Adsorption Behavior of a Gd-Based Metal–Organic Framework toward the Quercetin Drug: Effect of the Activation Condition

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ABSTRACT: A carboxylate gadolinium-based metal–organic framework (Gd-MOF) is an exceptional candidate for magnetic resonance imaging agents, but its low drug adsorption capacity hinders this MOF from being used as a theragnostic agent. In this work, the Gd-MOF was synthesized by a simple solvothermal method. Then, different activation situations, including various solvents over different time periods, were applied to enhance the specific surface area of the synthesized MOF. Different characterization analyses such as X-ray diffraction and Brunauer–Emmet–Teller along with experimental quercetin adsorption tests were done to study the crystalline and physical properties of various activated MOFs. In the following, the MOF activated by ethanol for 3 days (3d-E) was chosen as the best activated MOF due to its crystallinity, highest specific surface area, and drug adsorption capacity. More explorations were done for the selected MOF, including the drug adsorption isotherm, thermodynamics, and pH effect of adsorption. The results show that the activation process substantially affects the crystallinity, morphology, specific surface area, and drug adsorption capacity of Gd-MOFs. An optimized activation condition is proposed in this work, which shows an impressive enhancement of the specific surface area of Gd-MOFs just by simple solvent exchange method employment.

1. INTRODUCTION

Metal–organic frameworks (MOFs) are hybrid inorganic–organic porous materials. The inorganic part includes metal ions (clusters), and the organic part consists of bridging linkers between the metal ions.3−5 In recent years, MOFs have attracted the attention of researchers, especially those working in the biotechnology field including drug delivery, drug adsorption, image contrast agents (CAs), and tissue engineering.3−5 The popularity of MOFs is due to their crystalline structure, porosity, high surface area, ease of functionalization, and tunable size.5−7 Among various MOFs, lanthanide-containing MOFs are intriguing in the bioimaging field. The metal in this class of MOFs shows photoluminescence and magnetic properties, which can play the role of a CA in imaging and as a result make lanthanide MOFs promising multifunctional materials for treatments, biosensors, and imaging.4−6

Gadolinium-based MOFs (Gd-MOFs) are a common type of lanthanide MOF, which are considered preferred combination for CAs in magnetic resonance imaging (MRI) because Gd is a lanthanide transition metal that owns highly unique paramagnetic nature and acts as a positive CA in MRI.15 Negative CAs such as iron (Fe)-based materials used in MRI cause a low signal to noise ratio, appearance of a partial volume effect, and difficulty in cell tracking; they are not preferred among physicians for clinical uses.17 Therefore, Gd-based compounds are the most appropriate alternatives to be used as imaging agents compared to other paramagnetic (Mn)-18 or even superparamagnetic (Fe)-based materials.19

Gd complexes, used as commercial diagnostic CAs today, have some downsides such as low circulation time in the body, functionalization limits in case of need such as surface modification for crossing the blood–brain barrier, and toxicity due to high dose injection of Gd solution to get qualified contrasted images.20 To overcome these drawbacks, Gd-MOFs including Gd ions as nodes chelated with carboxylic ligands as struts are the best candidates for MRI agents21 thanks to their intense relaxivities due to the presence of a high concentration of Gd ions per MOF particle, biocompatibility because of the surrounding ligand which blocks interactions between toxic Gd ions and cell tissues,22 and facility of ligand modifications by specific peptides or polymers for targeted drug delivery, detection, or bioimaging.14,23 Although Gd-MOFs have attracted much attention in the MRI field, their low specific surface area, for example, 2−11 m²/g, is considered...
disadvantage for use in drug delivery systems and theragnostic agents.\textsuperscript{24–26}

