

# Rapid and Efficient Removal of Carbamazepine from Water by UiO-67

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## **ABSTRACT**

Carbamazepine is a persistent contaminant detected in surface and ground waters. In this study we present the adsorptive removal of carbamazepine from water in metal-organic frameworks UiO-66 and UiO-67 in comparison with a commercial activated carbon F400. While UiO-66 was ineffective in removing carbamazepine, UiO-67 showed superior performance by removing 95% of carbamazepine from a 100 mg L<sup>-1</sup> aqueous carbamazepine solution in just 2 minutes. In contrast, it took F400 more than an hour to remove 88% of the carbamazepine under the same conditions. We further show that UiO-67 can be regenerated repeatedly with no or negligible carbamazepine removal capacity loss, which demonstrates its potential as a durable and promising adsorbent that can be used for the removal of carbamazepine from water.

## INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) are classified as emerging class of environmental contaminants due to their presence in environmental water as a result of human excretion, disposal of drugs and discharge of wastewater plant effluents.<sup>1-2</sup> The occurrence of these organic contaminants, although found in water at very low concentrations, inevitably leads to environmental pollution and adverse effects on aquatic organisms and humans.<sup>1</sup>

Carbamazepine has been extensively used as an antiepileptic and antipsychotic drug and detected in wastewater treatment effluents, surface waters, groundwater and drinking water.<sup>3</sup> It is a persistent organic compound in the environment<sup>3</sup> and toxic to the aquatic system.<sup>4-7</sup> It is resistant to biodegradation and barely removed during conventional and biological wastewater treatments.<sup>8-10</sup>

Advanced treatment technologies studied for carbamazepine removal from aqueous solution include ozonation<sup>11-12</sup>, ultrafiltration<sup>9</sup>, oxidation<sup>13</sup> and photo catalytic degradation<sup>14</sup>. Photo catalysis and ozonation generate various byproducts. The effects of these derivatives are uncertain and they can be more persistent to biological degradation.<sup>12, 14</sup> Adsorption on porous materials is considered as an alternative technique in order to remove organic contaminants from water thanks to its low cost, ease of operation and practically no risk of releasing toxic byproducts to the environment.<sup>15-16</sup> Clays,<sup>3</sup> silica-based porous materials,<sup>5, 17</sup> carbon nanotubes,<sup>6, 18-19</sup> activated carbon,<sup>20-21</sup> mesoporous silica and functionalized polymers,<sup>22</sup> zeolites<sup>23</sup> and biochar<sup>24</sup> are adsorbents which have been previously studied for carbamazepine removal from aqueous solutions with limited success.

Metal organic frameworks (MOFs) are an intriguing class of hybrid porous crystalline materials that consist of inorganic nodes and organic linkers.<sup>25</sup> Over the past several years,

MOFs have shown excellent potential as promising adsorbents for liquid phase adsorption<sup>26-28</sup> due to their high surface area and porosity and tunable pore size and chemical functionality.

MOFs have been studied as adsorbents for the removal of a number of PPCPs,<sup>29-35</sup> herbicides and pesticides.<sup>36-38</sup> To the best of our knowledge, adsorptive removal of carbamazepine from water has not been studied in MOFs. In this work we considered two zirconium-based isostructural MOFs, UiO-66 and UiO-67, for carbamazepine removal from water due to their exceptional chemical, thermal, and water stability.<sup>39-41</sup> UiO-66 and UiO-67 are formed by  $Zr_6O_4(OH)_4$  inorganic clusters linked by 1,4-benzene dicarboxylate (BDC) and biphenyl-4,4'-dicarboxylate (BPDC) organic ligands, respectively.<sup>42-43</sup> UiO-66 has octahedral and tetrahedral pores, 12Å and 7.5Å in diameter, respectively,; whereas in the case of UiO-67, the longer linker results in larger octahedral and tetrahedral pores (16Å and 12Å, respectively).<sup>44</sup> For comparison purposes we also studied commercial granular activated carbon Filtrasorb 400 (F400) which has been commonly used for water treatment applications.<sup>20, 45-51</sup> Moreover, F400 has been used as a benchmark material in several studies which investigated the removal of organics using other porous materials, including MOF<sup>52</sup> and zeolite materials<sup>53-55</sup> as well as other carbonaceous materials.<sup>20, 45, 49, 51, 56-59</sup>

## EXPERIMENTAL METHODS

**Synthesis of MOFs:** UiO-66 was prepared with 3 missing-linker sites per node as reported previously.<sup>43, 60</sup>  $ZrCl_4$  (1.25 g, 5.4 mmol, Merck) was dissolved in 50 mL of *N,N'*-dimethylformamide (DMF,  $\geq 99.8\%$ , Sigma-Aldrich, SIAL) and 10 mL of concentrated hydrochloric acid modulator (HCl, 36.5-38 wt%, Sigma Aldrich) in a 250 mL glass bottle by ultrasonication for 20 min. Benzene-1,4-dicarboxylic acid (BDC, 1.23 g, 7.5 mmol, VWR) and 10 mL of DMF were then added to the solution and sonicated for further 20 min. The bottle was

placed in an oven at 80 °C overnight. The resulting white precipitates were separated by centrifugation after cooling to the room temperature. The solid was recovered by washing with DMF for 2 times and ethanol (Merck), for 3 times to remove unreacted linkers and DMF trapped from the pores, respectively and finally then dried at 90 °C in a vacuum oven.

