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1 **TAILORING THE PORE ARCHITECTURE AND CRYSTALLINE**
2 **STRUCTURE OF UiO-66 FOR THE SELECTIVE ADSORPTION OF ANIONIC**
3 **SPECIES IN AQUEOUS MEDIA**

4
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ABSTRACT26
27

28 Micropollutants such as organic dyes and pharmaceuticals have received much attention
29 in recent years due to their harmful effects on humans and wildlife, high stability against
30 natural degradation, and difficult removal in conventional water treatment plants. In this
31 work, we have optimized the adsorption of organic pollutants on UiO-66 metal-organic
32 frameworks by changing some synthesis parameters, which allowed the tuning of their
33 crystal structure and pore architecture. Samples with an extended microporous structure
34 and specific surface areas over $1300 \text{ m}^2 \cdot \text{g}^{-1}$ were prepared by a solvothermal approach,
35 which favored the access of the pollutant molecules to active adsorption sites. The
36 specific surface areas measured in this study are among the highest ever reported for UiO-
37 66. In batch adsorption tests conducted using aqueous solutions containing low initial
38 concentrations ($20 \text{ mg} \cdot \text{L}^{-1}$) of acid orange (AO7), ibuprofen (IBU), and methylene blue
39 (MB), the materials tested in this study exhibited preferential adsorption of the anionic
40 species AO7 ($192 \text{ mg} \cdot \text{g}^{-1}$) and IBU ($173 \text{ mg} \cdot \text{g}^{-1}$), resulting in AO7/MB and IBU/MB
41 selectivities of 9.6 and 8.7, respectively. The primary adsorption mechanism is most
42 likely a combination of electrostatic and Lewis acid-base interactions involving Zr-(-
43 SO_3^-) for AO7 and Zr-(- CO_2^-) for IBU. Subsequent tests with moderately higher
44 concentrations of AO7 ($50 \text{ mg} \cdot \text{L}^{-1}$) showed even higher adsorption capacities, exceeding
45 $340 \text{ mg} \cdot \text{g}^{-1}$. These results demonstrate that the optimized UiO-66 structure prepared in
46 this study exhibits high-performance adsorption capabilities for the removal of anionic
47 pollutants from aqueous media, thereby expanding the knowledge on the use of Zr-based
48 MOFs for water remediation.

49

50 **KEYWORDS:** Metal-organic frameworks; UiO-66; organic dyes; non-steroidal anti-
51 inflammatory drugs; adsorption.

52

53 **1. INTRODUCTION**

54

55 Metal-organic frameworks (MOFs) have received much attention in the past few decades
56 due to their promising application in different fields, including adsorption (Pedro H M
57 Andrade et al., 2022; Liu et al., 2021b; Madumo et al., 2023; Oladoye et al., 2021; Zango
58 et al., 2021), gas separation/storage (Basu et al., 2011; Hu et al., 2014; Ren et al., 2014;
59 Xie et al., 2018), membrane separation (Deng et al., 2021; Fang et al., 2020), sensing
60 (Koo et al., 2019; Li et al., 2022), drug delivery (Della Rocca et al., 2011; Gordon et al.,
61 2015), and catalysis (Pedro H. M. Andrade et al., 2022; Du et al., 2020; Liu et al., 2023;
62 Man et al., 2022; Rao et al., 2023; Rimoldi et al., 2017). The success of these materials
63 lies in their unique advantages, including very high porosity and specific surface area,
64 controllable pore size, tunable pore surface, and low density (Cao et al., 2021; Furukawa
65 et al., 2010; Oladoye et al., 2021; Zhou et al., 2012). These materials have a highly
66 interconnected three-dimensional pore structure, resulting in specific surface areas of up
67 to several thousand $\text{m}^2\cdot\text{g}^{-1}$ (Farha et al., 2012). They can be constructed from two
68 counterparts, namely secondary building units (SBUs) and linkers (Tranchemontagne et
69 al., 2009). SBUs are inorganic clusters containing one or more metal ions coordinated by
70 oxygen or nitrogen and connected by linkers (Butova et al., 2021). MOFs can be easily
71 modified by incorporating chemical groups into their structure and changing their surface
72 chemistry. Among the promising applications of MOFs, adsorption deserves to be
73 highlighted. Contaminants such as organic dyes, pharmaceuticals, and personal care
74 products have attracted considerable attention in recent years due to their harmful effects

75 on humans and wildlife, their high stability against natural degradation, and the difficulty
76 of removal in conventional water treatment plants (Drumond Chequer et al., 2013; Lin et
77 al., 2018; Rozada et al., 2003).

78

79 Several strategies have been used for treating wastewaters contaminated with organic
80 pollutants, including ozonation (Wang and Chen, 2020), electrochemical oxidation
81 (Martínez-Huitile and Panizza, 2018), photocatalysis (Gonçalves et al., 2019; Palhares et
82 al., 2020), filtration (Isawi, 2019; Lin et al., 2023), and adsorption (Dey et al., 2019; Lin
83 et al., 2023). Among these, adsorption has been considered a promising approach for
84 removing these and other pollutants due to its low environmental impact, ease of
85 operation, low cost, and high efficiency (Huang et al., 2022; Liu et al., 2021a, 2021b;
86 Wang et al., 2018).

87

88 The use of tetravalent metals and dicarboxylate ligands in MOFs is a relatively recent
89 development. First reported in 2008, UiO-66 is a zirconium-based MOF with cubic
90 symmetry and a three-dimensional pore system (Butova et al., 2019; Cavka et al., 2008).
91 This material is known for its good thermal and chemical stability, allowing it to
92 withstand adverse conditions without compromising its structural integrity. Although this
93 MOF has been tested in different applications, such works are generally based on standard
94 routes and barely investigate the influence of synthesis conditions on the structure and
95 properties of the prepared materials (Bambalaza et al., 2018; Bi et al., 2022; Castarlenas
96 et al., 2017; Chen et al., 2017; Dinh et al., 2021; Embaby et al., 2018; Li et al., 2020;
97 Nagarjun et al., 2021; Zhang et al., 2020, 1998). As far as we know, only a few works
98 have evaluated to some extent the influence of the synthesis route on the structure and
99 adsorption behavior of UiO-66 (Cao et al., 2021; Jrad et al., 2022; Qiu et al., 2017; Zhang

100 et al., 2017). Furthermore, only a few synthesis conditions were evaluated in these studies,
101 indicating the need for additional research to fully understand the structural parameters
102 that impact the adsorption behavior of this MOF. Therefore, this study contributes to a
103 better understanding of the correlation between the synthesis conditions, structure and
104 adsorption properties of UiO-66-based materials. We show here that depending on the
105 type and concentration of the additive used, as well as the relative amount of solvent,
106 structures with different types and degrees of defects can be produced, resulting in
107 different adsorption properties towards anionic and cationic molecules.

108

109 In this work, we investigated the structure and adsorption behavior of UiO-66 samples
110 prepared by a facile solvothermal route. The synthesis conditions were varied aiming to
111 obtain specimens with different structures and properties. Organic pollutants such as dyes
112 (acid orange 7, AO7, and methylene blue, MB) and a non-steroidal anti-inflammatory
113 drug (ibuprofen, IBU) were used in the adsorption tests. As mentioned earlier, these are
114 contaminants of great concern in recent years. The Lagergren kinetic model was
115 employed for evaluating the adsorption behavior of the tested samples. These materials
116 were examined by X-ray powder diffraction (XRD), N₂ sorption, thermogravimetry (TG),
117 and transmission electron microscopy (TEM).

118

119 **2. MATERIALS AND METHODS**

120

121 The following materials were used in this study as received and without further
122 purification: zirconium tetrachloride (ZrCl₄ / Aldrich / ≥ 99.5%), terephthalic acid
123 (H₂BDC / Aldrich / 98%), N,N-Dimethylformamide (DMF / Exodo / ≥ 99.8%),
124 hydrochloric acid (HCl / Vetec / 37%), glacial acetic acid (HAc / Synth / ≥ 99.7%),

125 absolute ethanol (EtOH / Synth / $\geq 99.5\%$), and deionized Milli-Q water. For the
126 adsorption tests, acid orange 7 (AO7 / Sigma-Aldrich), methylene blue (MB / Synth), and
127 ibuprofen (IBU / Florian Pharmaceutical Supplies, Brazil) were used as the pollutants.