One possible reason for low specific surface area in MOFs is the suboptimal removal of solvent molecules by activation methods.\textsuperscript{27} Through the activation process, solvent molecules, used for the synthesis of MOFs, are substituted by low-boiling point and low-surface tension solvents such as methanol, acetone, and ethanol.\textsuperscript{28} Therefore, the substituted solvent can be evaporated by applying low-temperature heat treatment in vacuum.\textsuperscript{27} The importance of post-synthetic activation methods for MOFs, specifically the solvent exchange method, has been increasingly regarded in very recent years\textsuperscript{29–31} because during this process, the pores of MOF particles can be evacuated by removal of the initial solvent, while its structure is preserved, and therefore, the pores of the MOF are more accessible to guest molecules following enhancement of specific surface area and stability of the MOF.\textsuperscript{28} To get a perfect porous MOF with structural integrity and the highest specific surface area, the activation conditions for each type of MOF should be optimized, including the time period of activation and the activation solvent used.\textsuperscript{31}

In this work, terephthalic acid (H\textsubscript{2}BDC) is considered the inorganic part of the Gd-MOF since it is a linear linker with a high affinity toward Gd metals to form a homogeneous network with excellent stability.\textsuperscript{32,33} In the structure of the Gd-MOF, there are two Gd metals in a lattice in which each metal is octacoordinated by four carboxylated oxygen atoms from bridged H\textsubscript{2}BDC ligands between the two Gd metals in a lattice, two from a distinct H\textsubscript{2}BDC ligand, and two oxygen atoms from solvent [N\textsubscript{2}N-dimethylformamide (DMF)] molecules forming the building block of the 3D structure.

The H\textsubscript{2}BDC ligand is non-toxic and surrounds the very toxic Gd metal, which acts as nodes in the MOF. As long as the organic linker encloses the nodes, the safety of the MOF is provided.\textsuperscript{34} Accordingly, since this type of Gd-MOF framework is rigid, the MOF is biocompatible with and suitable for bioapplications. As mentioned above, this MOF shows several advantages in bioapplications, such as biocompatibility, being a unique MRI CA, and high stability in aqueous solutions; however, the only disadvantage of the cited MOF is its low specific surface area for drug adsorption.\textsuperscript{35,36} Optimizing the activation conditions, including the type of solvent and time duration for a specific type of MOF, is necessary to get a fully porous MOF with the highest specific surface area.

This study focuses on improving the specific surface area of a synthesized 1,4-benzenedicarboxylic Gd-MOF by the solvent exchange activation method using various solvents (methanol, acetone, and ethanol) over different time periods (1, 3, and 5 days). Recently, several studies have been done on the 1,4-benzenedicarboxylic Gd-MOF, but none investigated the optimized conditions for the MOF activation following the enhancement of its adsorption capacity.\textsuperscript{20,21,37} For the first time, it is shown that the activation condition significantly affects the crystalline structure, morphology, size, specific surface area, and consequently adsorption behavior of the Gd-MOF, employing suitable characterization techniques.

Quercetin (Qt) is a natural bioflavonoid found in green tea, vegetables, and fruits. The Qt’s basic structure contains two benzene rings connected by a pyran ring (Scheme 1), and its charge is composed of positive and negative polar areas.\textsuperscript{38} Since it has a great potential to scavenge free radicals, it is popular as anti-inflammatory medicine.\textsuperscript{39} To investigate the adsorption behavior of all activated Gd-MOFs, Qt was chosen as the model drug. After this, the best Gd-MOF in terms of the morphology, specific surface area, and adsorption capacity was selected for more explorations, such as isotherm adsorption, pH, and thermodynamic effects on adsorption.

2. EXPERIMENTAL SECTION

2.1. Materials. Gadolinium nitrate hexahydrate \([\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}])\), 1,4-benzenedicarboxylic acid (H\textsubscript{2}BDC), and Qt (95%) were purchased from Sigma-Aldrich. DMF, ethanol, methanol, acetone, chloroform, hydrochloric acid (HCl, 0.1 M), and sodium hydroxide (NaOH, 0.1 M) were supplied by Merck. All chemicals were of reagent grade and used without further purification.

