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# Zirconium Based MOFs and Their Potential Use in Water Remediation: Current Achievements and Possibilities

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**ABSTRACT:** Water pollution and scarcity are two of the most serious problems humanity is currently facing. Therefore, it is important to develop effective and inexpensive technologies and treatments to remove key pollutants from water. Zr based Metal-Organic Frameworks (MOFs) are new materials with the potential to remove organic and inorganic pollutants. However, it is important to critically analyze their performance in laboratory trials to evaluate their scalability potential for wastewater treatment. This document presents a critical review of the most recent studies and advances regarding Zr based MOFs, specifically the UiO-66 and UiO-67 MOFs and analogous materials. We found that, although these materials are effective at removing inorganic and organic pollutants in water, there are still available research opportunities and knowledge gaps that need to be addressed. There is a need to further understand the mechanisms involved in the removal process to be able to develop more effective materials and/or to determine the best operating conditions during its implementation. Variations in removal efficiencies between the same MOFs also call for a more detailed description of the synthesis, as well as a better characterization of the material. This is because small variations in the characteristics of MOFs lead to non-homogeneous results, making accurate predictions of their removal capacity more difficult to determine. Finally, there is a need to better understand the stability of Zr based MOFs, as well as their removal capacity and reusability in wastewater with competitive ions, at standard pH and temperature operating conditions.

**KEYWORDS:** MOFs, UiOs, water pollution, removal, sorption

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## Introduction

### *Water Pollution and the Technological Challenge of Developing New Materials for Micropollutant Removal*

Water pollution is one of the main challenges that present day society needs to address (Schwarzenbach et al., 2010). Safe accessibility to this essential resource has become increasingly difficult for many communities worldwide. However, there are opportunities for solutions to come from many different angles, through the collaborative work of various sectors of society, including the development of advanced processes to remove organic and inorganic pollutants from water. Some of these contaminants can cause disruptions to the environment and/or living organisms, even in very small concentrations, which adds to the challenge of removing them. New technologies should remove contaminants effectively in the range of  $\text{mg L}^{-1}$ . These types of pollutants, also called micropollutants or emerging pollutants, are becoming more common due to changes in human consumption. Therefore, the ongoing development of technology to retrieve them and reduce their concentration in water, as much as possible, is key to reducing their impact on human health and the environment (Eggen et al., 2014; Margot et al., 2013).

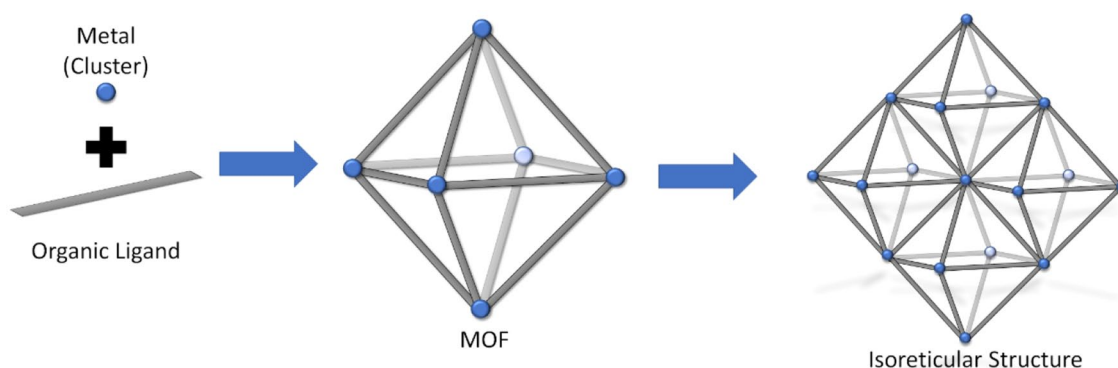
Among the technologies that are being developed, Metal-Organic Frameworks (MOFs), a new class of porous, hybrid materials, are showing a great potential in removing pollutants

in tertiary treatment processes. MOFs have been widely studied in different applications such as gas sorption, catalysis, photocatalysis, energy storage, drug storage and delivery, sensing and separation, among others (Gangu et al., 2016). The wide variety in the applications of MOFs is due to its structure and ease of functionalization (Figure 1). MOFs are mainly composed of inorganic metal clusters that are bound together by organic linkers via coordination bonds, which allows for the formation of an isoreticular structure. The relevance of the inorganic cluster for this material lies in the type of morphology that is obtained in the coordination material. This connection, called an organic ligand, can be easily modified with different functionalities, allowing the material to change its chemical properties within the design of the material itself while maintaining high porosity and surface area.

An important property of MOFs is the huge surface area that can be obtained with the combination of these materials, which has been expanded up to  $7,000 \text{ m}^2 \text{ g}^{-1}$  (Hönicke et al., 2018). The surface area of MOFs is larger than the values reported for other porous materials such as activated carbon or nanomaterials like silica, which ranges from  $950$  to  $2,000 \text{ m}^2 \text{ g}^{-1}$  (Lu & Xue, 2019) and  $1,700 \text{ m}^2 \text{ g}^{-1}$  (Thahir et al., 2019), respectively, however reported values for adsorption applications usually range below the  $1000 \text{ m}^2 \text{ g}^{-1}$ . Since MOFs are also highly porous, the high amount of available area sites on the surface of the MOFs allows them to adsorb or even catalyze the decomposition of different substances. In addition, through the



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**Figure 1.** Scheme of a MOF, formed by organic ligands and metallic clusters combining into an isorecticular structure.

particular selection of the inorganic cluster and the size of the inorganic ligand, it is possible to control the size and the shape of the cavities, which can increase or decrease the number of interactions with a given type of substance. This allows MOFs to be utilized in more specialized applications, as in the case of sorption of pollutants from water (Hasan & Jhung, 2015).

The relatively easy functionalization of MOFs is a distinct advantage over other types of porous materials such as zeolites and activated carbon, since the inclusion of different functional groups can completely change the chemistry of MOFs (Stock & Biswas, 2012). The inclusion of new functionalities can be achieved mainly by two routes: (a) by the design of the ligand and the formation of the as-synthesized MOF with the desired functionality (Fu et al., 2012); or (b) by the addition of active sites on the structure of the MOF that can be later modified by post-synthetic modification (Ali-Moussa et al., 2017). These two options widen the possibilities for these materials and their final application. Particularly, it could represent a huge improvement in the removal of small concentrations of pollutants by increasing the affinity or selectivity through the rationalized design of the material. This document is focused on the analysis of Zirconium based MOFs applied to water remediation. The objective is to critically analyze the results from different studies and identify knowledge gaps and areas of opportunity for research. This understanding will provide the basis for developing models to scale-up the application of MOFs to waste water treatment plants.

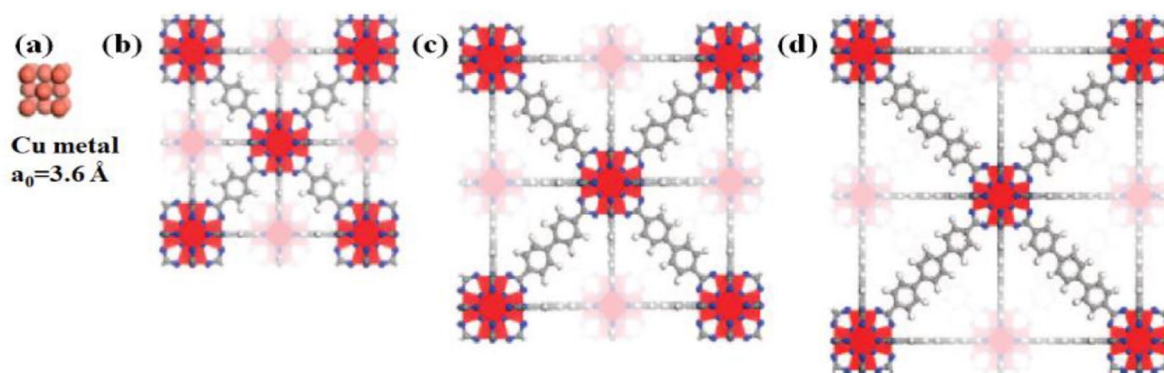
Even though MOFs are quite attractive in their potential use as adsorbents for the removal of different pollutants from water due to their high porosity and possibilities of functionalization, only a handful of materials have been researched for use in water treatment. This is mainly due to the instability of several MOFs in an aqueous environment (Wang, Yuan et al., 2016). Still, water stable MOFs have been widely studied to increase their capacity of adsorption. As mentioned earlier, selectivity and affinity are two factors that can be improved by the rational design of MOFs. MOFs based on metals that have been used for the decontamination of water, either as adsorbents, catalysts or both, include Al, Cu, Fe, Ti, and Zr. One of the first reports included the adsorption of Methyl Orange

with a Cr based MOF (Haque et al., 2010). After this, several attempts have been reported not only to remove pollutants by adsorption, but also to catalytically degrade some organic pollutants, as will be described next.

