in UiO-66 through replacement of the carboxylic group to coordinate with Zr-O bond [94]. A similar mechanism has been proposed to explain the adsorption of diclofenac anion on Zr-based MOFs, in which the diclofenac anion could replace the terminal OH/H₂O group in the metal cluster to establish coordination bonding [95]. The metal sites could also establish hydrogen bonding with PhACs. In this case, the metal cluster usually contains an oxygen atom that may also establish a hydrogen bond with the oxygen/nitrogen functional group in PhACs [90,93].

Various mechanisms that could occur with both AC and MOFs during the removal of PhACs from water systems are presented in Fig. 4. In general, three main mechanisms could occur: hydrogen bonding, electrostatic interaction, and π - π interaction. However, the presence of a metal cluster could add another possible mechanism, namely coordination bonding between the PhAC and the metal cluster as illustrated in Fig. 4(D). This interaction may be beneficial to improving the adsorption performance towards particular PhACs, such as tetracycline. Although AC does not contain any metal cluster within its structure, this particular interaction could still possibly be established if some metal residues are present and, thus, could establish a complex interaction with the PhAC [96].

3.3. Natural organic matter

The performance of adsorbents towards various PhACs could also be highly influenced by the presence of natural organic matter (NOM). In this case, humic acid (HA) could be used as a model for studying the effect of NOM on PhAC removal. For example, the adsorption performance of AC towards ibuprofen can be reduced up to 70 % in the presence of HA [97]. Such a reduction could be associated with pore blocking, which results in the inability of ibuprofen to access the adsorptive sites. A similar result was obtained when employing AC for the removal of carbamazepine and naproxen in post-sedimentation water from a water treatment facility [98]. The declining adsorption performance also depends

on the nature of the AC. During the naproxen adsorption study, the impact of NOM on the adsorption performance was greater in coal-based AC than in coconut shell-based AC. These results were confirmed by a number of studies involving various PhACs in wastewater and surface water, and the equilibrium adsorption of AC could be reduced up to 50 % [99–101]. There are two main mechanisms involved that may contribute to the declining performance of AC: adsorption competition and pore blocking. When the NOM is relatively small and more hydrophobic, there is a higher potential for it to competitively adsorb on AC rather than just blocking the pores of the AC [99]. The composition of the NOM is equally important when investigating the impact of NOM on the removal capacity of AC. In this case, the presence of fluorophore compounds is considered to impart the most negative impact on adsorption performance because they are a strong competitor for micropollutant adsorption by AC [101].

Although the presence of NOM is expected to reduce the adsorption performance of AC, a contrasting situation may also occur in which the presence of NOM does not impair the adsorption performance of AC. This has been observed in a study of ciprofloxacin removal [102]. There are several possible explanations for the phenomenon. First, the AC may have strong preferential adsorption towards the targeted molecule. Second, both the NOM and adsorbate have different adsorption sites on AC so they do not compete with each other, but a relatively high adsorbate/NOM ratio could be employed during the investigation, underestimating the competitive effect.

Despite the importance of studying the effect of NOM on the adsorption performance of adsorbents, a thorough investigation has not been carried out with MOFs. One investigation studied the impact of HA on ciprofloxacin adsorption by ZIF-8-derived carbon [103]. Unexpectedly, the adsorption of the ZIF-8-derived carbon was increased up to 5 mg L⁻¹ in the presence of HA. Afterwards, the adsorption remained stable and did not further increase when the HA concentration was increased up to 40 mg L⁻¹. This could be attributed to the formation of additional adsorption sites when the ZIF-8-derived carbon also adsorbed HA. The presence of HA allowed a hydrogen bond with ciprofloxacin, increasing the adsorption capacity.

3.4. pH

During the adsorption of PhACs, various parameters could affect the adsorption performance. One important parameter is pH, which can influence the state of both the adsorbate and the adsorbent. In the case of the former, the pH determines whether the adsorbate is protonated, neutral, or deprotonated. PhACs, such as ciprofloxacin, can also exist as zwitterionic species. Moreover, the solubility of the PhACs can also be affected by pH. For example, the solubility of diclofenac sodium is very limited in pH < 4 and, thus, the separation process that occurs below this pH can be attributed to precipitation of the diclofenac compound. Meanwhile for the latter, the pH can manipulate the surface charge of the adsorbent. In this case, pH is important to determining the isoelectric point of an adsorbent. Below this point, the adsorbent is positively charged, whereas the adsorbent is negatively charged when the pH is above its isoelectric point. Therefore, it can be safely assumed that a change in pH will influence the adsorption performance of both AC and MOFs, in particular by altering the electrostatic interaction between the adsorbents and PhACs. However, a negligible effect has been reported in the case of carbamazepine adsorption on UiO-67 [104]. This may then indicate the absence or negligible impact of electrostatic interactions during adsorption and that other interactions play a more dominant role. However, most studies have shown a non-negligible impact of pH change on the adsorption performance.

For instance, conducting the adsorption process at lower pH could beneficially impact the removal efficiency of AC towards various PhACs by altering the hydrogen bonding interaction between the adsorbates and AC. In this case, the presence of various AC functional groups, such as phenol and carboxylic groups, in protonated form is important because they are able to act as an H donor to interact with the PhACs with O or N sites to establish a hydrogen bond [105]. Therefore, negligible adsorption performance could be observed once the pH was increased because such functional groups are now in deprotonated form [105]. Similarly, a positive impact on the adsorption performance at acidic pH could also be expected when the adsorption mechanism in AC is governed by the electron donor–acceptor interaction, such as in the case of ibuprofen adsorption [70]. Differing from the electrostatic interaction that is unfavorable to be upheld in this condition due to the neutrally-charged ibuprofen, the donor–acceptor bond between the aromatic bond of ibuprofen and the carbonyl functional groups of AC could still be well-established at this pH and, thus, resulting in enhanced adsorption performance. Moreover, in a multicomponent system, an adsorbate–adsorbate interaction may also occur at acidic pH, which could aid in increasing the overall adsorption capacity of AC [106]. However, a decrease in adsorption capacity could also be observed at low pH, possibly due to a reduction in electrostatic interactions, particularly when the PhACs are positively charged [105]. In contrast, higher pH usually leads to a reduction in the efficiency of removing various PhACs [43,57,75,105,107–110]. In addition to being attributed to the deprotonated state of the various functional groups, this may also be due to the negative charge of the adsorbate and a repulsion effect being established between the adsorbate and negatively charged AC, leading to a reduction in the adsorption capacity. However, an increase in pH does not necessarily lead to a negligible adsorption capacity, as it only occurs when the electrostatic interaction is the main mechanism of adsorption. Therefore, considering the fluctuation in the adsorption performance in AC within a pH range, an optimum pH where the adsorption capacity of AC towards PhACs is the highest must sometimes be determined. This was demonstrated in a study using AC to remove amoxicillin [108,111].

A similar trend has been observed when an MOF is chosen as the adsorbent. In this case, higher pH usually leads to a reduction in the adsorption capacity of the MOF towards various PhACs [84,93,112–114]. As with AC, this performance of MOF towards PhACs could also be governed by an electrostatic interaction between the adsorbate and MOFs. At higher pH, the MOF is negatively charged and can establish a repulsion effect towards a deprotonated adsorbate. Furthermore, almost no adsorption could take place at a very high pH [112]. In this case, there are at least two plausible explanations. First, it may be caused by the adsorption process that is solely governed by electrostatic interactions between the MOF and adsorbate. The second possible explanation is degradation of the framework. Although the MOF is relatively robust at a wide range of pH, it can be degraded at a very basic pH. Therefore, the MOF structure could be partially degraded when applied at basic pH, resulting in a reduction in the adsorption capacity [31]. In contrast, at low pH, the adsorption capacity of the MOF towards various PhACs could be increased, stabilized, or decreased [91,94]. Therefore, as with AC, it is sometimes necessary to determine an optimum pH where the adsorption capacity of the MOF is maximized. This has been observed with UiO-66-NH₂, for which an optimum pH is required to establish a strong Lewis acid–base interaction between the MOF and adsorbate [59]. An optimum pH is also required to remove oxytetracycline using MIL-101(Cr)-ethylenediamine and MIL-101(Fe)-CNT because this condition will establish a strong interaction between the zwitterionic oxytetracycline and the MOF [86,115].

3.5. Temperature

A change in temperature could also affect the adsorption performance of PhACs in both AC and MOFs. Firstly, the temperature could be expected to affect the adsorption kinetics. When the operating temperature is elevated, adsorbate diffusion towards the adsorbent could be enhanced. This also means that the adsorption equilibrium could be reached faster. For example, in the diffusion of diclofenac in AC, increased temperature is accompanied by a significant decrease in the time for the adsorption to reach equilibrium [116]. Another investigation reported that a decrease in temperature could reduce the molecular diffusion of hydrophobic PhACs, inhibiting their access to the small pore region of the adsorbent [117]. Consequently, a reduction in the adsorption capacity was observed.