UiO-67 was synthesized according to previously reported procedure.<sup>43, 60</sup> Briefly, in a 250 mL glass bottle, 0.67 g of ZrCl<sub>4</sub> (2.7 mmol), 50 ml of DMF and 5 ml of concentrated HCl were added and ultrasonicated for 20 minutes followed by adding 0.90 g of 4,4'-biphenyldicarboxylic acid (BPDC, 3.8 mmol, 99%, Sigma Aldrich) and 100 mL of DMF and mixed ultrasonically for further 20 minutes. The resulting mixture was incubated at 80 °C overnight. The white solid was washed 3 times with DMF and 4 times with acetone by centrifugation (5000 rpm, 5 min). The powder was dried in a vacuum oven at 90 °C overnight.

**Characterization of adsorbents:** Powder X-Ray Diffraction (PXRD) patterns of the materials were obtained by a Stoe Stadi-P using Cu K $\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) in the range of  $2^\circ \leq 2\theta \leq 50^\circ$  with a  $0.5^\circ$  step size and a scan rate of 5 s / step. Powder X-Ray Diffraction (PXRD) was used to confirm the crystallinity of the synthesized isostructural UiO-66 and UiO-67 crystals and the stability of regenerated UiO-67.

In order to evaluate the BET surface areas, total pore volumes, micropore volumes and the pore size distributions, N<sub>2</sub> adsorption/desorption measurements of UiO-66 was performed on Quantachrome Autosorb IQ MP Physisorption analyzer and both UiO-67 and F400 were conducted on Micromeritics Tristar porosity analyzer at 77 K. Prior to analysis, UiO-66 was outgassed at 120 °C for 16 hours and UiO-67 and F400 were outgassed at 150 °C overnight under vacuum. At least 70 mg of sample was used in measurements. The specific surface areas were calculated using BET method at the range of 0.005-0.2 relative pressure range. The pore

size distributions of the adsorbents were derived by density functional theory (DFT) using the silica cylindrical-pore model for UiO-67 and UiO-66, and using the carbon slit-pore model for F400. The micropore volumes of all materials were calculated using the t plot method from N<sub>2</sub> adsorption isotherm.<sup>60</sup>

Scanning electron microscopy images were recorded on a Zeiss evolution MA10 SEM to assess the morphology and particle size of adsorbents. Samples were firstly coated with a thin layer of gold for conductivity and then operated in beam mode at a 15kV of acceleration voltage.

**Liquid phase adsorption experiments:** A 100 mg L<sup>-1</sup> carbamazepine stock solution (Sigma Aldrich) was obtained by dissolving carbamazepine in ultrapure water (18 M.Ω.cm) by ultrasonication until completely dissolved. The working solution concentrations for batch adsorption experiments were obtained with diluting the carbamazepine stock solution with ultrapure water. The initial and equilibrium carbamazepine concentrations in solutions were measured using a UV-visible spectrophotometer (Perkin Elmer, Lambda 950) according to the maximum absorbance at 285 nm of wavelength.

**Initial comparison of adsorbents for carbamazepine adsorption:** 6 mg of UiO-66, UiO-67 and F400 were introduced separately in to 5 mL aqueous solutions of carbamazepine with 100 mg L<sup>-1</sup> initial concentration. The carbamazepine solutions with adsorbents were shaken at 25°C at the speed of 250 rpm for 24 hours in an incubator shaker to ensure equilibrium was obtained. All experiments were performed in triplicate and the mean values are reported. Control experiments without adsorbents were also carried out to measure the initial concentration. The supernatants were separated from the adsorbents using a syringe filter (0.2 μm cellulose acetate membrane). The control solution was also filtered using syringe filter. The percentage removal of carbamazepine was calculated as below.

$$\text{Removal percentage (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_e$  are the initial concentration and the equilibrium carbamazepine concentration, respectively.

**Effect of adsorbent concentration on carbamazepine adsorption:** The effect of adsorbent amount on the removal efficiency was studied by introducing 3 mg, 6 mg, 9 mg, 10 mg and 12 mg of adsorbents into 5 mL of aqueous solution with 100 mg L<sup>-1</sup> carbamazepine concentration. Then the vials were placed in an incubator shaker and shaken at 250 rpm and 25°C for 24 hours. Control samples without adsorbents were also included.

**Kinetics of carbamazepine adsorption:** The adsorption kinetic studies on the removal of carbamazepine from water were performed by placing 48 mg of adsorbents in 40 mL carbamazepine solutions with an initial concentration of 100 mg L<sup>-1</sup>. Afterwards the solutions were shaken at 250 rpm at 25 °C. The supernatants were collected at predetermined time intervals using a syringe filter (0.2µm, cellulose acetate membrane). Kinetic experiments were carried out in triplicate and the results reported here are the mean values. The amount adsorbed ( $Q_t$ ) in mg of analyte per g of adsorbent as a function of time was calculated by using the following mass-balance relationship,

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where  $Q_t$  (mg g<sup>-1</sup>) is the amount adsorbed per unit mass of adsorbent at time  $t$ ,  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) are the initial concentration at time=0 and the residual concentration at time  $t$ , respectively.