Al, Cu and Fe-based MOFs have been studied and developed due to the availability and price of these metals, and because some of these materials are water stable and have shown a high thermal stability, making them suitable for water treatment with good regeneration of the adsorbent (Samokhvalov, 2018). These materials have been tested in the sorption of methyl orange (Wu et al., 2017), lead (Ricco et al., 2015), or azo dyes (Jung et al., 2018) and have shown great potential for the sorption of N-heterocyclic compounds and aromatic sulfur compounds (Samokhvalov, 2018), p-nitrophenol (Andrew Lin & Hsieh, 2015), Hg (Ke et al., 2011), dichromate (Lv et al., 2017), or some oils such as naphtha, diesel or gasoline from water (Zhang et al., 2019).

Iron-based MOFs are among the most promising upcoming materials for the decontamination of water due to the high availability of iron, its price and low toxicity. Green synthesis of these materials has been explored and studied for the sorption and catalysis of arsenates and dyes from water (Hou et al., 2018; Lv et al., 2015). In addition, similar to titanium-based MOFs, iron-based MOFs can participate in various photocatalytic applications (Wang & Li, 2017).

Interestingly, Cu-MOFs have also been explored due to their capacity to destroy by photocatalysis some organic pollutants (Taher et al., 2017). Still, in terms of photocatalysis titanium-based MOFs are some of the most studied materials in this area due to the low toxicity, high stability, and well-known photocatalytic properties inherent to  $\text{TiO}_2$ . However, synthesis of these materials is still challenging when compared with other MOFs. Due to the catalytic capacity of  $\text{TiO}_2$ , materials such as the MIL-125 and its amino functionalized version have been widely tested in the photocatalytic destruction of pollutants in water, such as organic pollutants (Huang et al., 2019), pharmaceuticals (Wang, Liu et al., 2016) or even in the reduction of metals such as Cr(IV) (Wang, Yuan et al., 2015). While the photocatalytic properties of these materials are promising, their synthesis is still a great challenge; therefore, its potential is still limited.



**Figure 2.** Structure of a: (a) unit cell of Cu in comparison to, (b) the UiO-66, (c) UiO-67, and (d) UiO-68 as reported by Cavka et al. (Cavka et al., 2008). Adapted with permission from J. Am. Chem. Soc. 2008, 130, 42, 13850–13851.

**Table 1.** Comparison of Surface Properties of UiO Zr-MOFs, Data from Cavka et al. (2008).

| MOF    | LIGAND                              | SURFACE AREA                          | WINDOW OPENING |
|--------|-------------------------------------|---------------------------------------|----------------|
| UiO-66 | Terephthalic acid                   | ~1,000 m <sup>2</sup> g <sup>-1</sup> | 6 Å            |
| UiO-67 | Biphenyl-4,4'-dicarboxylic acid     | ~3,000 m <sup>2</sup> g <sup>-1</sup> | 8 Å            |
| UiO-68 | p-Terphenyl-4,4''-dicarboxylic acid | ~4,170 m <sup>2</sup> g <sup>-1</sup> | 10 Å           |

Finally, Zirconium-based MOFs (Zr-MOFs) are some of the most widely used materials that have been tested for several applications, including the decontamination of water, mainly because of their stability, variety of structures, and relatively easy synthesis and modification while preserving the morphology of the pristine MOF.

### Zirconium-based MOFs, a Versatile Family of Materials with Potential for Water Decontamination

Zr-MOFs are widely used in water because they present relevant properties, such as good stability in water, variable pore size, a variety of structures, and relatively easy synthesis, modification, and functionalization while preserving the morphology of the pristine MOF. This document will focus on analyzing the advantages, limitations, and possibilities of the application of Zr-MOFs in the removal of pollutants from water, by analyzing several reported cases, focusing on the so-called UiO (University of Oslo) family of Zr-MOFs (Figure 2).

The water stability of the UiO Zr-MOFs has been attributed to factors such as the hydrophobicity of the pore, the coordination geometry and/or the high oxidation number of the Zr(IV) in the cluster (Bai et al., 2016). In addition, changes in the pore size of UiO-MOFs can be achieved by the rational selection of the ligand, providing the materials with selectivity. Finally, it is possible to add different types of functionalities on the organic ligands of the UiO MOFs to change the nature of the interactions on the surface of the material. The addition of different functional groups such as  $-NH_2$  or  $-OH$  allows

enhancement of the interactions between the surface of the MOFs and other substances (Lv et al., 2016; Sun et al., 2020). A comparison of some of the properties and structures of these materials is presented in Table 1.

The purpose of this review is to do a critical analysis of the current information regarding UiOs as a viable technology for water treatment. The focus of the document is on the following aspects: (a) uses and characteristics of the synthesized MOFs, including surface area, pore volume, charge, functionality, particle size, imperfections, and reusability; (b) an analysis of the sorption experimental condition, including pH, temperature, and competitive ions, as well as resulting sorption kinetics. The analysis of this information is crucial to applying MOFs at a larger scale for water decontamination, since the mentioned characteristics can affect the capacity and selectivity of MOFs in their application as adsorbents in tertiary water treatments.

#### *UiO-Zr MOFs in water decontamination: Uses and characteristics*

Due to the aforementioned properties of the UiO family of MOFs, specifically the UiO-66, UiO-67, and derived materials, they have been tested for the sorption of several pollutants that range from organic pollutants such as pharmaceuticals, organophosphorus substances, dyes, and hydrocarbons, as well as heavy metals or ions. In Supplemental Table S1, we have compiled information on the application of these materials in the sorption of different pollutants. The type and main characteristics of MOFs reported by the authors, including their maximum sorption capacity and the driving

force of the sorption of the pollutant, are included. In Supplemental Table S2 we have compiled key operating conditions that might affect removal mechanisms, relevant to evaluating the potential of MOFs in the removal of pollutants from water (such as temperature, pH, ion competitiveness), as well as their capability of regeneration. Both Supplemental Tables S1 and S2 are available in the Supplemental Information. Table 2 is a compilation of the pollutants addressed in Supplemental Tables S1 and S2.

From the analysis of the compiled information, it can be observed that several factors are important in choosing a MOF for the removal of a given pollutant. Key considerations are surface area, pore volume, window size, MOF charge (either on the ligand or on the metallic center), and the imperfections on the crystalline structure (either by missing linkers or missing clusters).

In the case of the surface area of the material and pore volume, these two factors are usually related, since the bigger the pore volume of the MOF, the greater the surface area of the material. It is also important to remember that the larger the surface area is, the more sites will be available for the pollutant sorption. In addition, a large pore size will increase diffusivity into the interior of the MOF. These two characteristics are some of the reasons why MOFs are being studied in the sorption of pollutants, since both can be relatively controlled by considering the coordination environment of the metallic cluster and the length of the ligand. An example of this is the case (Akpınar & Yazaydin, 2017) where the sorption of carbamazepine over the UiO-66 and the UiO-67 MOFs was studied. The reported surface areas and pore volumes for these materials were of  $1,640\text{ m}^2\text{g}^{-1}/0.656\text{ cm}^3\text{g}^{-1}$  and  $2344\text{ m}^2\text{g}^{-1}/1.069\text{ cm}^3\text{g}^{-1}$ , respectively for the UiO-66 and the UiO-67. While the UiO-67 showed a maximum adsorption of  $80\text{ mg g}^{-1}$  of the pollutant, in the case of the UiO-66 there was not a measurable removal of the pollutant. In this case, the authors reported that besides the bigger surface area, the large pore size of the UiO-67 allows carbamazepine to diffuse into the interior of the UiO-67 while the smaller pore of the UiO-66 did not.