Regarding the maximum adsorption capacity, the trend for both AC and MOFs can increase or decrease depending on the adsorption enthalpy of each adsorbent. The increase in adsorption capacity as the temperature increases indicates an endothermic phenomenon. This can then be caused by various phenomena. For example, this may indicate the importance of chemical interactions between the adsorbate and adsorbent [57]. In this case, the increase in temperature is useful to surpass the activation energy barrier of the adsorption process [38]. In addition, there is a possibility that materials may swell as the temperature increases, creating more access for the adsorbate to reach the adsorption sites [38]. The increase in adsorption capacity may also be assisted by the formation of adsorbate agglomeration. In this regard, there is a tendency for PhACs to aggregate as the temperature increases because the reaction is endothermic, resulting in an increase in the adsorption capacity of the adsorbents [118]. This has been observed, for example, in ibuprofen [70,119,120] and various antibiotics [38,109,121,122] using AC. Such a trend has also been observed with MOFs, such as during the adsorption of ciprofloxacin on various MOFs and MOF composites [123], tetracycline on ZIF-8 [80] and UiO-66 [94], carbamazepine on UiO-66 [94], and diclofenac on amino UiO-66 [124] and MIL-100(Fe) [112]. In contrast, the decrease in adsorption capacity as the temperature increases indicates that the adsorption process is an exothermic phenomenon and, thus, desorption process could occur by increasing the operating temperature. This has been observed in the adsorption of various NSAIDs by AC, MOFs, and MOF-derived carbon materials [29,113,125,126]. This trend also occurred in a study using a composite of UiO-66/graphene nanoplate to remove carbamazepine [127]. In this scenario, the decreased adsorption capacity at high temperature may be caused by an increase of the adsorbate solubility in water at high temperature, hindering the adsorption process.

Regardless of the trend in the adsorption capacity with changing temperature, it is always expected that the free energy change during the adsorption process will be negative. This indicates that the adsorption of PhACs is a spontaneous process. The free energy can usually be evaluated by calculating the magnitude of the Gibbs energy change at different temperatures. In an exothermic adsorption process, this value could increase and even get closer to a positive value as the temperature increases [114].

4. Performance of AC and MOFs in PhACs removal

Having discussed the various factors affecting the adsorption performance, the PhACs adsorption performance comparison between AC and MOF can be carried out. It should then be firstly noted that the values reported here were taken at an optimum condition, which are sometimes cannot be met in the real situation but could still be useful as a guideline to appropriately select the

potential adsorbents. Therefore, to achieve this, we consider the maximum adsorption capacity of the adsorbents as the most determining factor because it is the intrinsic adsorbent property. In most studies, this performance is usually approximated by employing Langmuir equation to obtain the maximum adsorption capacity. In addition, we also consider the Langmuir constant of the adsorbents, which highlights the indicates the affinity between the adsorbents and the adsorbates. This section will extensively discuss the adsorption performance of AC and MOFs towards various PhACs as listed in Table 1.

4.1. Non-steroidal anti-inflammatory drugs

One of the common classes of PhACs that has been widely investigated for removal from the environment is non-steroidal anti-inflammatory drugs (NSAIDs). This is because most NSAIDs can be accessed easily as over-the-counter medications, which do not require any prescription from a medical doctor. Excessive consumption that results in unused or expired products and incomplete metabolization of the drugs inside the human body may then cause their release and accumulation in the environment. In general, there are four widely used NSAIDs: ibuprofen, diclofenac, naproxen, and ketoprofen. They have high-volume production and are present in water systems and wild animals [138].

Ibuprofen is one of the most popular NSAIDs and been investigated as a target compound to be removed from aqueous waste. In water systems, ibuprofen can be detected as a whole compound or as metabolites. The latter come from the incomplete metabolization of ibuprofen in humans and animals and could be more toxic than its parent compound [139]. Exposure to a concentration of 1 mg L^{-1} of ibuprofen could cause various negative impacts in microorganisms, including growth inhibition and structural alteration [140]. AC can be used as an effective adsorbent to remove this particular compound from water systems. From a number of reports, the maximum ibuprofen adsorption capacity of AC usually falls within the range of $10\text{--}200 \text{ mg g}^{-1}$ [46,71,76,97,110,119,128,141–149]. The difference in the performance depends on various factors, such as the source of the AC and type of activation process because they can yield different surface properties of the AC. Although this capacity could be considered to be moderate, it is also possible to obtain a high-performance AC with higher ibuprofen adsorption capacity. This has been observed, for example, in an AC cloth and AC from cork waste, which had an ibuprofen adsorption capacity of $300\text{--}500 \text{ mg g}^{-1}$ [60,75,120]. The high adsorption capacity could be attributed to the higher surface area, though this must also be compensated by the slow time to reach equilibrium ($\sim 10 \text{ h}$) because of the small pore size, which builds resistance for the pore diffusion process [120]. This problem could be addressed by producing AC that has more mesopores to aid the diffusion and adsorption of ibuprofen because the size of the ibuprofen molecule hinders its diffusion through the micropores of AC [60].

A number of MOFs and their composites have also been investigated as candidates to remove ibuprofen from waste systems. Some of them have a similar adsorption capacity as AC, in the range up to around 200 mg g^{-1} [48,77,83,84,150–154]. However, a significant number of MOFs have a better reported ibuprofen adsorption capacity than AC, such as MOF-808 and UiO-66, which have adsorption capacities of 270 and 606 mg g^{-1} , respectively [78]. Employing MOFs with a large pore aperture is also beneficial to improving uptake. This was demonstrated, for example, when the adsorption capacity of both MIL-100 and MIL-101 were found to be 347 and 1576 mg g^{-1} respectively [79]. The unprecedented high ibuprofen uptake of MIL-101 is attributed to its large pore aperture (12 \AA) and pore volume ($12,700$ and $20,600 \text{ \AA}^3$). Another possibility for enhancing ibuprofen uptake is through a post-synthetic

modification. Using diaminstillbenedicarboxylate as the ligand for Zr-based MOFs, the MOF could be later functionalized with oxalyl chloride and terephthaloyl chloride [155]. The ibuprofen uptake capacity was 370–455 mg g⁻¹. Another strategy is to construct a carbon material that is derived from a MOF. A carbon material derived from MIL-53(Fe) has been reported to have an ibuprofen adsorption capacity of approximately 200 mg g⁻¹ [125]. In another study using ZIF-8 as the precursor material, an ibuprofen adsorption capacity of up to 320 mg g⁻¹ was achievable when induced by the abundance of a phenolic group [151].

Diclofenac is another popular NSAID that has been widely investigated as the targeted adsorbate to be removed from the environment. Its presence in water systems at various concentrations could then have negative impacts on aquatic lives. For example, exposure of *Oryzias latipes* in water to a diclofenac concentration of 1 µg/L has been reported to result in cellular toxicity, genotoxicity, and estrogenic effects [156]. Both AC and MOFs have been widely investigated to remove diclofenac from water systems. In most of the studies using AC as an adsorbent, the diclofenac adsorption capacity is in the range of 50–200 mg g⁻¹ or lower [29–31,34,35,37,41,57,110,116,126,157–161]. In addition, slow adsorption kinetics of AC towards diclofenac could occur because of its high microporosity [158]. To address the relatively low diclofenac adsorption capacity of AC, engineering the pore structure in AC seems to be important. For example, construction of a hierarchical pore structure in AC could be an effective strategy for improving the diclofenac adsorption capacity and kinetics [39]. In this case, parameter optimization of AC production, such as the carbonization temperature and activation method, seems to play a large role in obtaining AC with high surface area and mesoporous structure, which could have a diclofenac adsorption capacity of up to 700 mg g⁻¹ [149].