128

129 **2.1 MOF SYNTHESIS**

130

131 The UiO-66 samples were synthesized using a modified protocol of the standard
132 procedure described by Cavka *et al.* (Cavka et al., 2008). Typically, ZrCl₄ (1.6 mmol)
133 and H₂BDC (1.6 mmol) were initially mixed with DMF (40 mL). ZrCl₄, H₂BDC, and
134 DMF acted as the metal precursor, organic linker, and solvent, respectively. H₂O, HCl,
135 or HAc solutions (40 mL of DMF) were subsequently added to the previously prepared
136 solution. The effect of these additives on the structural properties and adsorption behavior
137 of the prepared MOFs was investigated. The additive/Zr molar ratio was adjusted between
138 0 and 150. To avoid overly acidic solutions and minimize the influence of large amounts
139 of water added to the reaction media, the molar ratio of additive/Zr was limited to 33
140 when HCl (37 wt%) was used. The as-obtained solutions were poured into a Teflon-lined
141 stainless-steel autoclave and kept at 120 °C for 24 h. After cooling to room temperature,
142 the obtained crystalline material was washed twice with DMF and then with EtOH. This
143 powder was subsequently sonicated for 30 min in EtOH (50 mL) before drying and finally
144 activated in air at 100 °C. The prepared materials were designated as UiO-66 (X_Y),
145 where X is associated with the additive/linker molar ratio and Y corresponds to the
146 additive used (H₂O, HCl, or HAc). For reference purposes, an additive-free sample was
147 prepared and referred to as UiO-66. In addition, another reference sample was synthesized
148 by reproducing the methodology described by Katz *et al.* (Katz et al., 2013), here
149 designated as UiO-66 (22_HCl_Katz) due to the HCl/Zr molar ratio used. This synthesis
150 method has become a standard in many other studies because it has been shown to

151 produce MOFs with high specific surface areas (about $1580 \text{ m}^2 \cdot \text{g}^{-1}$) and high adsorption
152 capacity (Katz et al., 2013; Zhang et al., 2017).

153

154 Samples were also obtained by increasing the concentration of metal precursor and
155 organic linker relative to the solvent content by a factor of five, resulting in higher yields
156 and more uniform crystal size. In this case, 8.0 mmol of ZrCl_4 and 8.0 mmol of H_2BDC
157 were initially mixed with 40 mL of DMF. The synthesis procedure used to prepare these
158 specimens is similar to that reported before. Samples obtained by this method were
159 labeled with the term “5×”. As discussed later, the addition of water provided an optimal
160 compromise between desirable structural properties, adsorption behavior, and feasibility.
161 For this reason, these samples were obtained using H_2O as the additive. In these highly
162 concentrated reaction media, another Zr-based MOF could be obtained in the absence of
163 an additive, namely MIL-140A (Guillerm et al., 2012); it has been reported that this
164 framework forms a monoclinic phase with a one-dimensional pore system (Butova et al.,
165 2019; Guillerm et al., 2012).

166

167 **2.2 CHARACTERIZATIONS**

168

169 X-ray powder diffraction (XRD) was conducted on a Philips-PANalytical PW1710
170 diffractometer at a scan rate of $0.03^\circ \cdot \text{s}^{-1}$, using CuK_α as the radiation source ($\lambda = 1.54 \text{ \AA}$).
171 N_2 sorption tests were conducted at -196°C on a BELSORP-max analyzer using samples
172 outgassed under vacuum at 100°C for 12 h. The specific surface area (SSA) was evaluated
173 by the multipoint BET (Brunauer-Emmett-Teller) model following the consistency
174 criteria (Ambroz et al., 2018; Guillerm et al., 2012). The non-local density functional
175 theory (NLDFT) and Barrett-Joyner-Halenda (BJH) method were employed to evaluate

176 the pore size distribution of the examined materials. The microporosity and mesoporosity
177 fractions of the tested samples were evaluated from Eq. (1) and (2), where V_{micro} , V_{meso} ,
178 and V_{total} represent, respectively, the micropore, mesopore, and total pore volumes ($\text{cm}^3 \cdot \text{g}^{-1}$).
179 ¹).

180

$$181 \quad \text{Microporosity} = \frac{V_{\text{micro}}}{V_{\text{total}}} \quad (1)$$

182

$$183 \quad \text{Mesoporosity} = \frac{V_{\text{meso}}}{V_{\text{total}}} \quad (2)$$

184

185 Thermogravimetry (TG) was performed on an Exstar 7200 thermal analyzer at a heating
186 rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and under N_2 flow ($20 \text{ mL} \cdot \text{min}^{-1}$). Transmission electron microscopy
187 (TEM) was conducted on an FEI Tecnai G2-20 SuperTwin microscope at an accelerating
188 voltage of 200 kV. The samples used in these tests were previously dispersed in absolute
189 ethanol and sonicated at room temperature for 5 min. The as-obtained suspensions were
190 dripped on carbon-coated grids (Holey Carbon) and then air-dried at room temperature.

191

192 **2.3 ADSORPTION TESTS**

193

194 Batch adsorption tests were carried out at room temperature using aqueous solutions
195 containing AO7, MB, or IBU. The adsorbent loading in these solutions was initially kept
196 constant at $200 \text{ mg} \cdot \text{L}^{-1}$, while the concentration of AO7, MB, and IBU was set at $20 \text{ mg} \cdot \text{L}^{-1}$,
197 unless otherwise specified. The initial pH of these aqueous solutions was about 5 and
198 remained nearly constant during the adsorption tests. The adsorption behavior of the
199 samples prepared in this study was evaluated using the Lagergren kinetic model. The

200 pseudo-nth-order kinetic law of Lagergren is expressed in Eq. (3), where k_n represents
 201 the rate constant for the nth-order adsorption ($\text{mg.g}^{-1}.\text{min}^{-1}$), q_e is the uptake capacity at
 202 equilibrium (mg.g^{-1}), and q_t is the adsorption capacity (mg.g^{-1}) at time t (min^{-1}) (Ho and
 203 McKay, 1998).

204

$$205 \quad \frac{dq_t}{dt} = k_n(q_e - q_t)^n \quad (3)$$

206

207 The integration of Eq. (3) from $t = 0$ and $t = t$ ($q_0 = 0$ and $q_t = q_t$) leads to Eq. (4) for the
 208 pseudo-second-order ($n = 2$) law. This model has been effectively used to describe
 209 adsorption systems similar to the one studied in this work (Guo et al., 2015; Li et al.,
 210 2018; Lin et al., 2018; Qiu et al., 2017).

211

$$212 \quad q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

213

214 Aliquots collected from these solutions after the adsorption step were centrifuged at 5000
 215 rpm for 10 min. The particle-free supernatant was then transferred to quartz cuvettes and
 216 examined by Ultraviolet-Visible (UV-Vis) spectroscopy on a Shimadzu UV-2600
 217 spectrometer at a resolution of 1 nm. The light absorption at 193 nm, 484 nm, and 664
 218 nm was used as a reference for IBU, AO7, and MB, respectively. The uptake of these
 219 pollutants on the prepared adsorbents ($q_t - \text{mg.g}^{-1}$) was calculated from Eq. (5), where C_0
 220 and C_t represent the initial concentration ($t_0 = 0$) and concentration at time t (mg.L^{-1}), V
 221 is the solution volume (L), and m is the adsorbent mass (g). The removal efficiency ($R -$
 222 %) was determined from Eq. (6), where C_e represents the concentration at equilibrium (t
 223 = t_e).

224

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (5)$$

226

$$R = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (6)$$

228

229 3. RESULTS AND DISCUSSION

230

231 3.1 INFLUENCE OF H₂O, HCl, HAc ADDITIVES

232

233 - STRUCTURAL CHARACTERIZATION

234

235 The XRD patterns and TEM micrographs obtained for UiO-66 samples are shown in Fig.
236 1 and 2. The XRD pattern of the UiO-66 reference and the other samples show a high
237 degree of similarity, indicating that these materials have similar crystalline structures.
238 UiO-66 has particles in the size range of 120-180 nm according to TEM images. In
239 general, the higher the amount of H₂O used, the smaller the particle size of the prepared
240 sample; UiO-66 (10_H₂O), UiO-66 (50_H₂O), and UiO-66 (150_H₂O) have particles in
241 the range of 30-50 nm, 15-25 nm, and 8-12 nm, respectively. This behavior is related to
242 the fast nucleation rate of Zr₆O₄(OH)₄ clusters (SBUs) when high concentrations of H₂O
243 are used, which favors the formation of the UiO-66 framework (Ragon et al., 2014;
244 Schaate et al., 2011). On the one hand, the addition of HCl up to 11 eq. decreased the
245 particle size of the prepared MOF; this behavior can also be observed from the broadening
246 of the XRD peak at $2\theta \approx 7.3^\circ$ when UiO-66 (2.2_HCl) and UiO-66 (11_HCl) are
247 compared to UiO-66. On the other hand, further additions of this acid caused a dramatic
248 increase in particle size. This seemingly contradictory behavior may be due to the