The same authors followed up with another interesting case the next year (Akpınar & Yazaydin, 2018). In their report, the authors studied the sorption of atrazine, an agricultural herbicide found in drinking water, to UiO-66 and 67. Interestingly, UiO-67 performed excellently by removing 98% of the pollutant within 2 minutes, which was faster in comparison to other similar materials such as the Zn-based material ZIF-8 (Zeolitic imidazolate framework) and activated carbon F400. However, it is important to mention that while the UiO-67 has a larger pore size and surface area than the UiO-66, its stability seems to be lower than its smaller counterpart. While in both publications (Akpınar & Yazaydin, 2017, 2018) the authors mention that the material can be reused, there is no discussion or deeper analysis on the stability of the UiO-67.

Among the most explored changes in the structure of MOFs is the surface charge to increase sorption, and in a few cases, selectivity. This is usually achieved by introducing a functional group, such as an amine or a hydroxyl group, on the organic ligand, which can increase the charge on this added functional group and therefore increase the interaction with charged substances. Usually, the as-synthesized UiO-66 seems to interact with pollutants by  $\pi$ -stacking or by interaction with the metallic cluster. However, introducing these new functional groups can completely change the nature of the interaction between the surface and the pollutant. Such is the case reported by Zhang et al. (2016). This publication reported the synthesis of UiO-66 and its analogs modified with 1 and 2 Br atoms on the organic ligand (UiO-66-Br and UiO-66-2Br). They also reported on the material's behavior toward the  $\text{Hg}^0$  sorption. While the surface area decreased with the addition of bromine groups from  $997\text{ m}^2\text{g}^{-1}$  to  $782\text{ m}^2\text{g}^{-1}$  and  $579\text{ m}^2\text{g}^{-1}$  for the UiO-66, UiO-66-Br and UiO-66-2Br, respectively, they reported that a higher amount of bromine on the MOF increased the amount  $\text{Hg}^0$  adsorbed on the adsorbent surface.

Another interesting example is how a change in the surface charge of the MOF led to an increase in its interaction with other substances, as reported by Sarker et al. (2018). In this study, the UiO-66 was functionalized with amine and carboxylic acid groups. These materials were tested in their ability to remove triclosan from water. They reported that the  $-\text{COOH}$  modified material adsorbed 2.4 times the amount of pollutant removed by activated carbon, and showed a higher kinetic constant in comparison. The UiO-66 and the amine-functionalized material performed in the middle range of the discussed materials, with an overall sorption capacity going from maximum to minimum as  $\text{COOH} > -\text{NH} > \text{UiO-66} > \text{activated carbon}$ .

As discussed earlier, Zr-MOFs have been modified with functional groups such as amines, carboxylates and some halogens, but usually these materials are compared only with the pristine UiO-66. An interesting example on the modification of MOFs was presented by Berger et al. (2020), where they synthesized a series of UiO-66 modified with halogens F, Cl, Br, and I. These modified MOFs have not been tested in water decontamination and could be interesting since the different size of the ions could lead to higher selectivity on the adsorption process. Some other options could be the inclusion of functionalities as phosphates. These organic functional groups are known to create highly energetic coordination bonds with metals, which could mean an improvement in the removal of this family of elements.

One more factor that should be considered when designing MOFs for pollutant sorption is the particle size of the synthesized material. Lv et al. (2016) analyzed the sorption of several nitrophenols over UiO-66 and UiO-66- $\text{NH}_2$ . In this publication, the authors analyzed the effect of pH and temperature in the environment and MOF's characteristics (such

**Table 2.** Different Pollutants Adsorbed on Zr MOFs.

| TYPE OF POLLUTANT | POLLUTANT                               | REFERENCE   |   |
|-------------------|---|---|---|
| Organic pollutant | Carbamazepine                           | Akpinar and Yazaydin (2017); Chen et al. (2017)   |   |
|                   | Atrazine                                | Akpinar and Yazaydin (2017)   |   |
|                   | Tetracycline                            | Chen et al. (2017)  |   |
|                   | Tetracycline hydrochloride              | Sun et al. (2020)   |   |
|                   | Phenol                                  | Lv et al. (2016)  |   |
|                   | 4-nitrophenol                           | Lv et al. (2016)  |   |
|                   | 2,4-dinitrophenol                       | Lv et al. (2016)  |   |
|                   | 2,4,6-trinitrophenol                    | Lv et al. (2016)  |   |
|                   | Benzene                                 | Navarro Amador et al. (2018)  |   |
|                   | Toluene                                 | Navarro Amador et al. (2018)  |   |
|                   | Ethylbenzene                            | Navarro Amador et al. (2018)  |   |
|                   | Xylenes                                 | Navarro Amador et al., (2018)   |   |
|                   | Glyphosate                              | Pankajakshan et al. (2018); Yang et al. (2017); Zhu et al. (2015)                                   |   |
|                   | Triclosan                               | Sarker et al. (2018)  |   |
|                   | Glufosinate                             | Zhu et al. (2015)   |   |
|                   | Heavy metal                             | Hg (II)   | Fu et al. (2019); Huang et al. (2016); Leus et al. (2017) |
|                   |   | Pb (II)   | Jamshidifard et al. (2019); Zhao et al. (2019)            |
| Cd (II)           |   | Jamshidifard et al. (2019)  |   |
| Cr (VI)           |   | Jamshidifard et al. (2019)  |   |
| Hg <sup>0</sup>   |   | Zhang et al. (2016); Zhao et al. (2021)   |   |
| Metalloid         | As (V)                                  | Audu et al. (2016); He et al. (2019); Huo et al. (2019); Qi et al. (2019); Wang, Yuan et al. (2015) |   |
|                   | As (III)                                | Audu et al. (2016); He et al. (2019); Huo et al. (2019); Qi et al. (2019); Wang, Yuan et al. (2015) |   |
|                   | Sb (III)                                | He et al. (2017)  |   |
|                   | Sb (IV)                                 | He et al. (2017); Qi et al. (2019)  |   |
|                   | Sb (V)                                  | He et al. (2017)  |   |
|                   | Se (IV)                                 | Wei et al. (2018)   |   |
|                   | Se (VI)                                 | Li et al. (2020); Wei et al. (2018)   |   |
|                   | B                                       | Lyu et al. (2017)   |   |
| Ion               | Fluoride                                | Lin et al. (2016)   |   |
|                   | Phosphate                               | Lin et al. (2015)   |   |
| Dye               | Methylene blue                          | Ali-Moussa et al. (2017); Chen et al. (2015); Molavi et al. (2018); Song et al. (2020)              |   |
|                   | Methyl orange                           | Chen et al. (2015); Molavi et al. (2018); Chen et al. (2015), Molavi et al. (2018)                  |   |
|                   | Rhodamine B                             | He et al. (2014)  |   |
|                   | Congo Red                               | Yang, 2017)   |   |
|                   | Malachite green                         | Yang, 2017)   |   |
|                   | Acid Orange 7                           | Zhang et al. (2017)   |   |
| Others            | <i>p</i> -Arsanilic acid                | Tian et al. (2018)  |   |
|                   | Diclofenac sodium,                      | Hasan et al. (2016)   |   |
|                   | Methylchlorophenoxypropionic acid MCPP) | Seo et al. (2015)   |   |

as functionality, pore size, and particle size), on the exothermic nature of the sorption process on different pollutant sizes. The size of the MOF had an important effect on the kinetics of the sorption process, where the smaller it was, the more rapidly saturation of the material was achieved. This was attributed to the increase of available adsorption sites on the outer surface of the MOF particles, resulting in a faster sorption process, since diffusion to the interior of the MOF was not the main mechanism of adsorption. Similarly, Li et al. (2017) also analyzed the effect of the particle size, concluding that the smaller the particle, the better the adsorption. Although the effect of this parameter is observed in the sorption performance of MOFs, it is rarely reported in most of the reviewed publications. Therefore, it is important to further explore the relation of this parameter with the adsorption phenomena of pollutants.