In contrast, MOFs seem to be more promising for eliminating diclofenac from wastewater systems. Although the diclofenac adsorption capacity of some MOFs, such as UiO-66 [65,124,162], FeBTC [163], MOF-801 [66], MOR-2 [95], and ZIF-8 [151], is comparable or even lower with AC, the incorporation of various functional groups, such as amine and acetate, can significantly improve the adsorption capacity to 400–600 mg g⁻¹, which is more than twice the capacity of AC [112,124,164]. Functionalization of the MOF with an acidic group, such as SO₃H and acetate, has also been observed to improve the MOF adsorption capacity towards this particular compound [92,162]. This capacity could be further enhanced in the presence of metal species in the functional group, such as iron and copper [92]. In addition, defect engineering strategy has also shown to be very effective in improving the diclofenac adsorption capacity in UiO-66 [65] and MOF-801 [66]. Compared with their non-defective counterparts, the defective MOFs have exhibited more than 4 times maximum diclofenac adsorption capacity which could reach up to around 680 mg g⁻¹ in the case of defective MOF-801 [66]. Despite this, high diclofenac adsorption uptake in MOF could not only be obtained in modified MOFs. Some unmodified MOFs have exhibited a higher diclofenac adsorption capacity than AC. For example, the maximum adsorption capacities of a Cu-based MOF [165], MIL-100(Fe) [130], MIL-101(Fe) [130], and MIL-53(Al) [166] have been reported to be in the range of 400–600 mg g⁻¹. Moreover, a maximum capacity of 833 mg g⁻¹ could be obtained by using zirconium-based MOF-808 [113]. Such a high capacity is attributed to the high surface area and large pore opening of MOF-808, which is highly suitable to adsorb diclofenac. For the removal of diclofenac, the use of MOF-derived carbon material could also be useful because its adsorption capacity could reach 400 mg g⁻¹, which outperforms commercial AC [151].

Naproxen is another NSAID that has been widely used; therefore, its removal from water systems has also been of increasing interest. Although its presence in the water could have various

negative impacts on aquatic life, its photoderivative products could pose more dangerous effects than its parent compound [167]. To remove naproxen, most types of AC and its composites could be deployed, and they usually have an adsorption capacity of up to 200 mg g⁻¹ [105,145,147,161,168–175]. However, some ACs with a combination of high surface area and mesoporous structure could exhibit higher adsorption uptake of approximately 300 mg g⁻¹ [142,176], and even up to 500 mg g⁻¹ [177]. Some of the reported MOFs have also demonstrated a similar naproxen uptake of approximately 100 mg g⁻¹ [84,168,178], though some unmodified MOFs, such as MIL-53(Al) [166], MIL-100(Fe) [130], and MIL-101(Fe) [130], have also demonstrated promising naproxen uptake of approximately 300 mg g⁻¹. However, this capacity can be improved when the MOF is functionalized. For example, the naproxen adsorption capacity of various functionalized MIL-101s, such as MIL-101-ethylenediamine, MIL-101-(OH)₃, and MIL-101-OH, could reach 154, 156, and 185 mg g⁻¹, respectively, compared to only 100 mg g⁻¹ with a non-functionalized MIL-101 [58,84,88]. A similar result has been achieved by constructing a composite that consists of graphene oxide and MIL-101 [170]. In this case, the naproxen adsorption capacity in the composite could be improved approximately 53 % (171 mg g⁻¹) compared to bare MIL-101. In another study, doping a metal ion in MIL-101 has the possibility of increasing the naproxen uptake capacity to approximately 396 mg g⁻¹ [179]. In this case, the presence of multiple ions in the MOF may help enhance the naproxen-MOF interaction. In another strategy, a composite adsorbent could also be used as an alternative approach to improve the adsorption capacity of MOFs. This has been observed in a composite consisting of graphene oxide (GO) and MIL-101 in which the naproxen adsorption capacity could be increased 50 % compared to the pristine MIL-101 [170].

Ketoprofen is another NSAID that is widely consumed worldwide. The use of this particular NSAID is popular when pain, such as that caused by rheumatoid arthritis and osteoarthritis, cannot be mitigated with the other common NSAIDs discussed above [180]. The presence of this particular compound in the water could have various negative impacts, such as growth inhibition of *Cyprinus carpio* embryos [181] and induction of metabolic toxicity in *Gyps coprotheres* [182]. Therefore, various studies have investigated removing ketoprofen from water systems. In this case, AC still usually has an adsorption capacity ≤ 100 mg g⁻¹ [42,119,131,183–186], though it is also possible to increase this capacity up to 300 mg g⁻¹ [187]. Using MIL-101(Cr) with a varying degree of hydroxyl functional groups, a higher adsorption capacity towards ketoprofen can be obtained by increasing the hydroxyl group in the MOF. However, the adsorption capacity only reaches up to 100 mg g⁻¹ and is not very competitive against AC [88]. Synthesizing a MOF composite could be a strategy for improving the adsorption performance, as observed in the use of MIL-101(Cr)/chitosan composite, which has a maximum adsorption capacity of approximately 157 mg g⁻¹ [153]. Although MOF may not outperform AC for this particular purpose, the employment of Zr-based MOFs could be beneficial. In this regard, Zr-based MOFs, such as UiO-66 and MOF-808, have shown a maximum adsorption capacity within the range of 300–600 mg g⁻¹ [188].

The adsorption performance of both AC and MOFs towards various NSAIDs is summarized in Fig. 5. As can be seen from Fig. 5(A), the maximum adsorption capacity of MOFs that have been studied for NSAID removal peaks at 251–500 mg g⁻¹. This is in contrast to the performance of AC, which peaks with a maximum adsorption capacity in the range of 101–250 mg g⁻¹, and up to 80 % of studies have shown that the maximum adsorption capacity of AC is only up to 250 mg g⁻¹. Moreover, some MOFs could even exhibit an adsorption capacity greater than 500 mg g⁻¹. For example, MOF-808 has a maximum adsorption capacity of 833 mg g⁻¹ towards

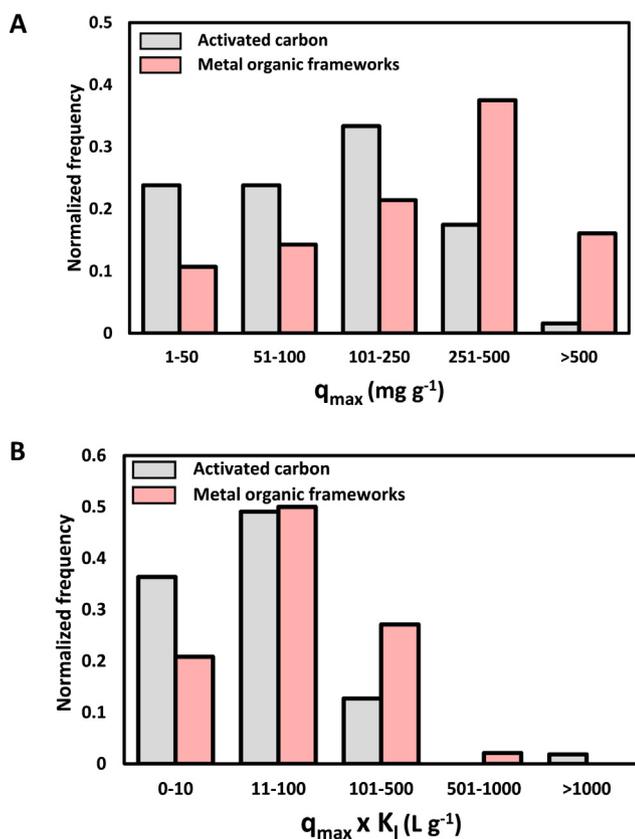


Fig. 5. Comparison of the adsorption performance of AC and MOFs for the removal of various NSAIDs based on maximum adsorption capacity (A) and the isotherm slope at low concentration (B).

diclofenac [113]. In addition, various functionalized UiO-66 frameworks have demonstrated an excellent adsorption capacity of up to 770 mg g⁻¹ towards the same compound [92].

Notably, most of the studies on NSAID removal have been conducted at a relatively high pollutant concentration. This is in contrast to the concentration of PhACs in the environment usually being very low. Consequently, the maximum adsorption capacity may not reflect the real adsorbent performance. Therefore, another performance comparison must be conducted in which the maximum adsorption capacity is not the sole determining factor. As has been stated in the beginning of this section, the use of Langmuir constant to obtain the Langmuir isotherm slope at very low concentration could be used to approach the adsorbent performance where the pollutant concentration is very low. This number contains the K_f value, indicating the affinity between the adsorbent and adsorbate. Therefore, in an ideal scenario, the maximum adsorption capacity is expected to be accompanied by a high K_f value and result in an adsorbent with high adsorption capacity and affinity.