The experimental data were fitted to Lagergren pseudo first order or pseudo second order linear kinetic model<sup>61</sup> to describe the kinetic rate constant of the system and kinetic models expressed in linearized form as below, respectively.

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 \times t \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

where  $Q_t$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed at time=  $t$ ,  $Q_e$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed at equilibrium,  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant,  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the pseudo second order rate constant,  $t$  (min) is the adsorption time.

**Adsorption isotherms of carbamazepine:** 6 mg of UiO-67 and F400 were placed separately in contact with 5 mL of carbamazepine solutions with concentrations in the range of 5-100  $\text{mg L}^{-1}$  and 30-100  $\text{mg L}^{-1}$ , respectively and then shaken at 250 rpm and 25°C for 24h. The supernatant was separated from adsorbents by filtering off with 0.2  $\mu\text{m}$  cellulose acetate syringe filter. The adsorbed amounts of carbamazepine were calculated by using Equation 5.

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (5)$$

where  $Q_e$  ( $\text{mg g}^{-1}$ ) is the amount adsorbed per unit mass of adsorbent at equilibrium,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration and  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration,  $V$  (L) is the volume of the carbamazepine solution and  $m$  (g) is the mass of the adsorbent.

Adsorption isotherm models Freundlich<sup>62</sup> and Langmuir<sup>63</sup> in their linearized forms were fitted to experimental data, which are given in Equations 6 and 7.

$$\ln(Q_e) = \ln(K_F) + \frac{1}{N} \ln(C_e) \quad (6)$$

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L} \times \frac{1}{C_e} + \frac{1}{Q_m} \quad (7)$$

where  $K_F$  ( $(\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/N}$ ) is the Freundlich adsorption constant,  $N$  is the adsorption intensity,  $Q_m$  ( $\text{mg g}^{-1}$ ) is the Langmuir maximum adsorption capacity and  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir adsorption constant.

**Effect of pH on carbamazepine adsorption:** To investigate the effect of pH on the adsorption of carbamazepine, 0.01 M hydrochloric acid (HCl, 36.5-38 %, Sigma Aldrich) or 0.01 M sodium hydroxide solution (NaOH, Sigma Aldrich) was used to adjust the pH of carbamazepine solutions. 6 mg of UiO-67 and UiO-66 were introduced to 5 mL of solutions with an initial concentration of  $100 \text{ mg L}^{-1}$  for 24 hours at  $25 \text{ }^\circ\text{C}$ . The adsorption capacities of UiO-67 were recorded as a function of pH.

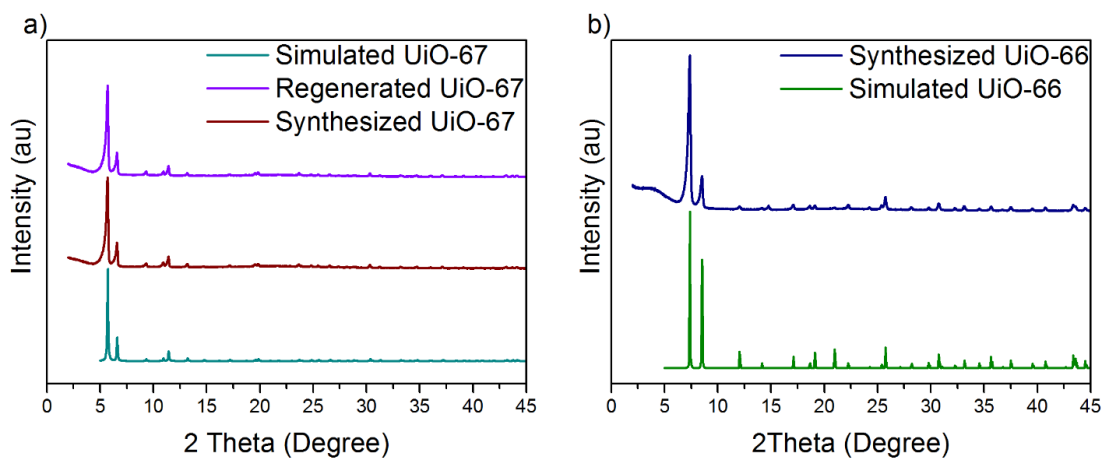
**Regeneration of UiO-67:** The spent UiO-67 was soaked in acetone and shaken at  $25 \text{ }^\circ\text{C}$  for 6 h and then supernatant was removed and re-soaked in fresh acetone and re-shaken at  $25 \text{ }^\circ\text{C}$  followed by removal of the acetone. Finally, the adsorbent was dried at  $90^\circ\text{C}$  overnight under vacuum. The regeneration of UiO-67 was repeated for at least six times following the above procedure prior to each adsorption.