Finally, one of the most important factors to consider and that should be addressed when analyzing MOFs in the adsorption of pollutants are the imperfections in the crystalline structure of the MOF, notably missing linkers or missing metallic clusters. This factor has only been analyzed in a handful of reviewed publications, and most of them are focused on the surface area, functionality, and general characteristics of the pores of the MOF. However, the work reported by Li et al. (2017) made a profound analysis on the effect of the imperfections of the UiO-66 in the sorption of selenate Se (VI). In this study, they made two types of analyses, one from an experimental and another from a theoretical point of view. Control on the defects was possible by changing the acid modulator during the material synthesis (acetic acid, HCl, among others) and its ratio to the metallic salt. The augmentation of the imperfections on the MOF increased the pore volume of the material and its surface area, which increased the adsorption capacity. This is because more imperfections increase the hydrophilic character of the MOF, which frees up M-OH and M-OH<sub>2</sub> sites to interact with other substances. In the same study, the authors also made the comparison with two other Zr<sub>6</sub> based MOFs, the NU-1000 and the MOF-808, and even when they performed better than the UiO-66 (almost double of its capacity) the same authors concluded that UiO-66 would be a better choice since it is cheaper and easier to synthesize. Also, by density functional theory calculations they predicted that HCl modulated UiO-66 would perform better than the other MOFs, since this material would contain a high number of defects.

It is important to mention that in the comparison between the characteristics of the UiO-66 in different publications, it is hard to address possible correlations due to the wide variety of values on the surface area for the same material. Reported values for UiO-66, for example, range between 486 m<sup>2</sup>g<sup>-1</sup> (He et al., 2017) and 1488 m<sup>2</sup> g<sup>-1</sup> (Lyu et al., 2017) (Table 3). It is likely that these differences could be due to synthesis procedures that depend on the modulator used during the self-assembling of the MOF, which in some cases produces less

**Table 3.** Different Surface Areas Reported for UiO-66 Zr Based MOFs.

| REPORTED SURFACE AREA M <sup>2</sup> G <sup>-1</sup> | REFERENCE                   |
|--|-----------------------------|
| 1,640  | Akpinar and Yazaydin (2017) |
| 1,188  | Lv et al. (2016)            |
| 1,082  | Hasan et al. (2016)         |
| 837.91   | Chen et al. (2015)          |
| 591.6  | Chen et al. (2017)          |
| 486  | He et al. (2014)            |

defective MOFs. However, it is also likely that the purification procedure used after the synthesis of the MOF could affect these values. Therefore, it is important to choose an appropriate MOF cleaning procedure, as well as the correct modulator, to obtain the proper information about the amount of defects present in the crystalline material, since in both cases the sorption capacity of the MOF could be affected. In the case of the defects, as was discussed earlier, missing linkers or metallic clusters could decrease the effect of diffusion in the interior of the MOF, thereby increasing the sorption capacity observed. In the case of the purification of the MOF, if the procedure is not done carefully, its surface area and available sites for sorption can decrease. More complete and detailed experimental procedures and material characterizations would allow for a better understanding of the differences observed between different studies and their reproducibility.

UiOs have also been used in combination with other materials to adsorb different pollutants. Such is the case reported by Yang et al. (2017), where they functionalized graphene oxide (GO) with the UiO-67. According to the authors, they enhanced the adsorption capacity of GO by growing the UiO-67 MOF over GO particles. This material was tested regarding the sorption of glyphosate and showed an excellent adsorption capacity, working within a wide range of pHs, resulting in a great advantage for its use in water treatment. This example points to new areas of research, such as combining MOFs with other materials. These composites could be helpful in increasing the sorption capacity or selectivity, reducing costs or implementing new methodologies to retrieve the composites after use. This last example is of high importance, since MOFs are usually obtained in a powdery state. Therefore, their recovery from effluents would be hard. Some mixtures could improve this, since the addition of magnetic nanoparticles/MOFs composites would allow for a faster recovery of the MOF. Another option is the growth of MOFs over surfaces. This last example would help to fix the MOF on a surface without another process to recover the MOF/pollutant system.

Besides the inherent sorption capacity of MOFs and their potential use as adsorbents, it is possible to include different functional groups or metals within the same structure, making

**Table 4.** Studies That Included Regeneration and the Type of Solvent Used.

| MOF                                       | POLLUTANT                 | REGENERATION NO. CYCLES /SOLVENT | REFERENCE                    |
|---|---------------------------|----------------------------------|------------------------------|
| UiO-67                                    | Carbamazepine             | 5/acetone                        | Akpinar and Yazaydin (2017)  |
| UiO-66                                    | Atrazine                  | 3/acetone                        | Akpinar and Yazaydin (2018)  |
| UiO-67                                    | Atrazine                  | 3/acetone                        | Akpinar and Yazaydin, (2018) |
| UiO-66                                    | Carbamazepine(CBZ)        | 4/chloroform, methanol           | Chen et al. (2017)           |
| UiO-66                                    | Rhodamine B (RhB)         | 7/DMF, water                     | He et al. (2014)             |
| UiO-66-NH <sub>2</sub>                    | Phosphate                 | 4/NaOH                           | Lin et al. (2015)            |
| UiO-66                                    | Phosphate                 | 4/NaOH                           | Lin et al. (2015)            |
| UiO-66                                    | 2,4-dinitrophenol         | 5/water, ethanol                 | Lv et al. (2016)             |
| UiO-66-NH <sub>2</sub>                    | 2,4-dinitrophenol         | 5/water, ethanol                 | Lv et al. (2016)             |
| UiO-66                                    | B                         | 4/HCl,water                      | Lyu et al. (2017)            |
| UiO-66_NH2                                | Fluoride                  | 5/methanol                       | Massoudinejad et al. (2016)  |
| UiO-67                                    | Glyphosate                | Lost integrity/water, acetone    | Pankajakshan et al. (2018)   |
| Fe <sub>3</sub> O <sub>4</sub> @TA@UiO-66 | As (III)/ Sb (III)        | Lost integrity/water, acetone    | Qi et al. 2019)              |
| UiO-66, UiO-66-NH, UiO-66 –NH-CO-COOH     | Triclosan                 | 4/ethanol                        | Sarker et al. (2018)         |
| UiO-67                                    | <i>p</i> -Arsanilic acid  | 4/NaOH, ethanol                  | Tian et al. (2018)           |
| UiO-67-NH <sub>2</sub>                    | <i>p</i> -Arsanilic acid  | 4/NaOH, ethanol                  | Tian et al. (2018)           |
| UiO-66, UiO-66-NH <sub>2</sub>            | Se (IV)/ Se (VI)          | 3/NaOH                           | Wei et al. (2018)            |
| UiO-67                                    | Congo Red/Malachite green | 7/NaOH                           | Yang et al. (2018)           |

it viable to carry out adsorption and photocatalytic degradation of the pollutants within the same material. For example, UiO-67 was modified with a Ru tris-bipyridine complex and the addition of Ti by post-synthetic exchange. By combining the absorption and catalytic properties of the Ru complex and Ti, respectively, the modified MOF could degrade methylene blue (Navarro Amador et al., 2017). This is a clear example of the versatility of MOFs that can be shown by adding rational changes to their structure.

To be competitive against other less expensive water treatment processes, regeneration and reusability of MOFs are needed, since most publications do not report these experiments and the ones that do report it, have not gone beyond seven cycles. Table 4 shows that several of the revised studies included regeneration and reusability of the synthesized UiOs. Although the average number of reusability cycles was four, some tested up to seven cycles. It is also important to mention that in all these studies, with the exception of Chen et al. (2017) for UiO-66, and Pankajakshan et al. (2018) for UiO-67, between cycles, more than 80% efficiency was observed. In the case of Chen et al. (2017), reusability was good for carbamazepine; however, because of the strong interaction between the MOF and tetracycline, it was not possible to desorb the latter. Regarding Pankajakshan et al.