The result of the above analysis of NSAID removal is shown in Fig. 5(B). As can be clearly seen, the majority of both AC and MOF adsorbents peak at a slope value between 11 and 100 L g⁻¹. A slope of 100 L g⁻¹ would mean that, in the case of a feed concentration of 1 mg L⁻¹, the adsorbent could reach a loading of 100 mg g⁻¹. This could indicate that some of the MOFs that have higher adsorption capacities are impaired by relatively low affinity. A contrasting situation could occur with AC, in which a low adsorption capacity is combined with high affinity. However, the second largest group of MOFs have values in the range of 101–500 L g⁻¹. This is in contrast to AC, in which the second largest group have

the lowest position, namely 0–10 L g⁻¹. This may indicate the superiority of some MOFs over AC for the removal of NSAIDs. Within this category, some MOFs, such as MOF-808 [113], Cu-doped-MIL-101(Fe) [179], and both functionalized and non-functionalized MIL-101(Cr) [58], could be good candidates that combine good adsorption capacity and adsorbent-adsorbate affinity. In addition to the large pore aperture and high surface area, the better adsorption performance of MOF than AC towards various NSAIDs could also be aided by the presence of carboxylic group in the investigated NSAIDs. Such a carboxylic group could then establish a coordination bonding with the exposed metal sites of the MOFs to significantly increase the adsorbent-adsorbate affinity and thus resulting in the higher adsorption capacity [189].

4.2. Antibiotics

Another class of PhACs that has been largely investigated for removal from water systems is antibiotics. Antibiotics were first introduced in 1930 as organic compounds used to eliminate pathogenic bacteria [190]. As in the case of NSAIDs, the presence of such compounds in water systems is highly concerning and poses a high risk to the aquatic environment [191,192]. In addition to the water ecosystem, there is also a concern that the presence of antibiotics may have negative impacts on the soil ecosystem, though clear evidence for such a concern is not yet established [193]. In addition to these risks, one of the greatest environmental concerns caused by antibiotic contamination is the rapid development of resistance in microbial communities because of unintentional and massive exposure to mass-produced antibiotics [193]. For example, municipal water treatment has been reported to be an important source of antibiotic resistance genes, which could have potential to pollute the surrounding surface water [194]. Therefore, removal from the environment is essential.

Sulfamethoxazole is one example of a sulfonamide antibiotic that has been widely used for both animals and humans. Because of its frequent usage, its potential to contaminate the surrounding environment cannot be neglected [195]. As a targeted adsorbate to be removed from the environment, the adsorption capacity of AC may vary from 50 to 200 mg g⁻¹ [32,107,196–199]. However, the maximum adsorption capacity of various types of AC estimated by Langmuir equilibrium could reach 400 mg g⁻¹ or greater [67,106,200–202]. Some types of AC exhibit a linear adsorption equilibrium in which more sulfamethoxazole is adsorbed as its concentration increases, which may indicate the involvement of a chemical reaction and interaction, not just limited to monolayer physical adsorption [32,201].

An investigation of the removal of sulfamethoxazole has also been conducted involving various MOFs, such as Cu-BTC [114], MIL-53 (Fe) [198], MIL-101 [114], NU-1000 [114], UiO-66 [114], UiO-66-NH₂ [114], UiO-67 [203], and ZIF-8 [114]. Most of the MOFs, including Cu-BTC, MIL-53(Fe), UiO-66, and ZIF-8, cannot really compete with the capability of AC because their adsorption capacity is < 50 mg g⁻¹. However, there are some promising MOFs with adsorption capacities of approximately 200 mg g⁻¹ because they have large pore windows (e.g., NU-1000 and MIL-101(Cr) [114,204]). In addition, the sulfamethoxazole adsorption process occurs very fast in MIL-101(Cr), with only 3 min required to reach equilibrium. To outperform AC, porphyrin-based MOFs MOF-525 and MOF-545 have been studied for this purpose [114]. The sulfamethoxazole adsorption capacity of both MOFs could reach 585 and 690 mg g⁻¹, respectively, which is significantly higher than that of their counterparts. In addition, a study was conducted by employing MOF-based nanoporous carbons. Various MOFs, such as MOF-5 [205] and ZIF-8 [74,206], have been investigated as starting materials to synthesize porous carbon for sulfamethoxazole removal. Compared to the normal AC and MOF used as the starting

material, the adsorption capacity of this material is higher and in the range of 300–700 mg g⁻¹ [74,205,206].

In addition to sulfamethoxazole, trimethoprim is another example of an antibiotic that has been widely used in the medical, veterinary, and aquaculture fields because of its cheap price and broad anti-bacterial spectrum [207]. As a consequence of its broad usage, it also has the potential to contaminate the environment. Therefore, its removal from water systems is one of the main recent research topics. Based on a number of studies on the use of AC as an adsorbent to remove trimethoprim, the reported adsorption capacity of AC could be as low as 50–100 mg g⁻¹ [198,208–210]. However, this capacity could be improved so AC has a maximum adsorption capacity in the range of 200–300 mg g⁻¹ [69,211,212], and even up to 500 mg g⁻¹ when a microporous AC is used because of the suitability of the trimethoprim molecule to fill the micropores [212]. In contrast to AC, only a few studies have investigated the use of MOFs to remove trimethoprim. MIL-53(Fe) [198] and Zr-bio-MOF [213] have been investigated as potential adsorbents to remove trimethoprim, but their adsorption cannot outperform AC.

Penicillin is another class of antibiotic that has been investigated for removal from the environment. One example compound is amoxicillin. The adsorption capacity of AC to remove this compound has been observed to be in the range of 50–200 mg g⁻¹, which shows the importance of not just the physical properties, but also the chemical properties of AC [36,108,111,118,121,128,214–216]. However, the maximum adsorption capacity of AC could be improved up to 500 mg g⁻¹ when chemically activated, such as by using KOH, NaOH, or NH₄Cl, or through suitable physical activation that assists in increasing the porosity of the AC [111,217–220]. The use of MOFs has been reported to remove amoxicillin from water system, though this is not as widely investigated as adsorption using AC. From these investigations, we conclude that some MOFs, such as MIL-101 [221], MIL-101-NH₂ [221], MOF-235 [221], MOF-235-NH₂ [221], UiO-66 [59], and Zn-MOF [222], are still not competitive enough to outperform AC because their adsorption capacity is comparable or below the capacity of AC. Differing from the rest, MIL-53(Al) could be a promising option because it has been reported to have an amoxicillin adsorption capacity of up to 759 mg g⁻¹ [91].

Ciprofloxacin is another type of antibiotic that has been investigated for removal from water systems. This particular compound is a fluoroquinolone antibiotic that has been widely used to treat diseases that occur in both humans and animals. The presence of this particular compound could result in a number of negative impacts. For example, the presence of ciprofloxacin could decrease the nutrient removal capability in wetlands and alter its microbial community, increasing the presence of anti-resistance genes [223]. Addressing this issue, various ACs and their composites have been investigated for removing this particular compound from water systems. In these studies, the ciprofloxacin adsorption capacity of AC has been in the range of 200–400 mg g⁻¹ [102,122,224–233] with the possibility of a maximum uptake of 600 mg g⁻¹ [234]. Despite this quite good performance, some types of AC still suffer from low adsorption uptake of < 100 mg g⁻¹ [26,235–239] and exhibited a slow kinetic response because more than 24 h are required for the adsorbent to reach equilibrium [224,234].

A number of MOFs have also been investigated for the removal of ciprofloxacin. However, some proposed MOFs, such as Cu-glutamate, Cr-fumarate, and UiO-66, do not exhibit satisfactory performance because their adsorption capacities are ≤ 100 mg g⁻¹ and, thus, not competitive to outperform AC [178,240–242]. Some MOFs, such as MIL-100(Fe) and MOF-235(Fe), have exhibited a more promising performance with adsorption capacities in the range of 200–300 mg g⁻¹ [123]. A study

involving various MOFs from the ZIF family and UiO-66 indicated the superiority of ZIF-67-SO₄ [243]. This may indicate the importance of functional groups in MOFs to remove ciprofloxacin. The ciprofloxacin adsorption capacity of MOFs could also be increased by synthesizing them as a composite because the other constituent material may provide additional adsorptive sites. This has been proven by synthesizing Fe₃O₄@MIL-100(Fe) and Fe₃O₄@MOF-235(Fe) [123]. In addition, the possibility of employing carbon-based material synthesized from MOF calcination has been studied. In this case, the MOF sources could be varied, such as HKUST-1 [244,245], MIL-53(Fe) [246], and ZIF-8 [103]. The ciprofloxacin adsorption capacity of this particular material has been reported to be significantly increased, reaching up to 400–800 mg g⁻¹ [245,246].