## RESULTS AND DISCUSSION

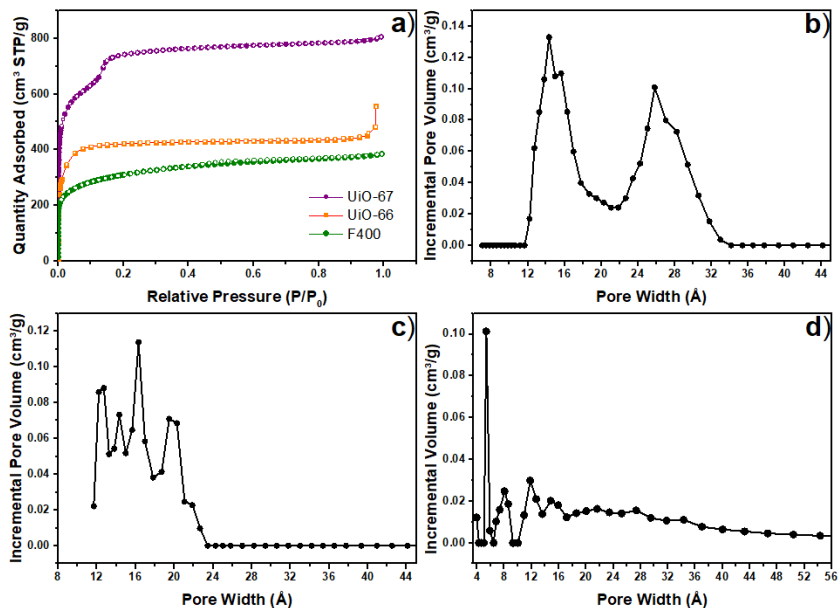
**Characterization of adsorbents:** Figure 1 shows that the PXRD patterns of the synthesized UiO-67 and UiO-66 are in good agreement with the simulated patterns which confirms the crystallinity. Figure 2 shows the  $\text{N}_2$  adsorption–desorption measurements in all adsorbents studied and their respective pore size distributions as a function of pore width. BET surface areas and pore volumes of UiO-67, UiO-66 and F400 are given in Table 1. UiO-67 has the highest specific surface area and the total pore volume among the three adsorbents, followed by UiO-66 and F400. UiO-67 and F400 possess both micropores and mesopores (i.e.  $> 20 \text{ \AA}$ ), whereas UiO-66 has only micropores. Because UiO-66 and UiO-67 were synthesized with the missing linkers



route they both exhibit pores slightly larger compared to those found in the defect free UiO-66 and UiO-67.<sup>60,49</sup> Finally, according to the SEM images given (Figure S1), UiO-66 and UiO-67 have similar average particle sizes, 0.233  $\mu\text{m}$  and 0.278  $\mu\text{m}$ , respectively, whereas F400 has a much larger average particle size of around 24  $\mu\text{m}$  (Figure S1c).



**Figure 1.** PXRD patterns of (a) UiO-67 and (b) UiO-66.

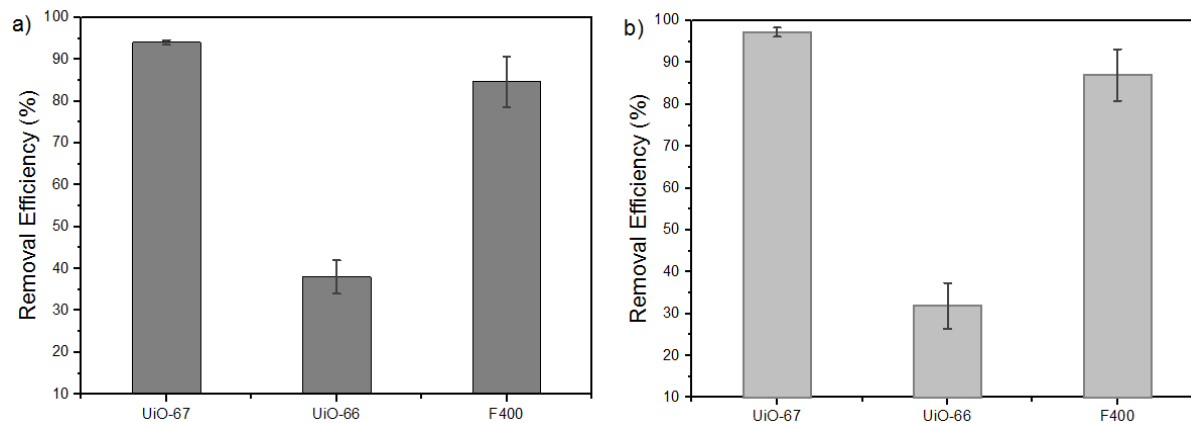


**Figure 2.** a) N<sub>2</sub> adsorption-desorption isotherms at 77 K for UiO-67, UiO-66 and F400 (filled and empty symbols represent adsorption and desorption, respectively) and pore size distributions of b) UiO-67, c) UiO-66, and d) F400.