(2018), the integrity of the UiO-67 was lost after the water and acetone wash. Still, these results are very encouraging, providing evidence for the stability of the structure of the UiO family in aqueous solutions, as well as regeneration and reusability potential.

From the presented regeneration procedures and solvents used, the most economical might be through a pH change. However, it is known that at higher pHs the stability of the MOF decreases. For this reason, it is important to further study changes in the physical and/or structural characteristics of the MOFs after regeneration, and not only changes in removal efficiencies.

While Zr MOFs possess interesting characteristics that would allow them to compete with other porous materials, their synthesis is still based on solvothermal conditions, which use toxic solvents such as DMF. Therefore, there is room for novel research synthesizing MOFs using less toxic solvents, or lower quantities, for their synthesis. Some attempts with interesting results have been reported to change the synthesis procedure toward greener options. The case reported by Hu et al. (2015), attempted to synthesized the UiO-66 and several derivatives by hydrothermal synthesis, by using water instead of DMF during the synthesis process. The materials they obtained were crystalline and retained the characteristics that make



**Table 5.** Maximum of Adsorption of Some MOF/Pollutant Systems Reviewed and the Driving Force Proposed by the Authors for the Adsorption Process.

| MOF                         | POLLUTANT       | DRIVING FORCE  | MAXIMUM OF ADSORPTION (MG/G) | REFERENCE                   |
|-----------------------------|-----------------|--|------------------------------|-----------------------------|
| UiO-66                      | Carbamazepine   | Pore size  | To low to be reported        | Akpinar and Yazaydin (2017) |
| UiO-67                      | Carbamazepine   | Pore size  | 80                           | Akpinar and Yazaydin (2017) |
| UiO-66                      | Carbamazepine   | Hydrophobic interactions (van der Waal forces in general)  | 37.2                         | Chen et al. (2017)          |
| UiO-66-NH <sub>2</sub>      | Hg (II)         | Functional group effect.   | 145.1                        | Fu et al. (2019)            |
| UiO-66-NH <sub>2</sub>      | Hg (II)         | Mass diffusion and functional group effect.  | 223.8                        | Zhao et al. (2021)          |
| UiO-66                      | Hg (II)         | Weak affinity of Hg to the active binding sites due to the lack of functionality.                                    | 61.6                         | Zhao et al. (2021)          |
| UiO-66                      | Hg <sup>0</sup> | Chemisorption  |                              | Leus et al. (2017)          |
| UiO-66                      | As(V)           | Two binding sites within the adsorbent framework are proposed for arsenic species, on the cluster and on the ligand. | 303                          | Wang, Yuan et al. (2015)    |
| HCl-UiO66-(SH) <sub>2</sub> | As(V)           | Missing linkers sites bind to As (V)   | 40                           | Audu et al. (2016)          |

MOF attractive. Another example was presented by Ali-Mousa et al. (2017), where the UiO-67 was synthesized and modified by mechanochemistry with minimum amounts of solvent. Still, most of the attempts of synthesis and use of UiO MOFs as adsorbents are based on the solvothermal procedure. It is important to address this feature in the synthesis of MOFs, since the solvent can remain trapped in the pores of the hybrid material, which in water-based applications could represent a risk of being released into the environment. While different approaches have been explored in the synthesis of MOFs as described earlier, these approaches usually lead to materials that are less crystalline than their analogous MOFs synthesized by solvothermal means. These differences should be measured in terms of their adsorption capacity to evaluate if the decrease of crystallinity affects greatly or not the adsorption capacity of MOFs, either positively or negatively.

In the case of the MOF/pollutant adsorption process, there is also the need to homogenize results. Table 5 includes maximum adsorption values and the driving force reported in selected studies, as reported by different authors. It is possible to observe that different authors propose different mechanisms for the same pollutant and the same type of MOF, as in the case of carbamazepine (CB) over UiO-66 MOF. Akpinar and Yazaydin (2017) reported that CB was not adsorbed at all due to the pore size, while C. Chen et al. (2017), reported that the UiO-66 could adsorb up to 37.2 mg of the same pollutant. Another example is the adsorption of Hg (II), where the metal was adsorbed on the surface of the UiO-66 and its modified analog UiO-66-NH<sub>2</sub> (Fu et al., 2019; Zhao et al., 2021). While the sorption capacity of the amine functionalized MOF remains higher than the capacity of the un-functionalized material, the difference between the values of the maximum of adsorption on the UiO-66-NH<sub>2</sub> range from 145.1 to 223.8 mg g<sup>-1</sup>

for different studies (Table 5). Finally, the last example is the adsorption of As(V), where the modification of the UiO-66 to HCl-UiO66-(SH)<sub>2</sub> (Audu et al., 2016) did not improve adsorption as predicted; on the contrary, adsorption decreased. Also, it is interesting to note that for UiO-66, adsorption was explained to have occurred in both the metallic centers and the ligand, while on functionalized MOF the sorption process was explained by the absence of organic linkers within the crystalline structure. The differences discussed earlier can be related to the lack of an extensive procedure to clean up the MOFs, different qualities of the crystals used for adsorption (imperfections) and/or different conditions at which the sorption experiments take place. This information is not always shared by the authors, so in order to improve or predict the properties of MOFs, it would be important to include this information.

To summarize, when designing MOFs for the sorption of pollutants from water, it is important to take into account the synthesis procedure, stability of the MOF, pore volume and surface area, imperfections, particle size, and charge of the MOFs, where in most cases, all of these factors would be present when selecting and adequate MOF. Still, other factors that should be taken into account are the nature of the material to be retrieved from water, the experimental conditions under which sorption takes place, as well as the reusability and regeneration of the MOF. In the following section, we discuss the use of MOFs for the sorption of pollutants, from the point of view of the adsorbate.

*Sorption experiment conditions, a key factor in understanding the sorption of pollutants in MOFs*

*pH and speciation.* MOFs adsorption capacity is mainly attributed to different parameters such as temperature, surface area,

**Table 6.** Pollutant Speciation at Different pHs and MOF's Pz ZP.

| MOF   | POLLUTANT                 | PH RANGE               | PZ ZP | REMOVAL AT PH=7-7.5 @ T <sub>amb</sub> (MG G <sup>-1</sup> ) | REFERENCE                   |
|---|---------------------------|------------------------|-------|--|-----------------------------|
| UiO-66  | Carbamazepine (CBZ)       | 2 to 10                | 4.81  | ~15  | Chen et al. (2017)          |
|   | Tetracycline (TC)         | 2 to 8                 | 4.81  | ~4   | Chen et al. (2017)          |
| UiO-66  | Sb (III)/Sb (V)           | 1.5 to 6/<br>1.5 to 12 | 7.2   | ~75  | He et al. (2017)            |
| UiO66-NH <sub>2</sub>                               | Sb (III)/Sb (V)           | 1.5 to 6/<br>1.5 to 12 | 8     | ~80  | He et al. (2017)            |
| UiO-66  | 2,4-dinitrophenol         | 2 to 10                | 5.5   | ~84  | Lv et al. (2016)            |
| UiO-66-NH <sub>2</sub>                              | 2,4-dinitrophenol         | 2 to 10                | 6.5   | ~86  | Lv et al. (2016)            |
| UiO-66-NH <sub>2</sub>                              | Fluoride                  | 3 to 11                |       | ~46  | Lin et al. (2016)           |
| UiO-66-NH <sub>2</sub>                              | Fluoride                  | 3 to 11                |       | 16.6   | Massoudinejad et al. (2016) |
| UiO-66  | Triclosan                 | 2 to 12                |       |  | Sarker et al. (2018)        |
| UiO-66-NH <sub>2</sub>                              | Triclosan                 | 2 to 12                |       |  | Sarker et al. (2018)        |
| UiO-66 -NH-CO-COOH                                  | Triclosan                 | 2 to 12                |       | ~130   | Sarker et al. (2018)        |
| UiO-66  | Se (IV)/Se (VI)           | 3 to 11                | 6     | ~45 /~ 7   | Wei et al. (2018)           |
| UiO-66-NH <sub>2</sub>                              | Se (IV)/Se (VI)           | 3 to 11                | 4.7   | ~5 /~37  | Wei et al. (2018)           |
| HCl-UiO66-(SH) <sub>2</sub>                         | As(v)/As(III)             | 2, 7, 12               |       | ~99 /~39   | Audu et al. (2016)          |
| Fe <sub>3</sub> O <sub>4</sub> @TA@UiO-66<br>UiO-67 | As (III)/Sb (III)         | 3 to 11                | 3     | ~24 /~24   | Qi et al. (2019)            |
| UiO-67  | Carbamazepine             | 3 to 9                 |       | ~ 79   | Akpinar and Yazaydin, 2017) |
| UiO-67  | Atrazine                  | 2.8 to 9.8             |       | 10.96  | Akpinar and Yazaydin, 2018) |
| UiO-67-HCl  | Se(VI)                    | 2.5 to 9.5             |       | ~100   | Li et al. (2017)            |
| UiO-67  | <i>p</i> -Arsanilic acid  | 3 to 10                | ~ 4.4 | ~225   | Tian et al. (2018)          |
| UiO-67-NH <sub>2</sub>                              | <i>p</i> -Arsanilic acid  | 3 to 10                | ~ 4.5 | ~ 138  | Tian et al. (2018)          |
| UiO-67-Graphene Oxide                               | Glyphosate                | 2 to 8                 |       | ~135.26  | Yang et al. (2017)          |
| UiO-67  | Congo Red/Malachite green | 2 to 8                 | 6.1   | ~ 1000/~ 280   | Yang et al. (2018)          |
| UiO-67  | Glyphosate /Glufosinate   | 2 to 9                 | ~2    | ~287 /~181   | Zhu et al. (2015, p. 67)    |