Another widely used antibiotic class is tetracyclines. Tetracycline is one of the most common antibiotics in the world because a high-quality and high-purity product can be industrially produced at low cost [247]. Tetracycline can be used in both humans and animals and is very effective for treating infections caused by various bacteria. However, this particular compound is difficult to metabolize and can be directly excreted. There is growing concern regarding the long-term exposure of microorganisms to this compound, despite the difficulty reaching an acute toxicity level [248]. For example, the presence of 2–5 mg L⁻¹ tetracycline could disturb the efficiency of nitrogen removal in biological wastewater treatment [249]. Therefore, its presence in the water system may be significant and its removal necessary. Some studies have used AC from various sources and found that the adsorption capacity of AC and its various composites is within the range of 200–500 mg g⁻¹ [33,44,62,109,122,250–256], though the performances of some types of AC are below this value [257–260]. This capacity of AC could even be increased to more than 700 mg g⁻¹ when its mesoporous structure is well-developed [61]. In addition, such an excellent performance could also be obtained due to the presence of metal residues in the adsorption system. Such an increase in adsorption capacity has been observed in the presence of copper ion in the solution [72], the presence of metal in the AC [96], or when it was produced as a magnetic AC composite [261] or in the presence of iron salt as dopant [262]. In this case, the presence of metal could help establish a chelate-coordination between the AC and tetracycline to improve its adsorption capacity [96].

Various MOFs, such as UiO-66 [64], UiO-66-(COOH)₂/GO composite [263], UiO-66-(OH)₂/GO composite [264], trimetallic MOF-74 [265], UiO-66 [90,94], UiO-66-NH₂ [90], and YCM-101 [266], have been found to have adsorption capacities ≤ 100 mg g⁻¹. This adsorption capacity may not be superior to AC, mainly due to the unsuitability of the pore opening of the MOF for tetracycline to penetrate [90,267]. This has been proven by modifying the synthesis conditions for the MOF. One approach is by embedding another metal during synthesis of the MOF. The addition of Mn metal in the synthesis of UiO-66 has been reported to increase its pore size and surface area, which could be caused by the presence of defects. This then results in improved tetracycline adsorption of Mn-doped UiO-66 up to 184 mg g⁻¹ [268]. In another study, a structure directing agent of poly(diallyldimethylammonium chloride) was used to obtain a hierarchically porous ZIF-8 with a larger pore opening. As a result, the tetracycline adsorption capacity could reach 977 mg g⁻¹, which was attributed to multilayer adsorption [269]. Another study using a mesoporous MOF-818 also demonstrated a relatively high tetracycline uptake capacity of 442 mg g⁻¹ combined with fast kinetics [270]. This has also been proven with the use of MOFs that have high surface areas and pore openings, such as NU-1000 and MOF-525, which have exhibited significantly higher tetracycline adsorption capacities than their UiO-66 counterpart, which could reach up to 600 mg g⁻¹ [64]. In addition, the use of other promising MOFs and MOF-based composites, such

as Fe/Co bimetallic MOF [271], MIL-101(Cr) composite [272], MIL-53(Fe) [273], MIL-53(Fe)-NH₂ [85], multi-walled carbon nanotube/MIL-53(Fe) composite [273], multi-walled carbon nanotube/MIL-53(Fe)-NH₂ composite [85], ZIF-8 [80], ZIF-8/MIL-53(Al)-NH₂ composite [274], and various Fe-based MOFs (MIL-88A, MIL-101, and MIL-53) [93] have exhibited promising performance because their tetracycline adsorption capacities fall into the range of 300–500 mg g⁻¹, which is highly competitive with the tetracycline adsorption exhibited by most types of AC. Furthermore, carbon material derived from various MOFs could be chosen because this strategy could increase the adsorbent surface area and pore volume, which could ease the penetration of tetracycline into the adsorbent. Although adsorbents with non-exceptional adsorption capacities could still be obtained [275,276], this strategy would produce adsorbents in which the tetracycline capacity falls in the range of 200–500 mg g⁻¹ when there is a combination of a well-developed mesoporous structure and functionality in the MOF-derived porous carbons [277–279].

Oxytetracycline is another popular antibiotic. The presence of this particular compound in the soil could lead to bioaccumulation in *Enchytraeus crypticus*, alter the composition of its gut microbiota, and increase the number of anti-resistance genes despite the absence of negative impacts on its growth and reproduction [280]. It has also been a target PhAC for removal from the environment. A number of studies using AC as an adsorbent have found that the adsorption capacity of AC for this particular compound could reach 300–600 mg g⁻¹ [38,199,281,282], though some of them have also reported a capacity of approximately 100 mg g⁻¹ [283]. One investigation reported an adsorption capacity of greater than 1300 mg g⁻¹, which may be attributed to the large micropore area [284]. Some MOFs, such as Co-ZIF-67 [285] and MIL-101(Cr) [86], have then been used to adsorb the compound, though their performance is still not satisfactory. However, the use of amino-functionalized MOFs, such as MIL-101(Cr)-ethylenediamine [86] and MIL-88B(Fe)-NH₂ [87], have been shown to be able to significantly increase the adsorption capacity for oxytetracycline compared to their non-functionalized counterparts. In addition, a MOF composite, such as Fe₃O₄@ZIF-8 [286], MIL-53 composite [273], and MIL-101(Fe)-CNT composite [115], and other promising non-functionalized MOFs, such as ZIF-8 [80], could also become a good option to remove oxytetracycline considering their relatively high adsorption capacities of approximately 300 mg g⁻¹.

A summary of the adsorption performance of both AC and MOFs towards various antibiotics is shown in Fig. 6. As can be seen from Fig. 6(A), both adsorbents peak at a maximum adsorption capacity of 251–500 mg g⁻¹. However, 24 % of MOFs studied for the removal of antibiotics have had a maximum adsorption capacity > 500 mg g⁻¹, compared to 12 % of studies on AC. MOFs with large pore apertures and surface areas, such as MOF-818 [270], MOF-545 [114], and MOF-525 [114], belong to this particular group. Notably, a high maximum adsorption capacity is also exhibited by carbon materials derived from various MOFs. This indicates the benefit of having a more structured pore before obtaining a carbon material to improve the adsorption capacity towards antibiotics.

However, further analysis of the adsorption performance (Fig. 6(B)) indicates that MOFs and their carbon derivatives may not actually be too beneficial in comparison to AC when they are to be applied in a real situation. Although both adsorbents peak at slope values between 11 and 100 L g⁻¹, the frequency of slope values in the range of 101–1000 L g⁻¹ is greater with AC than MOFs. This is in contrast to the previous performance for the removal of NSAIDs, for which MOFs might outperform AC. Moreover, despite their relatively high adsorption capacity, the affinity of various MOFs towards various antibiotics may be low and, thus, impair

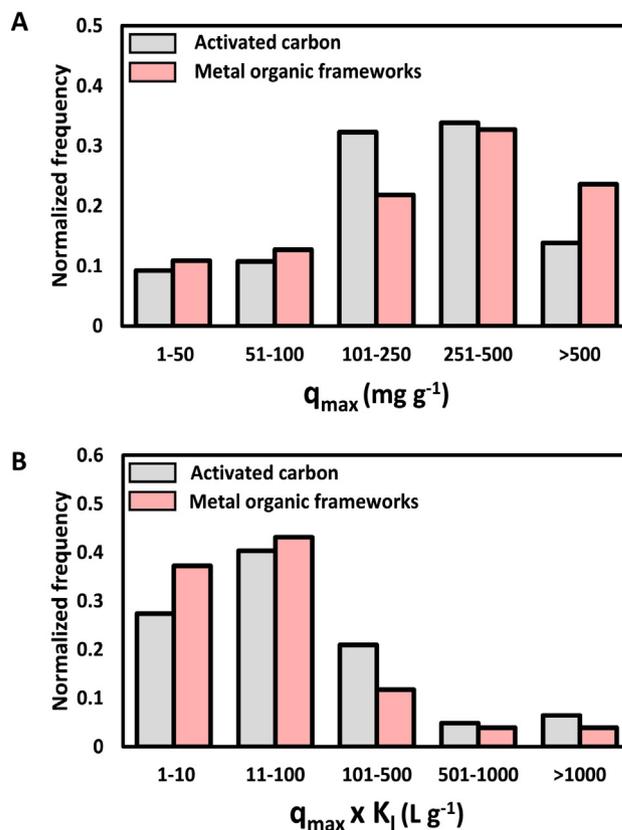


Fig. 6. Comparison of the adsorption performance of AC and MOFs for the removal of various antibiotics based on maximum adsorption capacity (A) and the isotherm slope at low concentration (B).

their performance when applied to very low concentrations. This could be caused by the absence of carboxylic group in most of the investigated antibiotics molecules and thus reducing the affinity between the MOF and the PhACs. However, it is also possible to have a MOF with relatively low adsorption capacity but high adsorbate-adsorbent affinity, such as UiO-66 [64]. Therefore, this particular MOF could be useful for antibiotic removal. However, the results suggest that AC may perform better than most of the studied MOFs for the removal of antibiotics from water systems.

4.3. Others PhACs

Both NSAIDs and antibiotics are drug classes that have been widely investigated for removal from water systems by both AC and MOFs. There have also been some investigations of other classes of PhACs that are not widely investigated, particularly with MOFs, but worth mentioning.