**Table 1.** Surface area and pore volume properties of UiO-66, UiO-67 and F400.

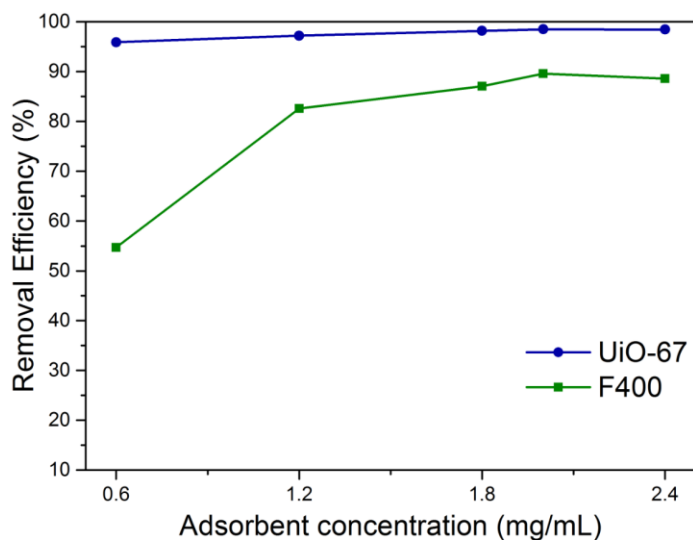
| Materials | Specific Surface Area, m <sup>2</sup> g <sup>-1</sup> | Total Pore Volume, cm <sup>3</sup> g <sup>-1</sup> | Micropore Volume cm <sup>3</sup> g <sup>-1</sup> |
|-----------|---|--|--|
| UiO-67    | 2344  | 1.069  | 0.930  |
| UiO-66    | 1640  | 0.656  | 0.621  |
| F400      | 1135  | 0.484  | 0.241  |

**Initial comparison of carbamazepine removal in UiO-67, UiO-66 and F400:** At first, the carbamazepine removal efficiency (%) of UiO-66, UiO-67 and F400 were compared by studying carbamazepine adsorption at two different initial carbamazepine concentrations, 10 and 100 mg L<sup>-1</sup>, with the same amount of adsorbent concentration (1.2 mg mL<sup>-1</sup>). Removal efficiencies given in Figure 3 show that UiO-67 and F400 removed around 95% and 85% of the carbamazepine initially present in the water at both concentrations studied. UiO-66 on the other hand, removed around 35% of the carbamazepine from water. The results clearly show that UiO-66 is ineffective in the removal of carbamazepine. This may be attributed to the narrow pore aperture (6 Å)<sup>64</sup> and relatively smaller pore size of UiO-66 which prevent carbamazepine (kinetic diameter of 7.4 Å)<sup>23</sup> from being adsorbed in its pores. Given its poor performance for carbamazepine removal from water, UiO-66 was excluded from the rest of the adsorption experiments in this study.



**Figure 3.** Removal efficiency of carbamazepine from water at initial carbamazepine concentrations of (a) 10 mg L<sup>-1</sup> and b) 100 mg L<sup>-1</sup>. Experiments were performed in triplicate and the mean values are reported. (Adsorbent concentration 1.2 mg mL<sup>-1</sup>).

**The effect of adsorbent concentration:** Figure 4 shows the carbamazepine removal efficiency of UiO-67 and F400 as a function of adsorbent concentration. UiO-67 removed effectively most of carbamazepine (around 96 %) from water at a very small adsorbent concentration of 0.6 mg mL<sup>-1</sup>, whereas F400 removed about 52 % at the same adsorbent concentration. For UiO-67 the increase in adsorbent concentration made only a small difference reaching to 98% within the range studied (Figure 4). For F400, although the removal rate increased with increasing F400 concentration, the maximum carbamazepine removal efficiency observed was around 85%. These indicate that UiO-67 has a much better removal efficiency of carbamazepine compared to F400.

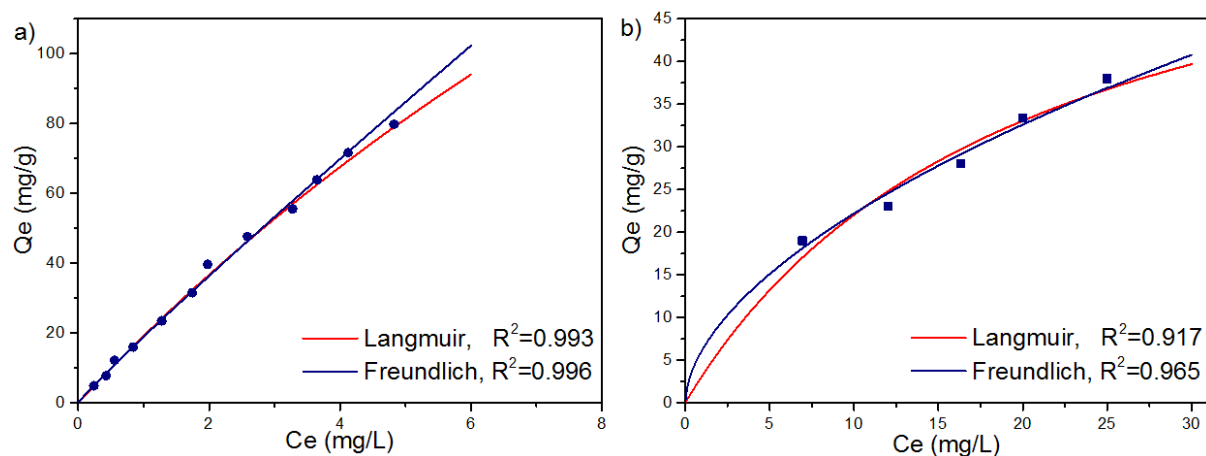


**Figure 4.** Effect of adsorbent concentration on carbamazepine removal. The initial carbamazepine concentration is  $100 \text{ mg L}^{-1}$ . Experiments were performed in triplicate and the mean values are reported. Errors are smaller than the symbols. The solid lines are given as guides to the eye.