functional groups, concentration, among others. Nevertheless, the speciation of pollutants in water is determined by pH of the solution, which will affect removal efficiencies. To understand removal mechanisms, a key aspect and challenge is to understand the solution phase speciation with varying pHs. Similarly, the MOFs' charge, which can change with varying pHs, could also have an effect on its sorption capacity for a given contaminant. Therefore, an accurate description of the pollutant speciation as well as MOFs' charge at a given pH are key to understanding removal mechanisms and efficiencies. Examples of studies, where pollutant speciation at different pHs or MOFs' point of zero Zeta Potential (Pz ZP, pH at which the net charge of the particle is zero) were considered or reported, are presented in Table 6.

Wang, Liu et al. (2015), studied the removal of As (V) from water with Zr-MOF UiO-66, which presented speciation ( $H_3AsO_4$ ,  $H_2AsO_4^-$ , and  $HAsO_4^{2-}$ ) at different pH values from 1 to 11. The maximum removal efficiency was observed at pH 2, where coordination processes are the main removal mechanism at low acidic conditions. However, electrostatic interactions appear to be relevant for removal efficiencies at higher pHs. Similarly, Audu et al. (Audu et al., 2016), studied the removal of As (V) and As (III) with HCl-UiO66-(SH)<sub>2</sub> MOF in aqueous media at pH 2, 7, and 12, demonstrating chemoselective capture of anionic and neutral As (V) and As (III), respectively. Furthermore, at pH 12, effective desorption could also be observed for both, As (V) and As (III). In contrast, Qi et al. (2019), when studying As (III) removal, found almost no

**Table 7.** Studies Where Changes With Temperature Were Reported.

| MOF                             | POLLUTANT                             | T VARIATION (°C) | CHANGES REMOVAL EFFICIENCY W/T INCREASE | REFERENCE           |
|---------------------------------|---------------------------------------|------------------|---|---------------------|
| UiO-66                          | Carbamazepine(CBZ)/ Tetracycline (TC) | 25, 35, 45       | Increase                                | Chen et al., (2017) |
| UiO-66                          | Rhodamine B (RhB)                     | 0, 30, 50        | Increase                                | He et al. (2014)    |
| UiO66/ UiO66-NH <sub>2</sub>    | Sb (III) /Sb(V)                       | 25, 35, 45       | Increase                                | He et al. (2017)    |
| UiO-66 /UiO-66-NH <sub>2</sub>  | Phosphate                             | 20, 40, 60       | Increase                                | Lin et al. (2015)   |
| UiO-66-NH <sub>2</sub>          | Fluoride                              | 20, 40, 60       | Decrease                                | Lin et al. (2016)   |
| UiO-66 / UiO-66-NH <sub>2</sub> | 2,4-dinitrophenol                     | 15, 35, 55       | Decrease                                | Lv et al. (2016)    |
| UiO-66                          | B                                     | 25, 35, 45       | Increase                                | Lyu et al. (2017)   |
| UiO-67                          | Congo Red/ Malachite green            | 20-45            | Increase                                | Yang et al. (2018)  |

variations in removal efficiencies across a pH range between 2 and 10.

Another speciation example is Se (IV) and Se (VI), which are inorganic species of Se, where in natural waters (pH 5-9)  $\text{HSeO}_3^-$  and  $\text{SeO}_3^{2-}$  dominate, as well as  $\text{SeO}_4$  for Se (IV) and Se (VI), respectively. The results of Zr-MOF application to Se (VI) removal indicate that the removal mechanism might depend on the pH and the MOFs' charge. Both Li et al. (2017), and Wei et al. (2018), observed a decrease in Se (VI) removal with an increase in pH, indicating a change in the surface charge of the MOF from positive to negative, before and after the Pz ZP. However, Wei et al. (2018), observed that for Se (IV) an increase in pH increased the removal for Se (IV). These observations were inconsistent with both UiO-66 and UiO-66-NH<sub>2</sub> surface charges within the pH examined, indicating that the removal mechanism was not affected by electrostatic attraction. Finally, Wei et al. (2018), reported that UiO-66 and UiO-66-NH<sub>2</sub> could be easily regenerated by adjusting the pH to 8.5, without affecting its adsorption capacity, indicating stability of the tested MOFs up to a pH of 10.4.

In natural water, at pHs between 6 and 8,  $\text{Sb}(\text{OH})_3$  and  $\text{Sb}(\text{OH})_6^-$  are the main species found for Sb (III) and Sb (V), respectively. He et al. (2017), observed variations in the removal efficiency of both Sb (III) and Sb (V), respectively. Similar to other heavy metals, Sb had higher removal mechanisms observed with a lower pH ( $\text{pH} < 2$ ), with no apparent effect on the compound speciation. However, at higher pH, the speciation affects removal efficiencies. For anionic Sb (V), removal efficiencies decreased after the Pz ZP of the MOF. For neutral Sb (III), a second removal efficiency maxima is found around the Pz ZP of the studied MOF; this observation was also presented by Qi et al. (2019).

The above discussion emphasizes the importance of addressing the metal or metalloid speciation to understand the possible removal mechanisms of the pollutants with the UiO under consideration. This evaluation is also relevant for other heavy metals such as  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Pb}^{2+}$ , where higher

sorption was present at pH values between 1 and 7, as well as for organic pollutants, as charged species can benefit or affect interactions with UiOs. As an example, methylene blue (MB) removal by UiO-66 is compared between different experiments. The first one carried out by Song et al. (2020), showed that the UiO-66 had a greater sorption capacity at higher pH values from 8 to 11, where an increase in pH promoted electrostatic attractions between the adsorbent and the cationic dye MB. In a second study by Molavi et al. (2018), the sorption capacity had a considerable decrease at higher pH values attributed to the electrostatic interaction as well as  $\pi$ - $\pi$  stacking.

As mentioned before, it is equally important to know the charge of the studied UiO during sorption experiments. This would help to understand if electrostatic repulsion or attraction might be present between the MOF and the pollutant. However, few studies present such a complete characterization of the synthesized UiO materials and report the Pz ZP for their material (Table 6). Future studies should make an effort to include the speciation of the solute and the Pz ZP of the sorbent.