4.3.1. Anticonvulsants

Carbamazepine is one popular example of an anticonvulsant drug used to treat epilepsy. This particular compound is one of the most frequently encountered pharmaceuticals in aquatic systems and has been well-known for inducing oxidative stress in marine bivalves [287]. The adsorption capacity of most types of AC and its composites is usually ≤ 100 mg g⁻¹ [104,161,288–292]. However, some studies have reported the possibility of obtaining an adsorption capacity in the range of 200–300 mg g⁻¹ for AC [45,293–299], which could be associated with the presence of a mesoporous structure of AC and increased surface area and pore volume to give carbamazepine better access to the adsorption

sites in AC. The removal of this compound from water systems has then been widely investigated using both AC and MOFs, including a composite of UiO-66/graphene nanoplate [127], UiO-66 [94,127], UiO-66-NH₂ [81], and UiO-66-F [81], which have a moderate adsorption capacity of $\leq 100 \text{ mg g}^{-1}$. A study using UiO-67 has reported that the isotherm exhibits a linear increase [104]. Therefore, a higher amount of carbamazepine can be adsorbed by UiO-67 as the concentration in the water increases.

4.3.2. Anticholesterolemic drugs

Anticholesterolemic drugs are used to lower plasma cholesterol levels. One common example of these drugs is clofibrac acid and its derivative clofibrate. The presence of this compound has been reported in water systems, and a number of investigations have investigated removing it from the environment. AC from various sources have demonstrated an adsorption capacity of approximately 100 mg g^{-1} [300] or lower [301,302]. Other studies have demonstrated an adsorption capacity of AC in the range of $200\text{--}300 \text{ mg g}^{-1}$ [28,137]. However, this capacity could only be reached with AC in which the pores were not dominated by supermicropores, despite the assumption that these pores are often associated with the strongest adsorption sites, indicating the importance of suitable pore size to accommodate clofibrac acid [137]. Another study reported that the maximum adsorption capacity towards this particular compound could reach 500 mg g^{-1} [303]. In this case, the contribution from multilayer adsorption indicated by the adsorption isotherm cannot be neglected. MOFs have also been used to remove this particular compound from water systems. MIL-101 has been reported to have an adsorption capacity of approximately 300 mg g^{-1} [58,89,168]. This adsorption capacity can be slightly enhanced when a hydroxyl or amine functional group is present, which may be attributed to the acid-base interaction. In contrast, a significant decrease in the adsorption capacity of MIL-101 has been observed in the presence of an acidic group [58].

4.3.3. Beta-blockers

An example of a beta-blocker is atenolol, which is mostly used to treat high blood pressure and heart-associated chest pain. The removal of this particular compound from water has been widely investigated by employing AC. The adsorption capacity of AC towards atenolol is usually $\leq 100 \text{ mg g}^{-1}$ [76,160,304–306]. This performance can be improved through several modification processes, such as oxidation [105]. However, some studies have shown that the atenolol adsorption capacity of AC could be improved to $> 500 \text{ mg g}^{-1}$ when a suitable chemical activation method is used [27]. Although MOFs are not yet as widely studied as AC, a recent study demonstrated the potential of MIL-163 and a defective Ni₈BDP₆ MOF to outperform AC in removing atenolol from the waste system [304]. The atenolol adsorption capacity of MIL-163 is estimated to reach 92.2 mg g^{-1} . This is then attributed to the proper channel dimensions of MIL-163 ($1.2 \times 1.2 \text{ nm}$) to let atenolol pass through the pore and get adsorbed. The framework stability of MIL-163 helps prevent ligand leaching and maintain adsorption performance. Another study was carried out using an adsorbent column employing defective Ni₈BDP₆. With an initial atenolol concentration of 73 mg L^{-1} , the column could maintain the adsorption performance up to 12 days without any sign of MOF degradation.

The performance of both AC and MOFs towards adsorbing these various PhACs is presented in Fig. 7. As can be seen in Fig. 7(A), the studies conducted with these PhACs were considerably smaller than the studies conducted for the other classes of PhACs. From the studies conducted thus far, the maximum adsorption capacity of AC falls within the range of $51\text{--}250 \text{ mg g}^{-1}$, whereas two peaks appear in the studies using MOFs as the adsorbent. In this case, the maximum adsorption capacity falling within $1\text{--}50 \text{ mg g}^{-1}$ can be

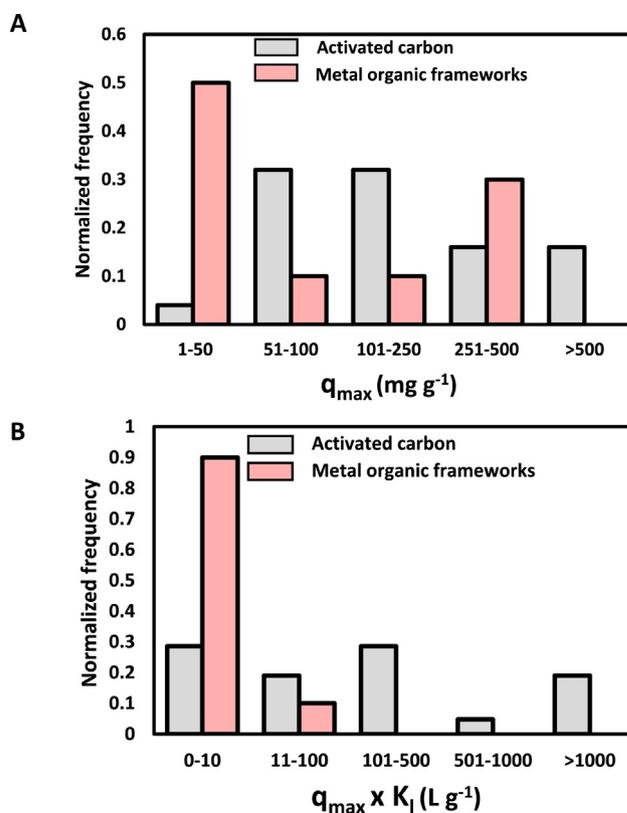


Fig. 7. Comparison of the adsorption performance of AC and MOFs for the removal of other PhACs based on maximum adsorption capacity (A) and the isotherm slope at low concentration (B).

assigned to various studies of MOFs for carbamazepine removal, and a relatively high adsorption capacity in the range of $251\text{--}500 \text{ mg g}^{-1}$ is exhibited by UiO-67 [104] and MIL-101(Cr) [58,89] for the removal of carbamazepine and clofibrac acid, respectively. However, the relatively high adsorption capacity of some MOFs towards these compounds is not accompanied by high affinity. As shown in Fig. 7(B), approximately 90% of MOFs exhibit a very low Langmuir isotherm slope ($0\text{--}10 \text{ L g}^{-1}$). This may indicate that the affinity of these MOFs towards these particular PhACs is relatively weak and could impair their performance when applied in a real-world situation. Moreover, this suggests that they are not yet able to outperform AC.

5. Outlook and future studies

Having extensively compared the adsorption performance between MOF and AC towards various PhACs, further suggestions and theme for further studies will also be provided here to obtain a more comprehensive view to compare the adsorption performance between AC and MOFs, which are summarized in Table 2.

5.1. Investigation in real and more complex environments

Although recent investigations have clearly shown the efficacy of both AC and MOFs in removing PhACs from waste systems, some issues and challenges still remain to be addressed in future research. The first issue is related to the performance of the adsorbents in real conditions. Until now, most of the studies in this field have been performed in controlled environments. Such conditions will not be met in real-world applications in which both adsorbents are going to be used. The adsorption performance of AC in

Table 2
Other factors and subjects for future studies to compare the adsorption performance of AC and MOFs for PhAC removal.