**Adsorption isotherms:** Adsorption isotherms of carbamazepine in UiO-67 and F400 are given in Figure 5. The range of equilibrium concentration,  $C_e$ , for UiO-67 is  $0.2$  to  $5 \text{ mg L}^{-1}$  whereas for F400 is  $7$  to  $25 \text{ mg L}^{-1}$ . This is because the initial concentration of carbamazepine does not exceed  $112 \text{ mg L}^{-1}$  due to carbamazepine's poor solubility in water and UiO-67 removes almost all of it, hence the relatively low range of  $C_e$  obtained. In contrast, F400 removes less carbamazepine under the same conditions yielding higher  $C_e$  values. The adsorption isotherms were fitted to the linearized forms of the Langmuir and Freundlich models (Figure S2) and the calculated Langmuir and Freundlich parameters are given in Table S2. Even though both models gave good fits for UiO-67 and F400, the Freundlich isotherm was deemed to be more applicable since the isotherms did not approach saturation regime within the studied concentration range.

Carbamazepine adsorption in UiO-67, in particular, shows almost a linear trend which indicates that UiO-67 can adsorb higher amounts with increasing concentration of carbamazepine.

Based on the greater  $K_F$  value, UiO-67 is predicted to have a carbamazepine adsorption capacity about 3 times larger than that of F400, which is in line with the pore volumes reported in Table 1. A comparison of the  $K_F$  values of carbamazepine by various adsorbents are given in Table 2, which shows that the adsorption capacity of UiO-67 is expected to be higher than those of other adsorbents including F400, mesoporous silicate, resin and polymer.



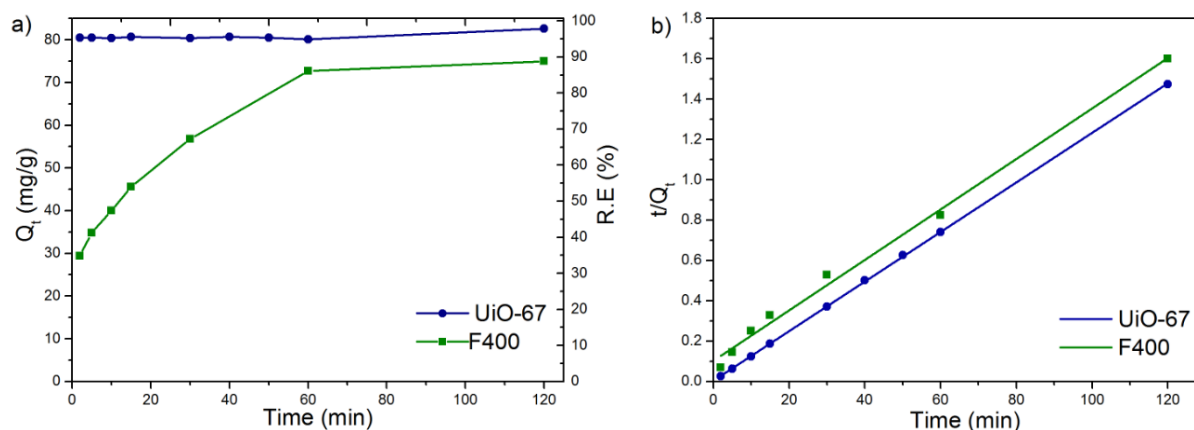
**Figure 5.** Adsorption isotherm of carbamazepine in (a) UiO-67 and b) F400. Solid lines show the Langmuir and Freundlich model fits. Experiments were performed in triplicate and the mean values are reported. Errors are smaller than the symbols.

**Table 2.** Comparison of Freundlich rate constant values ( $K_F$ ) for adsorption of carbamazepine by various adsorbents reported in the literature.

| Adsorbent  | Carbamazepine |   |       |               |
|--|---------------|---|-------|---------------|
|  | pH            | $K_F$ ( $\text{mg g}^{-1}$ )<br>( $\text{L mg}^{-1}$ ) <sup>1/N</sup> | N     | Refs.         |
| Hexagonal mesoporous silicate, HMS   | 7.0           | 0.113   | 0.835 | <sup>5</sup>  |
| Mercapto-functionalized HMS, M-HMS   | 7.0           | 0.747   | 1.106 | <sup>5</sup>  |
| Amine-functionalized HMS - (A-HMS)   | 7.0           | 0.047   | 1.106 | <sup>5</sup>  |
| Mesoporous silicate SBA-15   | 7.0           | 0.206   | 0.885 | <sup>5</sup>  |
| Mesoporous silicate MCM-41   | 7.0           | 0.143   | 0.860 | <sup>5</sup>  |
| Powdered activated carbon  | 7.0           | 1.852   | 1.072 | <sup>5</sup>  |
| Mesoporous silica SBA-15   | 5.0           | 1.10  | 1.34  | <sup>17</sup> |
| Single-walled carbon nanotubes   | n.a           | 62.5  | 0.35  | <sup>19</sup> |
| Molecularly imprinted polymer, MIP   | n.a           | 28.7  | 0.38  | <sup>22</sup> |
| Non-imprinted polymer, NIP   | n.a           | 10.2  | 0.32  | <sup>22</sup> |
| Y-zeolites modified with extra framework transition metal and surfactant cations | 6.0           | Low loading<br>n.a  | -     | <sup>23</sup> |
| Amberlite XAD-7 acrylic-ester-resin  | 7             | 5.56  | 0.744 | <sup>65</sup> |
| Activated carbon/Fe <sub>3</sub> O <sub>4</sub>                                  | 6.0           | 63.2  | 4.44  | <sup>66</sup> |
| Biochar/Fe <sub>3</sub> O <sub>4</sub>   | 6.0           | 23.1  | 3.73  | <sup>66</sup> |
| Activated Carbon F400  | 5.0           | 6.6   | 0.55  | This work     |
| UiO-67   | 5.0           | 18.9  | 0.94  | This work     |