249 combined effect of the pH decrease and the presence of water in the HCl solution (37
250 wt.% purity). At low pH, the nucleation rate of UiO-66 is slowed down because the
251 deprotonation of H₂BDC ($pK_a = 3.54$) is inhibited (Ding et al., 2019). However, as
252 discussed earlier, the addition of water has the opposite effect, favoring the nucleation of
253 metal clusters. Thus, HCl has a variable effect on the crystallite size of the prepared MOFs
254 depending on the concentration used. This controversial behavior of HCl has also been
255 discussed elsewhere (Ragon et al., 2014). The addition of either H₂O or HCl caused a loss
256 of the octahedral shape commonly observed for UiO-66 crystals (Fig. 2b-2e). The same
257 behavior was not observed for HAc and the addition of this modulator up to 150 eq.
258 resulted in large octahedral crystals of about 415 nm in size (Fig. 2f). Similar behavior
259 has also been reported in other studies (Bueken et al., 2017; Ragon et al., 2014; Schaate
260 et al., 2011). The peak marked with an asterisk in the XRD patterns displayed in Fig. 1c
261 is associated with a minor phase of unknown origin observed in the HAc-derived samples.
262

263 Table 1 brings the textural properties obtained in the N₂ sorption tests (Fig. S1). UiO-66
264 has a microporous structure (microporosity = 0.9), SSA = 948 m².g⁻¹, and V_{total} =
265 0.41 cm³.g⁻¹. These values are in agreement with those described elsewhere (Guillerm et
266 al., 2012; Hao et al., 2018). As a general trend, the use of the different additives slightly
267 expanded the typical micropore structure of the UiO-66 framework and increased the
268 mesopore volume (see NLDFT and BJH in Fig. S1). It can be observed that the use of
269 H₂O was more effective in creating mesoporosity, which can be related to the formation
270 of smaller crystals as discussed previously. This can be clearly seen by the formation of
271 hysteresis loops in the sorption isotherms and BJH distribution. The use of H₂O at 10 eq.
272 caused a dramatic increase in SSA to 1255 m².g⁻¹ and V_{total} to 0.64 cm³.g⁻¹. These
273 structural changes were accompanied by an increase in the mesoporosity from 0.10 to

274 0.22. Further additions of H₂O at 50 eq. or 150 eq. caused an increase in mesoporosity
275 fraction to about 0.8, but a decrease in SSA to 831 m².g⁻¹ and 782 m².g⁻¹. The higher
276 mesoporosity of UiO-66 (50_H₂O) and UiO-66 (150_H₂O) compared to UiO-66 and
277 UiO-66 (10_H₂O) can also be observed in the N₂ sorption isotherms (Fig. S1), as
278 evidenced by wider hysteresis loops. It has been reported that the hysteresis loop is due
279 to the capillary condensation of N₂ in mesopores (Thommes et al., 2015). This increase
280 in mesoporosity was accompanied by an increase in V_{total} to 1.42 cm³.g⁻¹ and 0.90 cm³.g⁻¹,
281 respectively. The use of HAc and HCl at 10 eq. and 11 eq., respectively, decreased the
282 microporosity of UiO-66 from 0.90 to 0.80. Nonetheless, further additions of these acids
283 increase the microporosity and SSA of this MOF, reaching values above 1300 m².g⁻¹.

284

285 From the results described so far, it can be observed that the preparation of UiO-66 MOFs
286 with small crystallites leads to samples with low microporosity and lower SSA. On the
287 other hand, specimens with large crystallites also have high SSA. This trend was observed
288 for all the additives used in this study. For instance, adding only 10 eq. of H₂O leads to
289 samples with about 40 nm crystal size and 1255 m².g⁻¹. Increasing this concentration to
290 50 eq. or 150 eq. results in the formation of materials with crystallites of 20 nm and 10
291 nm, respectively. The resulting samples have SSA of 831 m².g⁻¹ and 782 m².g⁻¹,
292 respectively. In the case of HCl and HAc, a higher amount of additive results in an
293 increased SSA. The high SSA of UiO-66 (22_HCl_Katz) has been assigned to the
294 presence of defects related to missing linkers in the MOF structure; Katz *et al.* (Katz et
295 al., 2013) estimated that about 1/3 of the linkers are missing in this material. The same
296 reasoning can be applied when water is used as an additive, where hydroxyl groups and
297 Cl⁻ from the ZrCl₄ precursor can partially replace the BDC linkers (Shearer et al., 2014).
298 Achieving high SSA requires the controlled formation of defects while maintaining the

299 integrity of the framework. However, the use of large amounts of water is not effective
300 for this purpose. Finally, it has been argued that the high SSA obtained with the addition
301 of HAc is more likely related to missing cluster defects (Shearer et al., 2016).

302

303 - ADSORPTION TESTS

304

305 AO7 was initially used as a contaminant in adsorption tests on UiO-66 samples prepared
306 with various additives. The pH remained stable at about 5 and no significant changes were
307 observed throughout the experiments. Table 2 summarizes the evaluated adsorption rate
308 (k_2) and uptake capacity (q_e) based on the adsorption curves obtained (Fig. S2). It can be
309 observed that the pseudo-second-order kinetic model fitted well to the experimental data,
310 displaying a goodness-of-fit (R^2) close to 1. In general, the use of H₂O, HCl, or HAc had
311 a positive effect on the adsorption behavior of UiO-66. As mentioned before, these
312 additives can cause the formation of defects such as missing linkers and missing clusters
313 in the MOF structure, which in turn can increase the total pore volume and improve the
314 adsorption performance. As it can be noticed, such an improvement was not observed for
315 UiO-66 (150_HAc) because this material showed a lower uptake capacity than UiO-66
316 (51.8 mg.g^{-1} vs. 80.2 mg.g^{-1}), despite having faster adsorption kinetics ($1.18 \text{ mg.g}^{-1}.\text{min}^{-1}$
317 vs. $0.54 \text{ mg.g}^{-1}.\text{min}^{-1}$). This result could be considered unexpected since
318 UiO-66 (150_HAc) is the sample with the highest SSA among those obtained in this work
319 ($1356 \text{ m}^2.\text{g}^{-1}$). However, as mentioned earlier, the use of HAc is often associated with the
320 presence of missing cluster defects in the MOF structure. According to Zhang *et al.*
321 (Zhang et al., 2017), zirconium ions act as open active sites and can coordinate with the
322 sulfonate groups contained in AO7 through Lewis acid-base interactions. Therefore, the
323 decrease in adsorption capacity observed in samples prepared with higher amounts of

324 HAc can be attributed to the presence of missing Zr clusters, leading to a reduced number
325 of active sites available for AO7 adsorption.

326

327 Zeta potential and thermogravimetric (TG) tests were performed on selected samples
328 (Fig. S3) to validate the adsorption mechanisms. The results were consistent with the
329 previous observation, indicating that the use of HAc is more likely to be associated with
330 the generation of missing cluster defects in the UiO-66 structure than with missing linker
331 defects. On the other hand, the use of H₂O and HCl at 10 eq. and 33 eq. caused a lack of
332 linkers in the MOF framework, which positively affected their adsorption behavior due
333 to the presence of open active sites. In the UiO-66/AO7 system, it was observed that
334 higher positive zeta potentials did not always correlate with increased adsorption of the
335 anionic AO7, contrary to what might have been expected. Again, it was expected that
336 UiO-66 (150_HAc) would have the highest adsorption capacity, but this was not
337 observed. Thus, both the TG and zeta potential results confirm that the primary adsorption
338 mechanism is based on more specific interactions than just electrostatic interactions. In
339 this case, AO7 coordinates with the readily accessible Zr-cluster, facilitated by the
340 presence of missing linker defects, through Lewis acid-base interactions (Zhang et al.,
341 2017).

342

343 The most promising adsorption behavior was observed for samples prepared with either
344 low amounts of H₂O (up to 50 eq.) or high additions of HCl (above 11 eq.). In both cases,
345 the pollutant was nearly completely removed from the solution after 180 min of
346 adsorption. UiO-66 (10_H₂O) and UiO-66 (33_HCl) were able to remove about 95% of
347 AO7 in the first 60 min of adsorption. Among the samples prepared with H₂O, it is worth
348 highlighting that UiO-66 (50_H₂O) had faster adsorption kinetics than UiO-66 (10_H₂O)

349 ($5.27 \times 10^{-3} \text{ mg.g}^{-1}.\text{min}^{-1}$ vs. $2.47 \times 10^{-3} \text{ mg.g}^{-1}.\text{min}^{-1}$), even though the latter exhibited a
350 higher adsorption capacity (96.3 mg.g^{-1} vs. 101 mg.g^{-1}). This result may be due to the
351 large difference in the pore structure of these samples (Table 1). The pore volume and
352 mesoporosity assessed for UiO-66 (10_H₂O) and UiO-66 (50_H₂O) were $0.64 \text{ cm}^3.\text{g}^{-1}$
353 and $1.42 \text{ cm}^3.\text{g}^{-1}$, 0.22 and 0.80, respectively (Table 1). On the other hand,
354 UiO-66 (10_H₂O) displayed a higher SSA ($1255 \text{ m}^2.\text{g}^{-1}$ vs. $831 \text{ m}^2.\text{g}^{-1}$). These results
355 strongly support the correlation between the adsorption kinetics and the pollutant
356 diffusion within the porous structure of the MOF, which in turn is influenced by the
357 presence of defects. Moreover, the adsorption capacity is influenced not only by the
358 accessibility of the SBUs (which serve as specific sites for the adsorption of anionic
359 species), but also by the abundance of these active sites, which, as previously discussed,
360 is related to both a high specific surface area and the presence of missing linker defects.