Factor	Activated carbon	Metal-organic frameworks
Real performance	A number of studies have been performed in real wastewater to obtain the real performance.	More studies are required to observe the real adsorption performance of MOFs in a more complex system rather than a single system. In particular, more investigations are required to study the effect of NOM on PhAC adsorption.
Adsorbent regeneration	More studies are required on the use of green solvents for AC regeneration.	More studies are required on the use of green solvents to regenerate MOFs. In addition, thermal regeneration is worthwhile for some robust MOFs to avoid the use of solvents.
Adsorbent separation	Granular AC could be directly used as an adsorbent in a column, avoiding the need for subsequent separation steps. However, whenever possible, the use of a binder to form a pellet should be avoided to minimize declining performance of the AC for adsorption.	MOFs are mostly produced as nanoparticles, rendering the separation process from water systems difficult. Therefore, to increase applicability, the performance as an adsorbent must be further investigated in other formats, such as structured adsorbent or membrane adsorber.
Adsorbent stability	AC has excellent framework stability. However, the integrity of the composite adsorbent must be evaluated.	The framework is more labile than AC. The framework stability must be thoroughly evaluated during the adsorption performance.
Economic viability	The economic viability of AC has been well proven, in particular regarding its production in large-scale.	The scale-up production for MOFs could be challenging, in particular for a specialized MOF that is designed with non-commercial ligand. Therefore, several aspects must be fully considered to make MOF production more competitive with AC.
Sustainability	There is an advantage in the use of various types of agricultural wastes and naturally-grown carbon waste.	Further investigations must be performed on the sustainability of producing MOFs for PhAC removal. More emphasis could be placed on evaluating the metal and ligand source for building the MOF.
Fundamental studies	Elucidation on the adsorption sites of AC	Elucidation on the adsorption sites of MOF

real wastewater could be significantly decreased from its performance in a controlled environment [294], suggesting the importance of studying the performance of the adsorbent in a real condition. In this case, various types of AC have been used to study the adsorption of various PhACs from real wastewater [108,121,196,200,288,289,294,297,298]. When such an investigation is not possible, a simulated condition that mimics the condition of a real waste system may be necessary to evaluate the true performance of the adsorbents. This has been studied, for example, by using a simulated effluent of various wastewaters to mimic the real conditions [29,216,219,307]. As the adsorption performance of a few numbers of MOFs looks promising and could outperform AC in certain cases, it is important to also study the performance of MOFs in this real environment. However, MOFs have not been as widely studied in real environments as AC [267,304]. Therefore, more investigations are needed in this field, especially in the use of promising MOFs.

Another possibility is to study the adsorption in a multicomponent environment. Although such an investigation is not as ideal as exposing the adsorbent in a simulated effluent or real wastewater, it is beneficial for investigating various phenomena that may occur because of the presence of other components in the system. At first glance, the adsorption capacity of both AC and MOFs may be expected to decrease because of the competitive adsorption phenomenon. This has been demonstrated with Fe_3O_4 -FeBTC MOF for three NSAIDs: diclofenac, naproxen, and ibuprofen [163]. During multicomponent adsorption, the removal efficiency of ibuprofen, diclofenac, and naproxen could only be maintained at 11 %, 61 %, and 85 %, respectively, compared to the single system, which is attributed to the competitive adsorption between the compounds and shows the selectivity towards naproxen. This has also been observed using AC in a bicomponent system containing ciprofloxacin and carbamazepine. Compared to the single system, the adsorption capacity of AC was significantly reduced up to 80 % because of the competitive adsorption [298].

However, competitive adsorption is not the only phenomenon to consider, as indicated by a study using AC in the presence of caffeine and diclofenac [157,308]. A possibility of the displacement of caffeine by diclofenac was suggested because of the lower affinity

of the former for AC [157]. In addition, there is a possibility that a higher adsorption capacity is present in the multicomponent system compared to the single system. This has been demonstrated for carbamazepine adsorption by UiO-66 in the presence of tetracycline [94]. A possible explanation is the establishment of an adsorbate-adsorbate interaction that results in a more favorable adsorption condition and increased adsorption capacity [308]. The presence of Pb(II) in a water system has been reported to be beneficial for increasing the oxytetracycline adsorption capacity of Fe_3O_4 @ZIF-8 through the complexation reaction that occurs between both adsorbates [286]. A similar observation was reported when the presence of copper ion increased the adsorption capacity of AC towards tetracycline because of the complex formation between the adsorbate and AC [72]. In a study of clofibrac acid adsorption the presence of calcium ions in the water system was beneficial for forming a complex adsorbate that could also enhance the adsorption on AC [300]. In another study, the presence of nickel ion was beneficial for improving the ciprofloxacin adsorption capacity of AC [225]. Thus, it is useful to be more selective in choosing the adsorbent to improve the actual performance.

In addition to investigations in a more complex environment, more studies need to be conducted in a more relevant concentration of PhACs than is usually found in real conditions. As stated previously, the concentration of PhACs in water systems is mostly in the range of nanogram or microgram per liter. This is in contrast to most of the investigations using AC and MOFs in which the PhAC concentration is usually set at ppm. Therefore, it is important to avoid overestimating adsorption performance, which may occur if the decision is based solely on the data obtained in the relatively high concentration range [98]. For example, one study on the capacity of AC towards carbamazepine and naproxen was performed by adjusting the concentration of both components in the range of 10–800 ng/L [98].

5.2. Adsorbent separation and regeneration

Another challenge that has to be addressed is the process of separating the adsorbents from the waste system. Although this issue applies to both AC and MOFs, it may be more applicable for

the latter than the former because most MOFs are mostly deployed as nano-adsorbents and could render its separation from the water a little bit more challenging. Some strategies have been proposed to address the issue, including the introduction of a magnetic property in both AC and MOFs [71,109,164,184]. This strategy could be very helpful in avoiding the release of nanoparticle adsorbents into the environment by easing the separation from the waste system when the adsorption process has finished [309]. However, embedding magnetic particles also poses a risk in reducing the surface area of the adsorbent, which could potentially result in reduced adsorption capacity.

Another strategy that could be used to address the separation process is the fabrication of a structured adsorbent. For AC, this has been done by adding a binder when structuring the AC. However, a disadvantage of this approach is a reduction in the number of effective adsorption sites, compromising the adsorption performance. This has also been investigated in various MOFs [113,310] by growing the MOF and immobilizing it on the surface of a substrate. This makes the adsorbent easier to handle and the separation of nanoparticles from the waste system can be avoided. Another possibility is to investigate the feasibility of fabricating an adsorptive membrane. In this case, the adsorbent can be incorporated inside a polymer matrix or stand alone on a porous support, which could also address the challenges related to separating the adsorbent from the water system after it is exhausted. However, it is probably more feasible to apply this strategy to MOF rather than AC because it is easier to engineer the particle size of the MOF and fabricate it as a continuous film. This strategy has been observed by using ZIF-8 membrane adsorbent, which can be used to adsorb various PhACs, such as acetylsalicylate acid, ibuprofen, and ketoprofen [311].

Regeneration is another issue that has to be addressed when an adsorbent is selected for PhAC removal. There are at least two issues regarding adsorbent regeneration. First, a reduction in the adsorption capacity is unavoidable. A decline in the adsorbent adsorption capacity often occurs once the adsorbent is regenerated, and a reduction of up to 50 % of the adsorption capacity can actually be expected [252]. Therefore, a study on the limitations of the adsorbent capability to remove contaminants must also be conducted. The second issue is related to the way the adsorbent is regenerated. Most of the adsorbents investigated for this purpose can usually be easily regenerated using solvent to regain the adsorption capacity after it becomes saturated. This then poses two other challenges. First, the right solvent must be carefully selected as a regenerant that depends upon the adsorbate. For example, strongly adsorbed molecules, such as tetracycline on UiO-66, could not be easily desorbed using chloroform, resulting in the impossibility of reusing the adsorbent [94]. Water could then be selected as the first option for regeneration. However, adjustments for the operating conditions (e.g., temperature or pH) are necessary to effectively desorb the PhACs from the adsorbents. Some alcohols could be chosen as promising alternatives, but the capability to desorb PhACs must be evaluated carefully. For example, regenerating AC with methanol is slightly more effective in sustaining the micropollutant removal capability than regenerating AC with ethanol [184]. In addition to the selection of an effective regenerant, there is another issue related to regenerant sustainability and the avoidance of harmful solvents. In this case, it is worth investigating a number of possible environmentally friendly regenerants.

Several studies have been performed to find various alternative possibilities for regeneration. For example, a combination of desorption methods using gamma irradiation to desorb PhACs from AC has been reported [202]. However, optimization of this technique is still required because the desorption capability is still relatively low. Another method uses persulfate in the regenerant

medium and ultrasonication [204]. In this strategy, the persulfate acts as an oxidizing agent to degrade the PhAC that is desorbed from the AC by the assistance of ultrasonication. This method could bring back the adsorption capacity of the adsorbent. Another strategy is to employ light to trigger the desorption process. This has been investigated using a composite adsorbent of UiO-66-NH₂/Ag₃PO₄ [312]. Upon irradiation of the adsorbent with visible light, the Ag⁺ ion is reduced to Ag⁰, which can then no longer act as an adsorptive site, triggering the desorption process.