**Adsorption Kinetics:** Figure 6a shows the adsorption of carbamazepine as a function of time with an initial carbamazepine concentration of  $100 \text{ mg L}^{-1}$ . After 2 hours, equilibrium uptake of carbamazepine was found to be  $82.61 \text{ mg g}^{-1}$  and  $75 \text{ mg g}^{-1}$  for UiO-67 and for F400, respectively, which correspond to 97 % removal efficiency for UiO-67 and 88.7 % for F400. More importantly, UiO-67 removed 95% of carbamazepine in just 2 minutes. In contrast, F400 removed only 35% of the carbamazepine in the first 2 minutes. The faster removal rate of carbamazepine in UiO-67 in comparison to F400 can be ascribed to several reasons including the active adsorption sites created by the missing-linker defects, UiO-67's smaller particle size (Figure S1b) and pore volume. The nodes of UiO-67 are twelve-linker-connected in the defect free sample; however, the connectivity around the node can intentionally be tuned to include less than twelve carboxylates. The carboxylate missing sites are capped with hydroxyl (-OH) and aqua ( $\text{H}_2\text{O}$ ) groups. Carbamazepine can make specific interactions with these functional groups on nodes. Additionally, missing linker defects lead to the enhanced porosity which may facilitate faster adsorption and greater adsorption capacity.<sup>67-69</sup>

The pseudo first order and the pseudo second order kinetic models were considered to analyze the experimental kinetic data (Figure 6 and Table 3). The adsorption kinetics of carbamazepine in both UiO-67 and F400 are well represented by the pseudo second order kinetic model. The pseudo second order rate constant ( $k_2$ ) of carbamazepine adsorption in UiO-67 was calculated to be  $0.04 \text{ mg g}^{-1} \text{ min}^{-1}$ , which is 27 times greater than that of for F400 ( $0.0015 \text{ mg g}^{-1} \text{ min}^{-1}$ ).



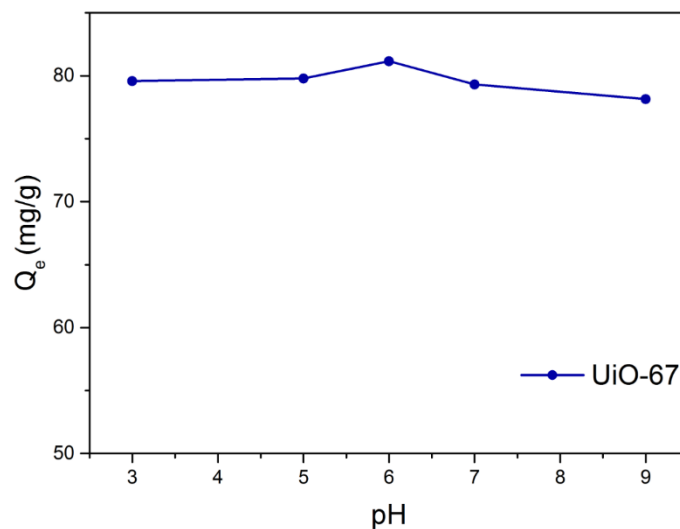
**Figure 6.** (a) Adsorption of carbamazepine in UiO-67 and F400 as a function of time and (b) the corresponding pseudo second order kinetic plots. Adsorbent concentration is  $1.2 \text{ mg mL}^{-1}$ . Experiments were performed in triplicate and the mean values are reported. Errors are smaller than the symbols. Solid lines are given as guides to the eye.