361

362 **3.2 INFLUENCE OF ZrCl₄ and H₂BDC CONCENTRATION**

363

364 **- STRUCTURAL CHARACTERIZATION**

365

366 Fig. 3a shows XRD patterns of samples prepared with a 5-fold increase in metal precursor
367 and organic linker concentration relative to the solvent amount. The XRD patterns of
368 MIL-140A and UiO-66 are also shown for comparison purposes. Although UiO-66 and
369 MIL-140A have similar XRD patterns, the latter has its main peaks shifted to larger 2θ
370 values (Butova et al., 2020). The coexistence of these MOFs in MIL-140A can be noted
371 in Fig. 3b, in which rectangular plates characteristic of the former and octahedral crystals
372 typical of the latter are observed (Butova et al., 2020). The addition of H₂O led to
373 specimens in which UiO-66 is the only phase present. As already observed, increasing

374 the water concentration decreases the particle size of the prepared MOF (Fig. 3c to 3e).
375 This behavior can also be observed in the XRD patterns displayed in Fig. 3a, where the
376 broadening of the main peak at $2\theta \approx 7.3^\circ$ occurs with increasing the water concentration.
377 The addition of H₂O at concentrations up to 10 eq. led to samples with well-resolved
378 XRD patterns, while further increases in this concentration resulted in specimens with
379 poorly-resolved peaks. Once again, water appears to play a key role in the crystallization
380 of UiO-66.

381

382 Fig. 4 shows the N₂ sorption isotherms and NLDFIT pore size distributions of the samples
383 prepared after increasing the concentration of ZrCl₄ and H₂BDC. Table 3 summarizes the
384 textural parameters obtained from these tests. The theoretical SSA calculated by other
385 authors for MIL-140A and UiO-66 were 360 m².g⁻¹ and 1125 m².g⁻¹, respectively (Butova
386 et al., 2020). The values obtained in this work were 597 m².g⁻¹ and 948 m².g⁻¹. This
387 difference can be due to the presence of structural defects in these samples, in addition to
388 the existence of additional phases in the MIL-140A sample (Fig. 3a and 3b). The addition
389 up to 10 eq. of water increased the microporosity of the prepared samples (Table 3) and
390 shifted their pore size distribution to larger sizes (Fig. 4b). As a result, UiO-66 (5_H₂O)
391 (5×) and UiO-66 (10_H₂O) (5×) displayed SSA of 1280 m².g⁻¹ and 1241 m².g⁻¹,
392 respectively. The use of water at higher concentrations (i.e., 50 eq. or 150 eq.) resulted in
393 samples with higher mesoporosities (up to 0.78) but much lower SSA (as low as 567 m².g⁻¹
394 ¹). From Fig. 4b it can also be seen that the micropores, which are the typical tetrahedral
395 and octahedral cages, are enlarged for all water-synthesized samples compared to the
396 standard UiO-66. In particular, the UiO-66 (5_H₂O) (5×) sample exhibited the most
397 significant expansion of the tetrahedral cage, leading to enhanced accessibility of the

398 SBUs to AO7 molecules.. This behavior is discussed in more detail in the following
399 sections.

400

401 - ADSORPTION OF AO7

402

403 The adsorption behavior of the samples prepared with a high concentration of precursors
404 is summarized in Table 4 (Fig. S4). MIL-140A had a lower uptake capacity (q_e) than UiO-
405 66, which can be related to its smaller micropores, SSA, and V_{total} of the former compared
406 to the latter ($597 \text{ m}^2.\text{g}^{-1}$ vs. $948 \text{ m}^2.\text{g}^{-1}$, and $0.31 \text{ cm}^3.\text{g}^{-1}$ vs. $0.41 \text{ cm}^3.\text{g}^{-1}$). This could result
407 in fewer adsorption sites on the MIL-140A surface, which could reduce its adsorption
408 performance. Regarding the UiO-66 materials obtained with water, their adsorption
409 behavior is positively influenced by increasing the precursor concentration as long as the
410 water addition is maintained up to 10 equivalents. UiO-66 (5_H₂O) (5×) was the sample
411 with the best adsorption performance, displaying a much higher adsorption rate (0.078
412 $\text{g}.\text{mg}^{-1}.\text{min}^{-1}$). This material was able to remove 97% of AO7 after 5 min of adsorption,
413 and 99% after 15 min. It is worth recalling that this MOF exhibited a very high SSA (1280
414 $\text{m}^2.\text{g}^{-1}$) and the largest expansion of the tetrahedral cage to about 1.1 nm (Fig. 4b), which
415 was attributed to the presence of missing linker defects. Considering the dimensions of
416 the AO7 molecule ($1.57 \times 1.00 \times 0.54 \text{ nm}^3$) (Zhao et al., 2013), also shown in Fig. S4), it
417 can be inferred that the observed expansion allows the longitudinal access of the dye
418 molecules into the small cages. This in turn not only increases the mobility of the organic
419 molecules within the microporous structure, but also increases the number of accessible
420 adsorption sites (based on Lewis acid-base interactions). The combination of both
421 features explains the high adsorption efficiency of the sample UiO-66 (5_H₂O) (5×).
422 Besides, it showed a well-resolved XRD pattern with sharp peaks (Fig. 3a), which

423 suggests that it has a highly crystalline structure. The same trend was not observed for
424 UiO-66 (50_H₂O) (5×) and UiO-66 (150_H₂O) (5×). These samples had a sharp decrease
425 in SSA, which is consistent with their poor adsorption performance.

426

427 Since UiO-66 (5_H₂O) (5×) showed the most promising adsorption behavior, additional
428 tests were performed with this sample. In these tests, the concentration of adsorbent in
429 the starting solution was systematically varied, from 50 mg.L⁻¹ to 200 mg.L⁻¹ (Table 5
430 and Fig. S5). Additionally, the dye concentration was increased from 20 mg.L⁻¹ to
431 50 mg.L⁻¹. When used at a concentration of 50 mg.L⁻¹, UiO-66 (5_H₂O) (5×) showed an
432 outstanding adsorption capacity of more than 300 mg.g⁻¹ after only 60 min. Notably, this
433 performance exceeds that of previously reported studies, especially under similar test
434 conditions (Yoon et al., 2019; Zhang et al., 2017).

435

436 **3.3 SELECTIVE ADSORPTION OF ANIONIC SPECIES**

437

438 Several studies have suggested that these organic contaminants are adsorbed onto the
439 MOF's surface through a combination of hydrophobic, π - π , electrostatic, and hydrogen
440 bonding interactions (Cao et al., 2021; Chen et al., 2017; Oladoye et al., 2021; Panda et
441 al., 2020). To further investigate the main adsorption mechanism of UiO-66 (5_H₂O)
442 (5×), it was used in adsorption tests conducted with aqueous solutions containing AO7,
443 MB, and IBU. UiO-66 was also employed in these tests for comparison purposes. Both
444 MB and AO7 are organic dyes with comparable molecular sizes of 1.63×0.79×0.40 nm³
445 and 1.57×1.00×0.54 nm³, respectively (Zhao et al., 2013). Moreover, MB is cationic
446 while AO7 is anionic. IBU, a non-steroidal anti-inflammatory drug, is a compound of
447 significant global concern (Rahman and Aziz, 2022). It is anionic and has molecular

448 dimensions significantly smaller than those of AO7 and MB ($IBU = 1.03 \times 0.52 \times$
449 0.43 nm^3 (Mestre et al., 2007)). Fig. 5 shows the adsorption behavior of UiO-66 and
450 UiO-66 (5_H₂O) (5×) as well as the structure of the different molecules tested. It can be
451 seen that the adsorption of both anionic species IBU and AO7 was greater on
452 UiO-66 (5_H₂O) (5×) compared to UiO-66, following the same trend previously
453 observed for AO7 (Table 4). However, an opposite behavior was observed for the cationic
454 MB. UiO-66 (5_H₂O) (5×) showed AO7/MB and IBU/MB selectivities of 9.6 and 8.7,
455 respectively, indicating a greater preference for AO7 and IBU adsorption over MB. These
456 selectivities are much higher compared to those obtained for UiO-66 (2.2 and 2.6,
457 respectively).