*Temperature.* Among the different parameters mentioned that affect the adsorption of pollutants, temperature is also important, as removal efficiencies may change with its variations (Table 7). However, the effect is not always the same. In most cases, it has been shown that increasing the temperature decreases the adsorption capacity. Such is the case studied by Jamshidifard et al. (2019), in which temperature was increased from 25°C to 45°C and the permeation flux increased through UiO-66-NH<sub>2</sub> loaded- PAN/chitosan nanofibers, which presented a slight decrease in its adsorption capacity for metal ion removal. In other words, the increase in temperature generated an increment in the size of the pores that resulted in a greater flux in the membrane matrix, causing the lower incorporation of metal ions in the pores. Another proof of this is stated by He et al. (2019) where the increase in temperature from 25°C to 45°C in As (III) and As (V) resulted in the decrease of the

**Table 8.** Competitive Ions Present in Evaluated Studies.

| MOF                                       | POLLUTANT                                | INCLUDE COMPETITIVE ION INTERACTIONS  | REFERENCE                   |
|---|--|---|-----------------------------|
| UiO-66                                    | Carbamazepine(CBZ)/<br>Tetracycline (TC) | Humic acids (enhance), Na <sup>+</sup> (no effect), K <sup>+</sup> (inhibit), Ca <sup>2+</sup> ,<br>and Al <sup>3+</sup> (no effect on CBZ but suppressed TC)   | Chen et al. (2017)          |
| UiO66-NH <sub>2</sub>                     | Sb (III)                                 | Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> (no effect) | He et al. (2017)            |
| UiO-66                                    | Sb (III) / Sb (V)                        | Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> (no effect) | He et al., (2017)           |
| UiO-66-HCl                                | Se(VI)                                   | KNO <sub>3</sub> (decrease)   | Li et al. (2017)            |
| UiO-66-NH <sub>2</sub>                    | Phosphate                                | BrO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> (no effect)   | Lin et al., (2015)          |
| UiO-66                                    | Phosphate                                | BrO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> (no effect)   | Lin et al. (2015)           |
| UiO-66-NH <sub>2</sub>                    | Fluoride                                 | Cl <sup>-</sup> , Br <sup>-</sup> (no effect), cationic surfactant (increase); anionic<br>surfactant (decrease)   | Lin et al. (2016)           |
| UiO-66-NH <sub>2</sub>                    | Fluoride                                 | NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>3</sub> <sup>-</sup> (no effect) HCO <sub>3</sub> <sup>-</sup> (decrease)  | Massoudinejad et al. (2016) |
| Fe <sub>3</sub> O <sub>4</sub> @TA@UiO-66 | As (III)/Sb(III)                         | CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , SiO <sub>3</sub> <sup>2-</sup> and PO <sub>4</sub> <sup>3-</sup> (no effect)  | Qi et al. (2019)            |
| UiO-66                                    | As (V)                                   | Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> (no effect)  | Wang, Yuan et al. (2015)    |
| UiO-66                                    | Se (IV)                                  | NaNO <sub>3</sub> , KNO <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , NaCl, Na <sub>2</sub> SO <sub>4</sub> (no effect),<br>Mg(NO <sub>3</sub> ) <sub>2</sub> (increase) Na <sub>3</sub> PO <sub>4</sub> (decrease)    | Wei et al. (2018)           |
| UiO-66                                    | Se (VI)                                  | NaNO <sub>3</sub> , NaCl, KNO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>3</sub> PO <sub>4</sub> , Mg(NO <sub>3</sub> ) <sub>2</sub> (decrease),<br>Ca(NO <sub>3</sub> ) <sub>2</sub> , (increase)            | Wei et al. (2018)           |
| UiO-66-NH <sub>2</sub>                    | Se (VI)                                  | NaNO <sub>3</sub> , NaCl (no effect), KNO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , Na <sub>3</sub> PO <sub>4</sub> (decrease),<br>Ca(NO <sub>3</sub> ) <sub>2</sub> , Mg(NO <sub>3</sub> ) <sub>2</sub> (increase)  | Wei et al. (2018)           |
| UiO-66-NH <sub>2</sub>                    | Se (IV)                                  | NaNO <sub>3</sub> , KNO <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , NaCl, Na <sub>2</sub> SO <sub>4</sub> (no effect),<br>Mg(NO <sub>3</sub> ) <sub>2</sub> (increase) Na <sub>3</sub> PO <sub>4</sub> (decrease)    | Wei et al. (2018)           |
| UiO-67                                    | Congo Red/ Malachite<br>green            | S-Citrate, Glucose, S-Benzoate, NaCl, CaCl <sub>2</sub> (no effect)   | Yang et al. (2018)          |
| UiO-67                                    | Glyphosate                               | CaCl <sub>2</sub> , NaOAc, MgSO <sub>4</sub> , KNO <sub>3</sub> (no effect)   | Zhu et al. (2015)           |

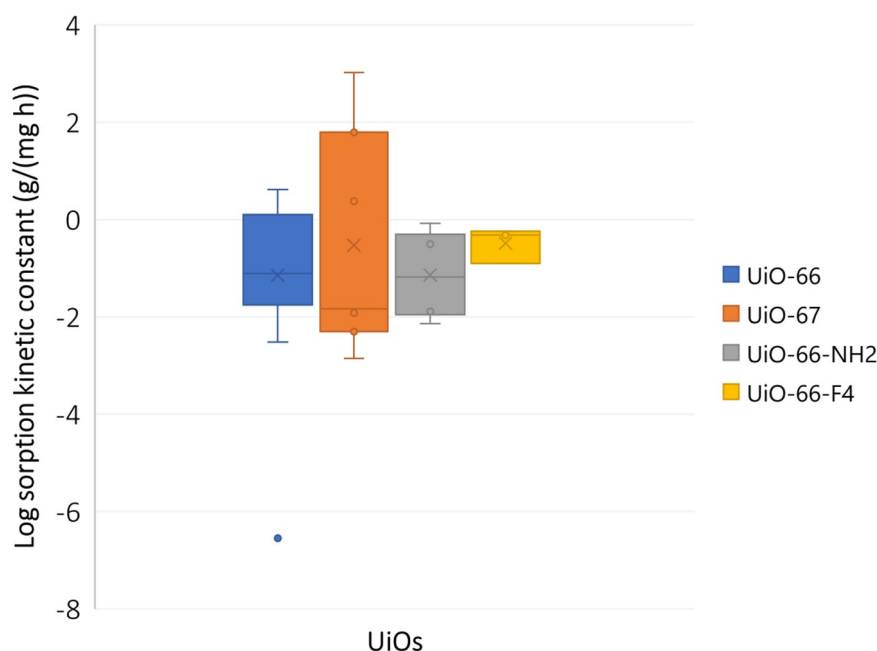
maximum adsorption capacities for UiO-66, from 204.38 and 68.19 mg g<sup>-1</sup> to 68.21 to 41.81 mg g<sup>-1</sup>, respectively; a similar behavior was observed for UiO-66(NH<sub>2</sub>).

Dye removal is not an exception to the effect of temperature since Molavi et al. (2018) demonstrate that the adsorptive interactions of MO and MB with UiO-66 at different temperatures (25°C, 35°C, and 45°C) show changes in their adsorption capacity. MO's adsorption capacity is unstable at higher temperatures, indicating an exothermic process, while MB displays a favorable behavior when increasing the temperature. On the same basis, Yang and collaborators (2018) point out that temperature has an effect on dye removal for UiO-67 at ranges from 20°C to 45°C, where removal efficiencies for Congo Red and Malachite green increase with rising temperature.

These observations point to differences regarding inherent energetic changes associated with the adsorption process that vary between MOFs and pollutants, which needs to be better understood to predict future removal processes. Nevertheless, not all evaluated studies included temperature variations since most studies have a fixed temperature, so that other parameters could be evaluated like pH and speciation.