It is also possible to regenerate the adsorbent in the absence of solvent by employing thermal regeneration. In this process, the use of organic and harmful solvents can be avoided and the adsorbents regenerated by exposing them to a high temperature condition in which the adsorbates are thermally degraded. This method may be suitable for AC and has been proven in a number of studies [71,196], but it is a challenge when a MOF is chosen as the adsorbent because the organic part of the MOF can degrade during the thermal regeneration process, partially destroying the framework, which can render the MOF useless for the next adsorption cycles. Therefore, the use of this method is limited and only MOFs with high thermal stability are able to be thermally regenerated. In this respect, a study employing a MIL-53(Al) Raschig Ring (RR) adsorbent has successfully shown the possibility to thermally-regenerate the MOF after the adsorbent was saturated with ibuprofen [154]. Because the MIL-53(Al) RR could retain its structure up to around 500 °C, the ibuprofen adsorbed in the MIL-53(Al) RR could be thermally degraded by heating the adsorbent at 330 °C. The thermally-regenerated MIL-53(Al) RR could then be reused with only a slight compromise observed in its adsorption capacity.

5.3. Adsorbent stability and integrity

In addition to investigations of adsorbent regeneration, it is also important to assess the material stability and integrity. In this regard, AC may outperform MOFs because the latter contain organic linkers that could reduce the robustness of the framework. This has been shown by the instability of numerous MOFs in various conditions, particularly once they are exposed to water or humid environments [313]. The metal–ligand bonding may also be prone to structural deterioration after several cycles of adsorption–desorption. Therefore, MOFs that are going to be applied for PhAC removal in water systems have to be more judiciously selected not only regarding their performance, but also an intact structure after a number of adsorption cycles.

Material integrity should also be carefully considered. This issue is particularly important when AC or MOF composites are used for PhAC removal, especially when the composite merely relies on the physical bonding between constituents without the presence of any covalent bonding. For example, the structural integrity of an AC composite could be compromised even after just one cycle of regeneration based on the change in X-ray Diffraction (XRD) pattern [314]. This indicates the importance of continuously evaluating not just the adsorption performance after regeneration, but also the material integrity, which then acts as a driving force to produce a composite that has stronger bonding between its components.

5.4. Economic viability and sustainability

Another important parameter that has to be considered in future investigations is the economic viability and sustainable production of both AC and MOFs. Both issues are essential because, eventually, the adsorbents will have to be industrially produced in a sustainable way in order to avoid further contamination of the water systems. In this regard, AC may have a significant edge over MOFs because AC was already well developed before the birth

of MOFs. Therefore, its large-scale production and hence its economic viability is currently not an issue. In addition, AC can also be produced using various types of agricultural wastes or naturally grown carbon sources and thus offering a more sustainable approach than MOFs. In this case, the main drawback probably lies in the use of high temperature during the production process that requires a large amount of energy. However, this could be simply addressed by adjusting the pyrolysis temperature of AC and the utilization of renewable energies.

In contrast, MOF may be slightly behind of AC in both aspects. Although some MOFs have been successfully produced at large scale, such as proven by BASF [315], it must be admitted that the economic viability of MOF production is still not as well-proven as AC, in particular in the production of a specific MOF that is specially designed to remove certain PhACs. Therefore, more studies are required to assess the possibility of scaling up the production of the targeted MOF that should also go hand in hand with the sustainability assessment. Several aspects then need to be considered so the MOF production could be competitive with AC. Firstly, the use commercially-available material that could be synthesized in large scale is much preferred than a specialized ones. Moreover, in respect to the metal source, the use of metal acetate, hydroxide, oxide, or sulfate should be preferred and could also be an additional consideration because they are less harmful to the environment [316]. As in the production of AC, the use of waste as raw material could also be a promising option to increase the economic viability and sustainability MOF production. This has been observed, for example, by employing PET as a raw material to synthesize various MOFs, such as UiO-66 [317] and MIL-53(Al) composite [318]. In this case, the PET acts as the source of terephthalate ligand to construct the MOF. The resulting MOF could be further used to produce a carbon-based adsorbent that contains metal species that could be beneficial for removing diclofenac from water systems [318]. In another investigation, polylactic acid plastic cups could also be used as a ligand source to construct a chiral MOF [319]. Lastly, the minimization of energy input during MOF production should always be prioritized. This particular point could actually be the main advantage of MOFs over AC because of the possibility of synthesizing MOFs in a very benign condition (e.g., room temperature) with minimum energy input, such as through sonochemical or mechanochemical methods. Recently, such a possibility has been proven by large-scale production of MOF CALF-20 that combines the utilization of commercially available starting materials, relatively benign synthesis condition (i.e. using water/methanol as solvent), high product yield up to 90 % and high space-time-yield around $550 \text{ kg m}^{-3} \text{ day}^{-1}$ [320]. Although this MOF is specially designed to capture CO_2 , it has undoubtedly shown the economic viability of MOF as a promising adsorbent to target low-value adsorbate, which could then be potentially translated in the case of MOF for PhACs removal from water streams.

5.5. Investigation regarding the adsorption sites both in AC and MOFs

Last but not least, further studies could also be directed to investigate the fundamental aspect during the adsorption process, namely to gain more insight regarding the adsorption sites of AC and MOFs. For example, until now, it is often assumed that the adsorption process in AC and MOFs occur both inside the pore and on the outer surface of the adsorbents since both of them are rarely differentiated. It could be then more insightful when the occurrence of both phenomena could be separated and more elucidated. In this case, various analytical techniques could be used. For example, it has been documented that the use of confocal microscopy is possible to determine whether an adsorbate is adsorbed on the surface or inside the pore of MOFs [321]. Another

possibility is to construct the adsorbent as a film to study then employing the quartz crystal microbalance (QCM) to investigate the real mass increase during adsorption process [322]. After the equilibrium condition is reached, the value could be compared with the expected value of mass increase in the case of full pore occupation. However, this technique might only be suitable to be applied for MOF since the material could be readily produced as a thin film on the QCM.

6. Conclusion

During the last few years, there has been increasing concern regarding the presence of PhACs in water systems. Although they are present at relatively low concentrations, their accumulation poses a threat to aquatic life. Therefore, their removal from water systems is essential to preserving the water ecosystem. Among the available strategies that can be used to remove them, adsorption could be considered as the most feasible because of its numerous advantages. Until now, AC has been commonly used as the main adsorbent to accomplish removal. With the increasing interest in MOFs during the last two decades, the adsorption performance towards various PhACs has also been widely studied.

This article has empirically and comprehensively reviewed the performance of both adsorbents to remove various PhACs from water systems. From the compilation of the results, we infer that the adsorption performance of MOFs is slightly better than that of AC in some areas. This is particularly obvious when the MOF is applied to remove various NSAIDs. This could be the case because the pore size of MOFs is tailorable and, thus, the MOF could also be rationally selected to perform a particular separation process. However, there are some cases in which the adsorption performance of AC is comparable or even better than that of MOF, such as shown in the performance towards removing antibiotics or other PhACs. In most cases, this happens when the molecular size of the targeted PhAC is relatively small and can be easily accommodated by AC. For example, AC has shown relatively good performance in removing carbamazepine, as indicated by its better adsorption capacity than various MOFs. This is also the case when the mesoporous structure in AC can be well developed and, therefore, does not hinder the diffusional process of the PhACs. In addition to AC and MOFs, there is another class of porous carbon-based adsorbent that is derived from MOFs. This particular adsorbent could actually offer a good alternative between AC and MOF. Most of them usually exhibit better adsorption performance than AC, partly because their porosity is more developed and they are derived from MOFs, which have a structured framework.

However, further studies are required to clearly assess which adsorbents are the best for PhAC removal. Although some MOFs could outperform AC in removing various PhACs, such as NSAIDs, it does not necessarily mean that the former is the best option for this particular purpose. In this case, further assessments are required to obtain a complete perspective. For example, even though a particular MOF shows better performance in adsorbing certain PhACs, its major challenge is related to its economical aspect because its production is still limited to lab scale. This is in contrast to AC, whose economical aspect of its production has been proven and could also be readily produced from various types of biomass waste and thus avoiding further pollution of the environment. Furthermore, this is also exacerbated by the fact that MOF is not as robust as AC and thus could limit its applicability for the adsorption process in water treatment. Therefore, from the current practical perspective, AC could still be much more attractive than MOF as an adsorbent. On the other hand, it does not mean that AC cannot be replaced by MOFs in the future. This is particularly because of the possibility of synthesizing various

MOFs in a benign way in contrast to AC, which has to be produced at high temperature. In addition, recent investigations have shown the possibility of producing MOF at large scale using commercially-available materials or using various types of industrial waste, which could also improve the sustainability aspect of the MOFs. When these aspects are fulfilled, there is a great opportunity for MOFs to be applied in the removal of PhACs from water systems. Moreover, there is great potential in developing MOF-derived carbon-based material. Recent studies employing this material has shown promising performance that combines the high adsorption capacity, kinetics, and material robustness.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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