458

459 The adsorption of MB was much less pronounced compared to AO7 and IBU, suggesting
460 that electrostatic interactions may also play an important role in the adsorption
461 mechanism of these pollutants on UiO-66 when comparing oppositely charged species.
462 Figure 6 depicts the zeta potential as a function of pH for UiO-66 and UiO-66 (5_H₂O)
463 (5×). The zeta potential of these materials at pH 5 is positive and equal to $10 \pm 4 \text{ mV}$
464 (UiO-66) and $15 \pm 10 \text{ mV}$ (UiO-66 (5_H₂O) (5×)). While the adsorption mechanism of
465 different samples cannot be fully explained by the surface charge alone, as discussed in
466 the previous section (3.1 - Adsorption Tests), the consideration of the opposite charges
467 can certainly help to justify the observed adsorption differences. The positively charged
468 surface of the MOF initiates an electrostatic interaction with the guest molecules,
469 resulting in the repulsion of cationic molecules such as MB, while favoring the
470 penetration of anionic molecules such as AO7 and IBU into the microporous network.
471 Subsequently, more specific interactions can occur leading to the increased adsorption

472 capacity of anionic species as discussed above. Therefore, the greater surface positivity
473 of UiO-66 (5_H₂O) (5×) contributes to its higher selectivity compared to UiO-66.

474

475 As discussed earlier, the porous structure plays a key role in the adsorption process by
476 favoring the diffusion of target molecules into the adsorbent's pore structure, thereby
477 accelerating the adsorption process. This behavior occurs for both anionic (AO7 and IBU)
478 and cationic (MB) species, as evidenced by the increased kinetic rate constants observed
479 for UiO-66 (5_H₂O) (5×) (Fig. 5c), which has an optimized porous structure when
480 compared to that of UiO-66. Also, the adsorption behavior of UiO-66 and
481 UiO-66 (5_H₂O) (5×) was different concerning the anionic pollutants; while the
482 adsorption rate and uptake capacity of UiO-66 is higher when using IBU, the opposite is
483 observed for UiO-66 (5_H₂O) (5×) with AO7 being more adsorbed. UiO-66 exhibited
484 higher adsorption affinity for IBU, which can be attributed to the greater accessibility of
485 IBU to the active adsorption sites due to its smaller molecular size compared to AO7. On
486 the other hand, because UiO-66 (5_H₂O) (5×) has larger micropores, this effect is less
487 pronounced. In fact, its adsorption capacity is even higher for AO7, although the
488 accessibility of IBU is still higher, as suggested by its size and confirmed by the faster
489 kinetic constant. However, it is important to note that when these values are converted to
490 molar capacity, the adsorption capacity of UiO-66 (5_H₂O) (5×) would be 0.59 mmol.g⁻¹
491 for AO7 and 0.84 mmol.g⁻¹ for IBU. The values obtained are more representative
492 because adsorption occurs at a finite number of active sites. In this case, both kinetics and
493 adsorption capacity would be higher for IBU compared to AO7. The adsorption
494 differences suggested here are schematically displayed in the inset of Fig. 6.

495

496 The adsorption capacities of various adsorbents, including similar MOF structures such
497 as UiO-66 isostructures, are shown in Table 6. It can be observed that the optimized
498 sample, UiO-66 (5_H₂O) (5x), exhibits an excellent adsorption capacity towards anionic
499 pollutants even at relatively low pollutant concentrations at equilibrium (up to 33 ppm).
500 The only other studies that reported similar or higher adsorption capacities used pollutant
501 concentrations much higher than those used here, which was beyond the scope of this
502 investigation. Our optimized material shows not only a significant improvement in
503 adsorption capacity, but also a remarkable increase in adsorption selectivity. The selective
504 adsorption of AO7/MB increased from 2.2 to 9.6 compared to regular UiO-66, indicating
505 a more than 4-fold increase in selectivity.

506

507 **4. CONCLUSION**

508

509 We have shown that both crystallinity and porous structure play an important role in the
510 adsorption capacity of organic pollutants on the UiO-66 framework. It was observed that
511 as the SSA and crystallinity increased, the number of active sites for adsorption also
512 increased, resulting in higher adsorption capacity. The intrinsic microporous channels of
513 the framework were also found to be critical in facilitating the access of the adsorbate to
514 the active sites. An optimal number of defects, in the form of missing linkers, resulted in
515 expanded micropore structures with increased specific surface area and exposed cationic
516 Zr active sites. As a result, materials with higher adsorption capacity and faster kinetics
517 could be obtained. The samples that best combined these two properties were obtained
518 using small amounts of water (i.e., 5 eq. or 10 eq.) in a highly concentrated reaction
519 medium. Loading capacities of up to 341 mg.g⁻¹ for AO7 and 173 mg.g⁻¹ for IBU were
520 achieved at relatively low pollutant concentrations, which are significantly higher

521 compared to other reports. In addition to the incredibly high adsorption capacity for
522 anionic species, the optimized UiO-66 framework showed outstanding selectivity for the
523 separation of anionic and cationic species, which can be associated with the expanded
524 micropore structure and the increased zeta potential. The main adsorption mechanism
525 involves an initial electrostatic interaction that repels cationic species and restricts their
526 interaction to a few sites on the surface, while allowing anionic species to interact
527 throughout the micropore structure. Subsequently, such anionic molecules can interact
528 more specifically with the defective Zr cluster through Lewis acid-base interactions
529 involving Zr(-SO₃⁻) for AO7 and Zr(-CO₂⁻) for IBU. The AO7/MB⁺ adsorption
530 capacity ratio was remarkably high, reaching 9.6, which is more than 4 times higher than
531 that of the UiO-66 reference sample.

532

533

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535

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539

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840 TABLES

841

842 Table 1: Textural properties evaluated from the N₂ sorption.

| Sample | SSA (m ² .g ⁻¹) | V _{micro} (cm ³ .g ⁻¹) | V _{meso} (cm ³ .g ⁻¹) | V _{total} (cm ³ .g ⁻¹) | Micro- porosity (V _{micro} /V _{total}) | Meso- porosity (V _{meso} /V _{total}) |
|-------------------------------|---|---|--|---|---|---|
| UiO-66 | 948 | 0.37 | 0.04 | 0.41 | 0.90 | 0.10 |
| UiO-66 (10_H ₂ O) | 1255 | 0.50 | 0.14 | 0.64 | 0.78 | 0.22 |
| UiO-66 (50_H ₂ O) | 831 | 0.28 | 1.14 | 1.42 | 0.20 | 0.80 |
| UiO-66 (150_H ₂ O) | 782 | 0.20 | 0.70 | 0.90 | 0.22 | 0.78 |
| UiO-66 (2.2_HCl) | 593 | 0.23 | 0.12 | 0.35 | 0.66 | 0.34 |
| UiO-66 (11_HCl) | 833 | 0.33 | 0.08 | 0.41 | 0.80 | 0.20 |
| UiO-66 (22_HCl_Katz) | 1349 | 0.55 | 0.10 | 0.65 | 0.85 | 0.15 |
| UiO-66 (33_HCl) | 1292 | 0.51 | 0.07 | 0.58 | 0.88 | 0.12 |
| UiO-66 (10_HAc) | 1223 | 0.52 | 0.12 | 0.64 | 0.81 | 0.19 |
| UiO-66 (50_HAc) | 1305 | 0.58 | 0.12 | 0.70 | 0.83 | 0.17 |
| UiO-66 (150_HAc) | 1356 | 0.56 | 0.04 | 0.60 | 0.93 | 0.07 |

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846 Table 2: Summary of AO7 adsorption by various samples using pseudo-
 847 second-order kinetics, with the removal efficiency evaluated at 180 min.

| Sample | $k_2 \times 10^{-3}$ ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) | q_e ($\text{mg}\cdot\text{g}^{-1}$) | R^2 | Removal Efficiency (%) |
|-------------------------------|---|---|-------|------------------------------|
| UiO-66 | 0.54 | 80.2 | 0.97 | 75 |
| UiO-66 (10_H ₂ O) | 2.47 | 101.0 | 1.00 | 100 |
| UiO-66 (50_H ₂ O) | 5.27 | 96.3 | 1.00 | 97 |
| UiO-66 (150_H ₂ O) | 2.52 | 95.5 | 0.99 | 96 |
| UiO-66 (2.2_HCl) | 1.24 | 76.9 | 0.99 | 74 |
| UiO-66 (11_HCl) | 2.20 | 95.6 | 1.00 | 95 |
| UiO-66 (22_HCl_Katz) | 2.68 | 102.8 | 1.00 | 98 |
| UiO-66 (33_HCl) | 3.25 | 102.6 | 1.00 | 98 |
| UiO-66 (10_HAc) | 3.72 | 101.5 | 0.99 | 93 |
| UiO-66 (50_HAc) | 1.51 | 98.9 | 0.96 | 90 |
| UiO-66 (150_HAc) | 1.18 | 51.8 | 0.97 | 51 |

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851 Table 3: Textural properties of samples prepared using water as an additive
 852 at higher concentrations.