**Table 3.** Pseudo first order and pseudo second order kinetic models fitting parameters

| Model  | Pseudo First Order Kinetic Model |                             |       | Pseudo Second Order Kinetic Model |   |        |
|--------|----------------------------------|-----------------------------|-------|-----------------------------------|---|--------|
|        | $Q_e$<br>( $\text{mg g}^{-1}$ )  | $k_1$ ( $\text{min}^{-1}$ ) | $R^2$ | $Q_e$<br>( $\text{mg g}^{-1}$ )   | $k_2$<br>( $\text{g mg}^{-1} \text{min}^{-1}$ ) | $R^2$  |
| UiO-67 | 2.9                              | 0.0244                      | 0.79  | 82.64                             | 0.04  | 0.9998 |
| F400   | 58.2                             | 0.0511                      | 0.967 | 80                                | 0.0015  | 0.9946 |

**Effect of pH:** The solution pH is a crucial parameter in practical water treatment which affects the adsorption capacity possibly by altering the electrostatic interactions between adsorbents and adsorbates. Figure 7 shows the change in the adsorbed amount of carbamazepine with respect to varying pH. It was found that the amount of carbamazepine adsorbed did not significantly change within the pH range studied. This may be due to the fact that carbamazepine exists almost exclusively as a neutral compound at pH 3.0- 9.0 since acid association constant (pKa) of carbamazepine is 13.9.



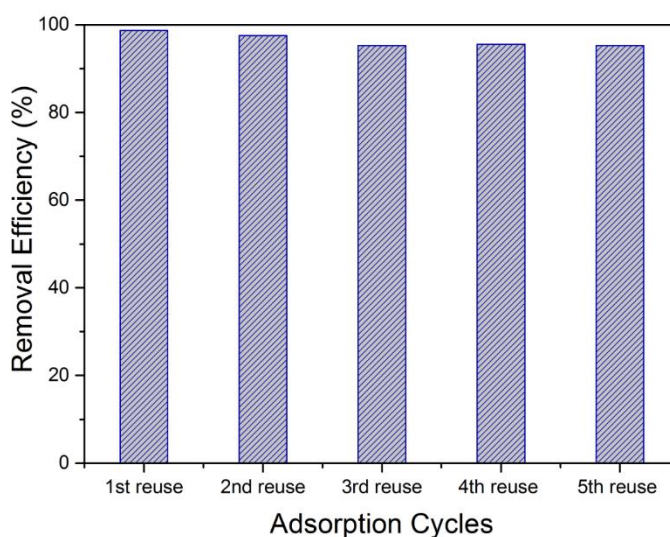


**Figure 7.** The effect of pH on adsorptive removal of carbamazepine. Experiments were performed in triplicate and the mean values are reported. Errors are smaller than the symbols. The solid lines are guides to the eye.

**Adsorption Mechanism:** Hydrogen bonding was previously used to explain the adsorptive removal of organic contaminants using MOFs.<sup>70-71</sup> However, the insensitivity of carbamazepine adsorption in UiO-67 (Figure 7) with respect to varying pH values indicates that the electrostatic interactions do not play a significant role and the contribution of hydrogen bonding is expected to be negligible and that it is rather the hydrophobic and  $\pi$ - $\pi$  interactions between the benzene rings of carbamazepine and the UiO-67 linkers which dominate. Carbamazepine has amine group (-NH<sub>2</sub>) that is a strong electron donating group,<sup>6</sup> this electron-rich,  $\pi$  donor, benzene rings of carbamazepine can strongly bind with the electron acceptor,  $\pi$  acceptor, of the oxygen containing functional group on the surface of UiO-67. Similar interactions have been reported for carbamazepine adsorption in other adsorbents in the literature.<sup>6, 65, 72</sup>

**Regeneration of UiO-67:** Regeneration of used adsorbents is of significant importance in terms of water remediation applications. The feasibility of regenerating UiO-67 was investigated using

the solvent assisted desorption technique. UiO-67 was tested for the adsorption of carbamazepine after the spent adsorbent soaked in acetone, shaken at room temperature and re-activated under vacuum at 90°C. This process was repeated five times and at the end of the 5th cycle, adsorption capacity of UiO-67 showed only an insignificant decrease (Figure 8). The crystallinity of the regenerated UiO-67 was also confirmed by XRD patterns (Figure 1a) indicating that UiO-67's structure was not destroyed after soaking with acetone and reactivating at 90°C. Overall, these prove that UiO-67 not only removes carbamazepine effectively and rapidly but also it is a durable adsorbent which can be used several times, which is absolutely a requirement for a practical and economical operation.



**Figure 8.** The adsorbed amount of carbamazepine by UiO-67 after consecutive regeneration cycles. (12 mg UiO-67 was in contact with 5 mL solution of 100 mg L<sup>-1</sup> initial concentration)

## CONCLUSIONS

We studied the removal of carbamazepine from water by using two water stable MOFs, UiO-66 and UiO-67, and a commercial activated carbon F400. UiO-67 showed superior performance in comparison to the other two adsorbents. The rapid and highly efficient removal of

carbamazepine in UiO-67 has been attributed to the active adsorption sites formed by the missing linker defects, well defined crystalline particles which are relatively small in size and high surface area and pore volume. Carbamazepine adsorption was found to be independent of pH, therefore, not the electrostatic but the hydrophobic and  $\pi$ - $\pi$  interactions were deemed to dominate the adsorption mechanism. Overall, fast adsorption kinetics, good solvent stability and reusability reveal that UiO-67 can be considered as a promising adsorbent for the carbamazepine removal from water.

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## **SUPPORTING INFORMATION**

Chemical structure and physicochemical properties of carbamazepine, SEM images of the synthesized MOFs and F400, and Freundlich and Langmuir adsorption isotherm model fittings for carbamazepine adsorption in UiO-67 and F400.

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