*Competitive Ions.* In natural waters, other components that can compete with the solute for sorption, mainly dissolved ions, are commonly present. In order to address if removal efficiencies would decrease when testing the MOFs in natural waters, it is important to consider natural organic matter and the possibility of competitive ions, mainly anions, present in natural water. As seen in Table 8, some studies include competitive ions, and for the most part, there was no observed decrease in removal efficiencies (He et al., 2017; Lin et al., 2015; Qi et al., 2019; Wang, Yuan et al., 2015; Yang et al., 2018; Zhu et al., 2015). However, there were other cases where competitive ions or organic matter had an important effect on the pollutant removal efficiencies. For example, Chen et al. (2017) observed that the presence of humic acids facilitated the removal mechanism for both CBZ and TC, Na<sup>+</sup> had no effect and K<sup>+</sup> inhibited the removal. However, different findings were observed in the presence of Ca<sup>2+</sup> and Al<sup>3+</sup>, which suppressed TC removal but had no effect on CBZ.

Similarly, Wei et al. (2018) observed that while the presence of ions slightly affected or had no effect on the removal of Se (IV) using UiO-66 or UiO-66-NH<sub>2</sub> (with the exception of Na<sub>3</sub>PO<sub>4</sub>), important negative effects were observed for the



**Figure 3.** Box plot results of sorption kinetic constant ( $y$  axis) for various metal organic frameworks from the UiO family ( $x$  axis).

removal of Se(VI) using both, UiO-66 or UiO-66-NH<sub>2</sub>. Furthermore, Li et al. (2017) also saw an important decrease in Se(VI) removal efficiencies in the presence of KNO<sub>3</sub>. Tian et al. (2018) and Yang et al. (2018) also considered other possible interferences present in the systems of interest, such as dissolved organic matter (DOM), or S-Citrate, Glucose, and S-Benzoate. In such studies, only small effects were observed.

Finally, Lin et al. (2016) also addressed the presence of cationic (CS) and anionic surfactants (AS) present in the medium. A removal increase was observed with CS and a decrease with AS, further corroborating the relevance of the charge of both the sorbate and the sorbent, as well as the presence of competitive ions.

From the previous analysis, we can conclude that in most cases the presence of competitive ions and/or interferences, at relevant concentrations, will not affect removal efficiencies. However, it is important to assess the system of interest and address possible interactions based on pH, pKa, and the point of zero charge of the sorbent, as well as possible ions and interferences. In addition, it is important to recognize that all the studies tested one ion or interference at a time, and that different results might be obtained from mixtures of multiple ions and/or interferences. Also, none of the studies tested the removal in naturally occurring waters.

**Sorption kinetics.** To understand the main sorption mechanisms present in the removal of the tested contaminants, most studies fitted their data to first-order and pseudo-second-order (ps) sorption models. Not surprisingly, in the reported cases the models fit best with ps sorption, indicating the presence of chemisorption or ion exchange. To understand

which characteristics from the sorbate or the sorbent affect the sorption kinetics, we evaluated the influence of the type of MOF, the sorbate concentration, the charge, and the molecular weight.

Figure 3 presents the overall results observed for the pseudo-second order kinetics constant ( $k_{psk}$ ). As seen, all the values fall relatively closely between the different studied UiOs. However, we can see less dispersion in the values for UiO-66 and UiO-66-NH<sub>2</sub> than for UiO-67, where large variability is observed between studies. This is probably due to greater data sets for UiO66, as well as fewer variations in the synthesis between studies.

From the analyzed studies, one can observe that the  $k_{psk}$  increases when the temperature increases. This was observed by Lin et al. (2015), and Lv et al. (2016) (see Table S2). However, the trends are not as straightforward with increasing concentrations. While Lyu et al. (2017), observed an increase in the  $k_{psk}$  with an increasing concentration, Zhang et al. (2016), saw a decrease, and Zhang et al. (2017) did not see an increase or a decrease. This can also be observed in Supplemental Figure S1 (in terms of concentrations), where no strong general trends can be observed for the analyzed studies.

Considering the properties and characteristics of the studied UiOs, some of the possible removal mechanisms include the introduction of chemicals into UiO pores (absorption), electrostatic interactions between charges of UiOs and chemicals of interest (adsorption), and/or chemisorption. If absorption is a generally important mechanism, it should be possible to observe a decrease in the  $k_{psk}$  for increasing molecular weight; Figure S2 presents a slight trend in decreasing  $k_{psk}$  with increasing molecular weight for UiO-66, but not for

UiO-67, indicating a poor relationship between the studied variables, or that both, adsorption and absorption, are happening simultaneously.

On the other hand, to understand whether or not the pollutant's charge affected or contributed to  $k_{psk}$ , we graphed the kinetics constant against the charge. However, no general trend is observed between differently charged pollutants (Supplemental Figure S3). This might be difficult to address, since such electrostatic interactions also depend on the charge of the UiO; furthermore, some pollutants might be zwitterions or might have different charges throughout the structure (such as glyphosate or organic salts). Although Supplement Figure S3 does not show a trend, further research should be done in this area, since differences in adsorption maximums were observed at different pHs for some of the analyzed pollutants (eg, Lv et al. (2016); Sarker et al. (2018); Qi et al. (2019)). Possible estimations of  $k_{psk}$  with changing pH would provide such information.

## Conclusions

While MOFs have shown great potential toward the sorption of several pollutants, there are still several areas of improvement needed to up-scale their application and make them competitive against other sorbents in the market. The first challenge lies in the MOF itself. While Zr MOFs have a great potential in the field thanks to their exceptional stability in water, synthesis and the particular treatment of the materials can yield crystals with different properties that greatly affect the capacity of adsorption of these materials. Considering the differences in the surface area reported for the same material or in the capacity of adsorption for a given pollutant, it is evident that these factors should be considered when reporting the sorption capacities of MOFs to have more reliable information. This review points out the importance of a systematic way of synthesizing and characterizing the produced material and the sorbate, being able to compare variations among different materials, identifying sorption removal mechanisms, as well as understanding the sorption kinetics.

Crystalline imperfections can also affect MOFs' capacity and the research around this is still young; only a handful of papers explain this. Also, little has been discussed on the stability and reusability of Zr-based MOFs, which could be a big challenge for these materials.

The functionalization of surfaces or the implementation of different types of composites should also be explored more to overcome the issues of the powder properties of MOFs, since in this state, it would be harder to recover them, making their application in the field more difficult. Here we also point out opportunities for future research, improving the material capabilities or recovery, as well as the possibility of using less solvent or less toxic solvents for the synthesis of MOFs.

It is also very important to pay close attention to possible MOF and sorbate charge(s) that might affect removal efficiencies and sorption kinetics, as well as variations in temperature and the presence of competitive ions. For the latter, although there have been studies with different ions, no study has been reported using naturally occurring water.

All the presented studies fitted their data to a pseudo-second order sorption model, indicating the presence of chemisorption or ion exchange. No clear trends are observed to explain the removal mechanisms responsible for the observed sorption kinetics. However, the data set included may be too small, and that differences in the characteristics of UiOs may have changed because of synthesis variations. We suggest including in future studies the role of sorption kinetics with varying pH.

Finally, when considering the UiO family as candidates for the removal of organic and inorganic pollutants in water treatment systems, it is important to address MOFs' stability and removal efficiencies in conditions commonly found in wastewater treatment plants (WWTP) such as temperature, pH, and co-ions. This is especially true as we observed that most studies considered acidic conditions when increasing the removal efficiency, which would require additional steps and reagents, resulting in higher costs. Furthermore, the presence of co-pollutants might represent a challenge and affect removal efficiencies. For the most part, MOFs have only been tested for one pollutant at a time under controlled conditions. This might be a crucial step that will determine if MOFs are suitable in tertiary water treatment processes.

It is important to consider that regeneration might not be possible for strongly sorbed pollutants, and that some regeneration processes might compromise the stability of the MOFs. Still, the analyzed studies indicate a high reusability rate for the UiO family, making them good candidates against other less expensive alternatives.

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## Authors' Contributions

RNA and CMM analyzed the information of the MOFs regarding synthesis and physical properties of the material (first section of the paper). DFC and NRC analyzed the data regarding the interactions of MOFs and adsorption conditions (second section of the paper).

## Availability of Data and Materials

All data generated or analyzed during this study are included in this published article [and its Supplementary Information files].

## Declaration of Conflicting Interests

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## Supplemental Material

Supplemental material for this article is available online.

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