| Sample | SSA ($\text{m}^2 \cdot \text{g}^{-1}$) | V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$) | V_{meso} ($\text{cm}^3 \cdot \text{g}^{-1}$) | V_{total} ($\text{cm}^3 \cdot \text{g}^{-1}$) | Micro- porosity ($V_{\text{micro}}/V_{\text{total}}$) | Meso- porosity ($V_{\text{meso}}/V_{\text{total}}$) |
|------------------------------------|---|---|--|---|---|---|
| UiO-66 | 948 | 0.37 | 0.04 | 0.41 | 0.90 | 0.10 |
| MIL-140A | 597 | 0.24 | 0.07 | 0.31 | 0.77 | 0.23 |
| UiO-66 (5_H ₂ O) (5x) | 1280 | 0.49 | 0.04 | 0.53 | 0.92 | 0.08 |
| UiO-66 (10_H ₂ O) (5x) | 1241 | 0.47 | 0.04 | 0.51 | 0.92 | 0.08 |
| UiO-66 (50_H ₂ O) (5x) | 890 | 0.31 | 1.11 | 1.42 | 0.22 | 0.78 |
| UiO-66 (150_H ₂ O) (5x) | 567 | 0.18 | 0.22 | 0.40 | 0.45 | 0.55 |

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856 Table 4: Summary of AO7 adsorption kinetics on samples synthesized with
 857 H₂O and a 5-fold increase in precursor concentration, evaluated with pseudo-
 858 second-order kinetics, with the removal efficiency measured at 180 min.

| Sample | $k_2 \times 10^{-3}$ (g.mg ⁻¹ .min ⁻¹) | q _e (mg.g ⁻¹) | R ² | Removal Efficiency (%) |
|------------------------------------|--|---|----------------|------------------------------|
| MIL-140A | 1.56 | 57.8 | 0.97 | 58 |
| UiO-66 | 0.54 | 80.2 | 0.97 | 75 |
| UiO-66 (5_H ₂ O) (5x) | 78.31 | 102.1 | 1.00 | 100 |
| UiO-66 (10_H ₂ O) (5x) | 7.23 | 100.7 | 1.00 | 100 |
| UiO-66 (50_H ₂ O) (5x) | 2.47 | 80.3 | 0.99 | 80 |
| UiO-66 (150_H ₂ O) (5x) | 1.83 | 61.5 | 0.98 | 61 |

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863 Table 5: Summary of AO7 adsorption kinetics on UiO-66 (5_H2O) (5×)
864 optimized sample at different concentrations, using pseudo-second-order
865 kinetics and measuring removal efficiency at 180 min.

| Adsorbent concentration (mg.L⁻¹) | k₂ × 10⁻³ (g.mg⁻¹.min⁻¹) | q_e (mg.g⁻¹) | R² | Removal Efficiency (%) |
|--|---|--|----------------------|-------------------------------|
| 50 | 0.47 | 341.10 | 0.99 | 34 |
| 100 | 0.70 | 295.10 | 0.99 | 59 |
| 150 | 1.21 | 262.50 | 1.00 | 78 |
| 200 | 1.67 | 230.00 | 1.00 | 92 |

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868 Table 6: Comparison of the adsorption performance of the samples prepared
 869 in this study and others reported elsewhere.

| Adsorbent | Pollutant | Adsorption Condition C_{eq} in $mg.L^{-1}$ | Adsorption Result | Ref. |
|-------------------------------------|-----------------------|---|--|----------------------|
| | | | Q_e and Q_{max} in $mg.g^{-1}$ k_2 in $\times 10^{-3} g.mg^{-1}.min^{-1}$ | |
| UiO-66 | AO7 – | -Langmuir isotherm C_{eq} up to 230 (298K) -Kinetics – pseudo 2 nd order $C_{eq} = 28$ | - $Q_{max} = 332$ - $Q_e = 220$ ($k_2 = 0.025$) | (Zhang et al., 2017) |
| UiO-66 UiO-66 (NH ₂) | AO7 – | -Kinetics – pseudo 2 nd order $C_{eq} = 39$ -Kinetics – pseudo 2 nd order $C_{eq} = 41$ | - $Q_e = 107$ ($k_2 = N/S$) - $Q_e = 85$ ($k_2 = N/S$) | (Yoon et al., 2019) |
| UiO-66(Ce) | AO7 – MO – MB + | -Langmuir isotherm C_{eq} up to 130 -Langmuir isotherm C_{eq} up to 150 -Langmuir isotherm C_{eq} up to 160 | - $Q_{max} = 427$ - $Q_{max} = 298$ - $Q_{max} = 249$ | (Zhao and Cai, 2021) |
| UiO-66 | MO – MB + | Langmuir isotherm C_{eq} up to 500 | - $Q_{max} = 176$ - $Q_{max} = 22$ | (Yang, 2017) |
| UiO-66-P | MO – MB + | Langmuir isotherm C_{eq} up to 500 | - $Q_{max} = 3.5$ - $Q_{max} = 95$ | (Yang, 2017) |
| UiO-66 | MO – MB + | -Kinetics – pseudo 2 nd order $C_{eq} = 6$ -Kinetics – pseudo 2 nd order $C_{eq} = 7$ | - $Q_e = 70$ ($k_2 = N/S$) - $Q_e = 67$ ($k_2 = N/S$) | (Qiu et al., 2017) |
| UiO-66 (HCl) | MO – MB + | -Kinetics – pseudo 2 nd order $C_{eq} = 2$ -Kinetics – pseudo 2 nd order $C_{eq} = 17$ | - $Q_e = 85$ ($k_2 = N/S$) - $Q_e = 13$ ($k_2 = N/S$) | (Qiu et al., 2017) |

| | | | | |
|----------------------------------|-------|---|-------------------------------|-----------------------|
| UiO-66-NO ₂ | MB + | -Langmuir isotherm C_{eq} up to 160 | $Q_{max} = 41.7$ | (Dinh et al., 2021) |
| | MO – | -Langmuir isotherm C_{eq} up to 160 | $Q_{max} = 142.9$ | |
| -UiO-66 | IBU – | -Kinetics – pseudo 2 nd order $C_{eq} = 1.8$ | $Q_e = 73$ ($k_2 = 11$) | (Cao et al., 2021) |
| -D_UiO-66 | | -Kinetics – pseudo 2 nd order $C_{eq} = 0.3$ | $Q_e = 79$ ($k_2 = 558$) | |
| -UiO-66 | IBU – | -Kinetics – pseudo 2 nd order $C_{eq} = 3$ | $-Q_e = 128$ ($k_2 = 0.56$) | (Sun et al., 2019) |
| -NH ₂ -UiO-66 | | -Kinetics – pseudo 2 nd order $C_{eq} = 6.5$ | $-Q_e = 51$ ($k_2 = 0.85$) | |
| Silica | MB + | -Kinetics – pseudo 2 nd order $C_{eq} = 8$ | $-Q_e = 37$ ($k_2 = N/S$) | (Gomes et al., 2021) |
| | DIP – | -Kinetics – pseudo 2 nd order $C_{eq} = 79$ | $-Q_e = 8.5$ ($k_2 = N/S$) | |
| Activated Carbon CPAC | IBU | -Kinetics – pseudo 2 nd order $C_{eq} = 0.5$ | $Q_e = 89$ ($k_2 = 5.2$) | (Mestre et al., 2007) |
| Zeolite | MB + | -Langmuir isotherm C_{eq} up to 135(298K) | $Q_{max} = 78$ | (Brião et al., 2018) |
| | CV + | -Langmuir isotherm C_{eq} up to 185(298K) | $Q_{max} = 86$ | |
| UiO-66 (5_H ₂ O) (5x) | AO7 | -Kinetics – pseudo 2 nd order $C_{eq} = 33$ | $-Q_e = 341$ ($k_2 = 0.5$) | This work |
| | | -Kinetics – pseudo 2 nd order $C_{eq} = 20$ | $-Q_e = 295$ ($k_2 = 0.7$) | |
| | | -Kinetics – pseudo 2 nd order $C_{eq} = 0.8$ | $-Q_e = 192$ ($k_2 = 2.9$) | |
| UiO-66 (5_H ₂ O) (5x) | IBU | Kinetics – pseudo 2 nd order $C_{eq} = 2.9$ | $Q_e = 173$ ($k_2 = 4.3$) | This work |
| UiO-66 (5_H ₂ O) (5x) | MB | Kinetics – pseudo 2 nd order $C_{eq} = 18$ | $Q_e = 20$ ($k_2 = 15$) | This work |

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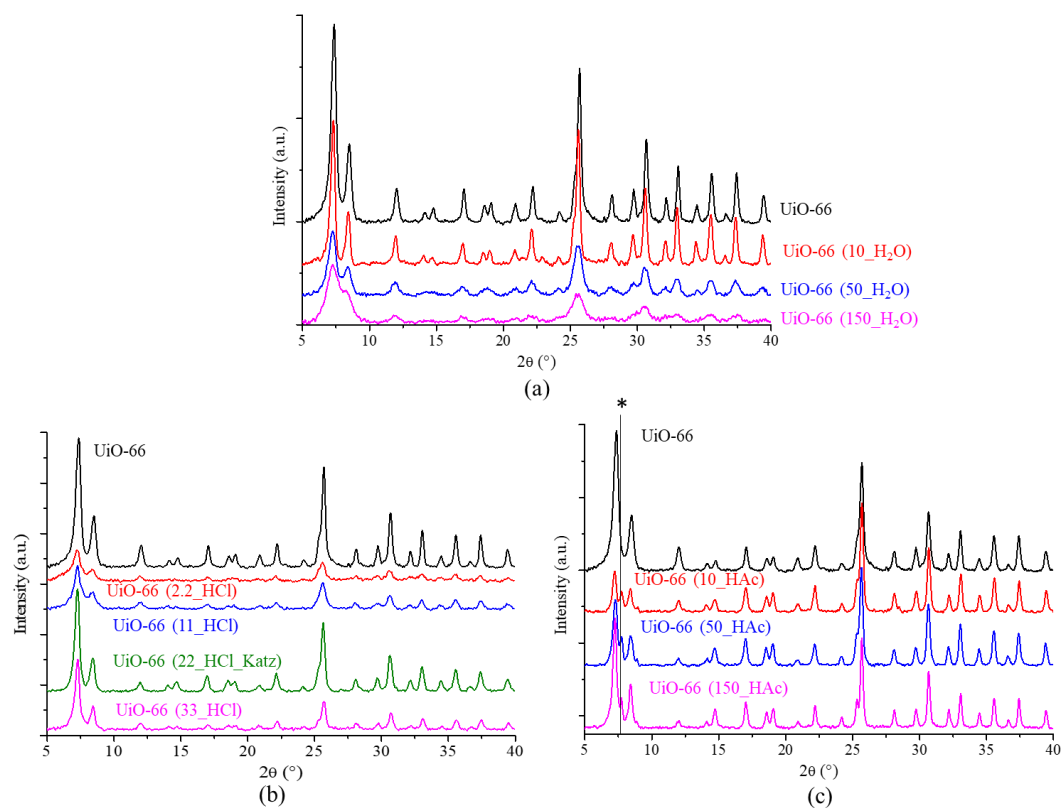
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874 FIGURES

875

876 Figure 1



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878 **Figure 1:** XRD patterns of UiO-66 specimens prepared using (a) H₂O, (b) HCl, and (c)
879 HAc as additives. The peak marked with the symbol “*” is assigned to minor phases
880 observed in the HAc-derived MOFs.

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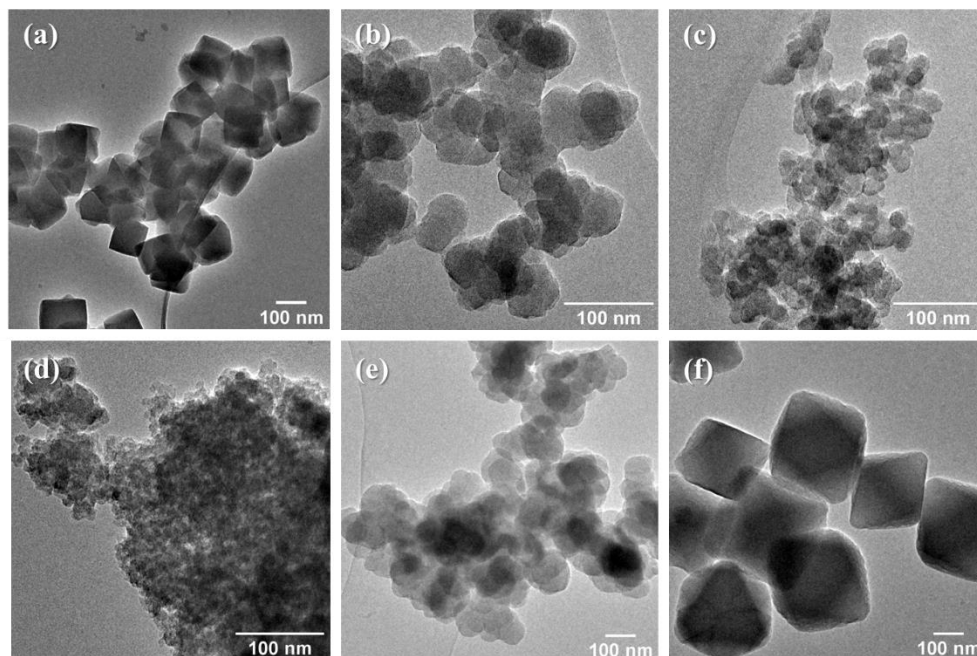
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892 **Figure 2**

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896 - **Figure 2:** TEM micrographs of UiO-66 samples obtained in this work. (a) UiO-66, (b)
897 UiO-66 (10_H₂O), (c) UiO-66 (50_H₂O), (d) UiO-66 (150_H₂O), (e) UiO-66 (33_HCl),
898 and (f) UiO-66 (150_HAc).

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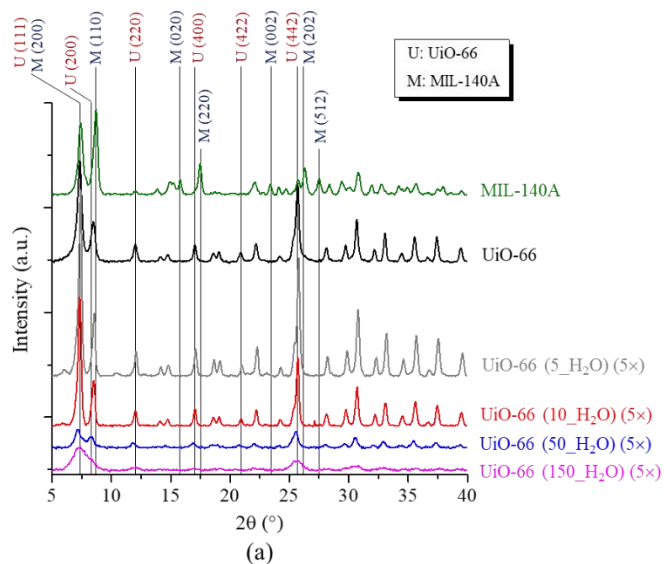
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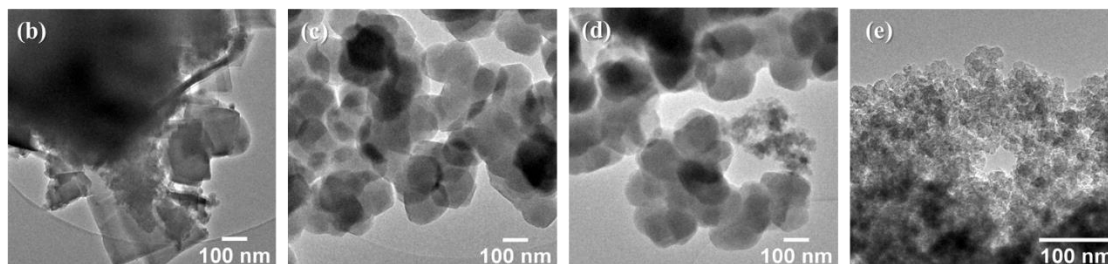
902 **Figure 3**

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(a)



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906 - **Figure 3:** (a) XRD pattern of samples obtained after a 5-fold increase in the
 907 concentration of $ZrCl_4$ and H_2BDC . The XRD patterns of UiO-66 and MIL-140A are also
 908 displayed for reference purposes. The highlighted diffraction peaks have been indexed
 909 according to the work of Butova *et al.* (Butova et al., 2020). TEM micrographs of (b)
 910 MIL-140A, (c) UiO-66 (5_H₂O) (5×), (d) UiO-66 (10_H₂O) (5×), and (e)
 911 UiO-66 (50_H₂O) (5×) are also exhibited.

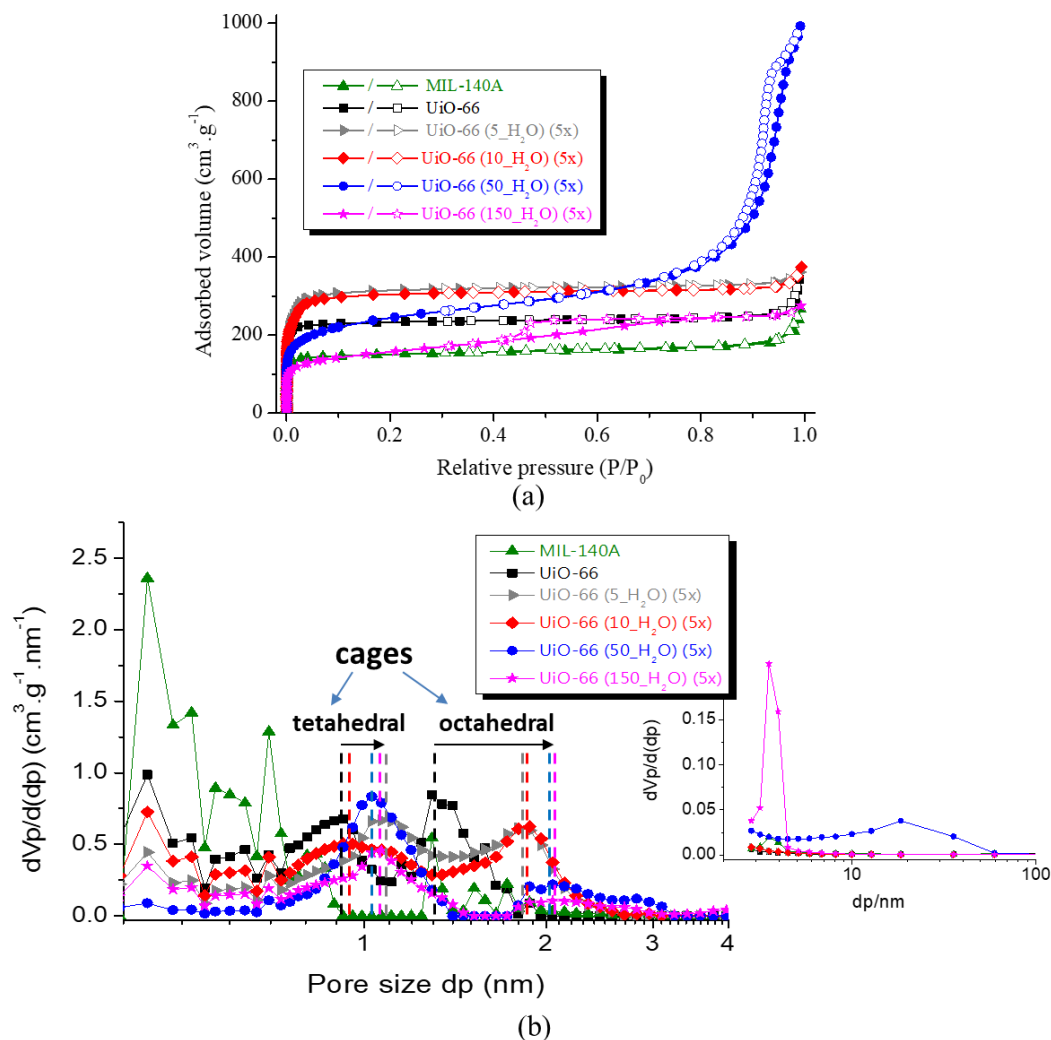
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915 **Figure 4**

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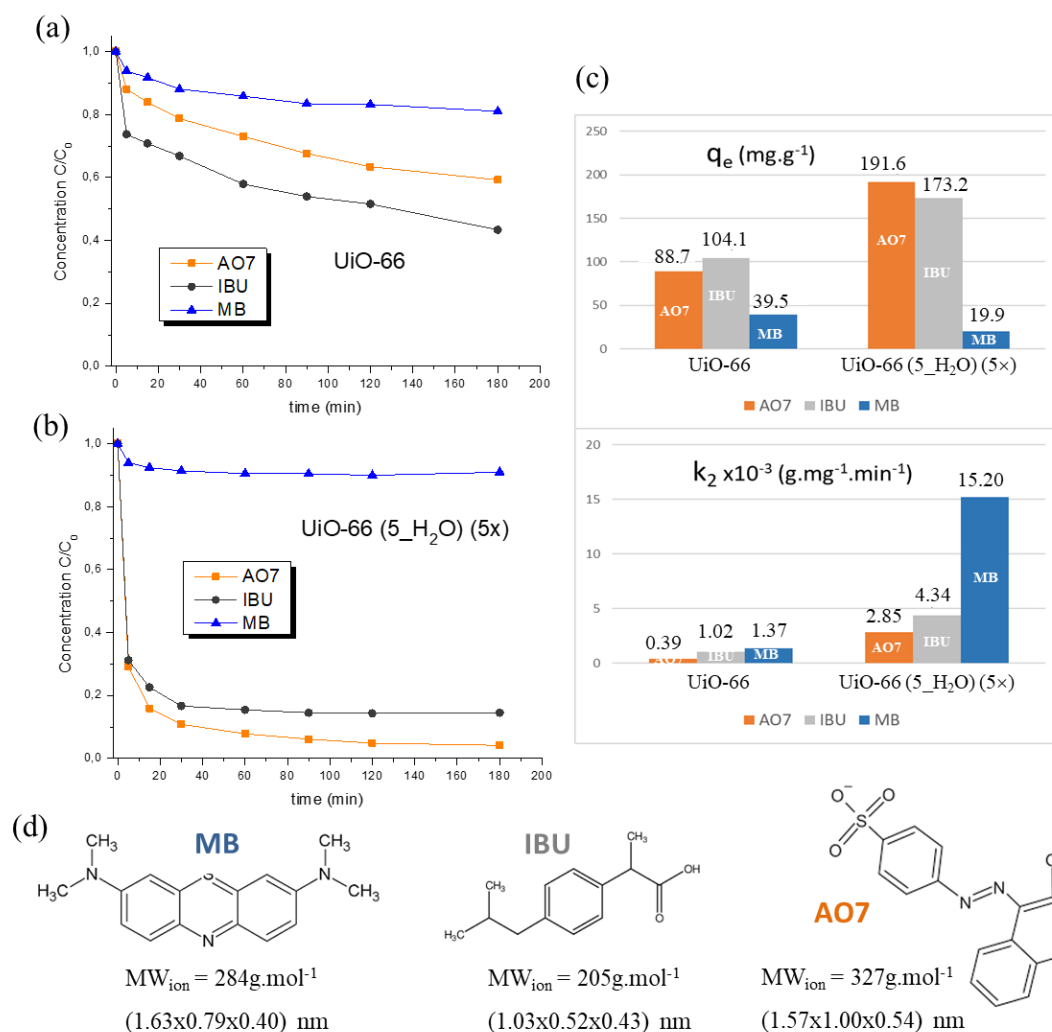
918 - **Figure 4:** (a) N₂ sorption isotherms and (b) NLDFT and BJH (inset) pore size
 919 distributions of samples obtained after a 5-fold increase in the concentration of ZrCl₄ and
 920 H₂BDC relative to DMF. The closed and open symbols are related to the adsorption and
 921 desorption branches, respectively. The data ascribed to UiO-66 and MIL-140A are also
 922 depicted for comparison purposes.

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924

925 **Figure 5**

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928 **- Figure 5:** Adsorption behavior of (a) UiO-66 and (b) UiO-66 (5_H₂O) (5x) in aqueous
 929 solutions containing AO7, IBU, and MB. The concentration of adsorbent and pollutants
 930 was kept at 100 mg.L⁻¹ and 20 mg.L⁻¹, respectively. (c) Comparison of the pseudo-second-
 931 order adsorption rate constant (k₂) and uptake capacity at equilibrium (q_e) evaluated for
 932 these MOFs. (d) Structural representations of the different pollutants used.

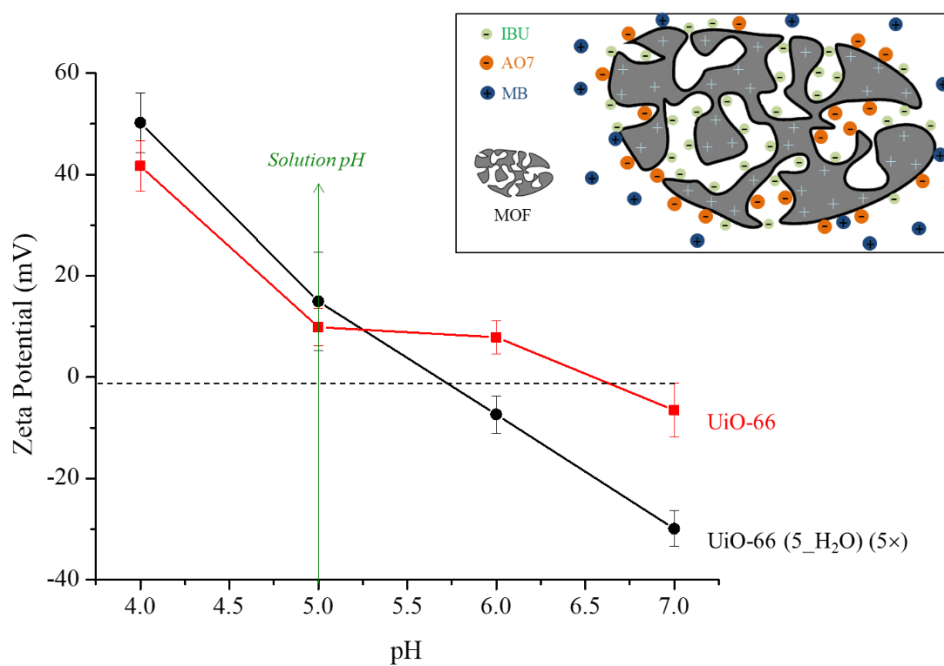
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936 **Figure 6**

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939 **- Figure 6:** Zeta potential as a function of pH for UiO-66 and UiO-66 (5_H₂O) (5×). Inset:
940 schematic representation comparing the adsorption mechanism of AO7, IBU, and MB on
941 the optimized porous structure of UiO-66 (5_H₂O) (5×).

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