2.2. Synthesis of Gd-MOFs. The synthesis procedure is performed based on Lorusso’s work.\textsuperscript{40} To synthesize Gd-MOFs by terephthalic acid, 300 mg of Gd(NO\textsubscript{3})\textsubscript{3} \cdot 6H\textsubscript{2}O and 166 mg of H\textsubscript{2}BDC were dissolved in 10 mL of DMF separately. After 10 min, both solutions were mixed and stirred at room temperature for 30 min. Then, the resultant solution was poured into a cell culture tube (diameter 18 mm and height 180 mm) and placed in an oven at 120 °C for 20 h. Afterward, the white nanoparticles were separated from the solution by centrifugation (4000 rpm for 5 min) and washed with DMF three times. Then, the whole obtained nanoparticles were subdivided into five subdivisions. One of the subdivisions, which is referred to as Gd-DMF hereafter, was used as obtained. However, the rest of the subdivisions were subjected to further washing under sonication with four low-boiling point solvents, including ethanol, methanol, acetone, and chloroform, at three different washing cycle times. Particles washed with chloroform got destroyed upon adding the solvent, so chloroform was eliminated from the selected solvent series. For each activation solvent, the nanoparticles were soaked in the solvent for three different times, for example, 1, 3, and 5 days at room temperature. Each day, the particles were washed with the fresh solvent under sonication for 15 min. At the end of the washing cycle, particles were dried in an oven at 50 °C for 12 h. The as-synthesized particles were named x:y where x refers to the time of activation in terms of the day (1, 3, and 5 days) and y abbreviated the name of the solvent used, that is, E stands for ethanol, M for methanol, and A for acetone. Table 1 summarizes the list of Gd-MOF nanoparticles activated by various washing cycles.

2.3. Adsorption Experiments. First, the calibration curve of the Qt drug was drawn by measuring the characteristic absorbance of Qt at \(\lambda = 370\) nm using a UV–vis spectrophotometer for a series of Qt solutions with pre-specified concentrations of 2.5, 5, 10, 15, 20, and 25 ppm. A linear curve was drawn by the concentration of the solution against its absorbance intensity at \(\lambda = 370\) nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Scheme1.pdf}
\caption{Quercetin Structure}
\end{figure}

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Table 1. List of Gd-MOF Nanoparticles Activated by Various Washing Cycles along with Their Sample Code Used in This Study

| sample       | activation solvent | duration of activation (days) |
|--------------|--------------------|-----------------------------|
| 0d-DMF       | DMF                | 0                           |
| 1d-M         | methanol           | 1                           |
| 3d-M         | methanol           | 3                           |
| 5d-M         | methanol           | 5                           |
| 1d-A         | acetone            | 1                           |
| 3d-A         | acetone            | 3                           |
| 5d-A         | acetone            | 5                           |
| 1d-E         | ethanol            | 1                           |
| 3d-E         | ethanol            | 3                           |
| 5d-E         | ethanol            | 5                           |

A stock solution of Qt in ethanol at a concentration of 100 ppm was prepared. To analyze the adsorption kinetics of the activated Gd-MOFs, 10 mg of nanoparticles was poured into 50 mL of Qt solution at a concentration of 20 ppm and stirred at room temperature for 75 min. For each predefined time interval, 5 mL of the solution was taken from the solution and centrifuged to get the supernatant. The concentration of the supernatant was determined by measuring the intensity of UV−vis spectroscopy at λ = 370 nm. The kinetic experiments were performed three times to get reliable data. Finally, the adsorption capacity of the Gd-MOFs against Qt was calculated using the following formula\(^{41}\)

\[
q_t = \frac{(C_0 - C_t) \times V}{T}
\]  

(1)

where \(C_0\) (mg/L) and \(C_t\) (mg/L) are the initial concentration and the concentration at time \(t\) of Qt, respectively, \(V\) (mL) is the volume of the solution, and \(T\) (g) refers to the weight of the Gd-MOF.\(^{37}\) To further investigate the kinetic adsorption of Qt onto Gd-MOFs, three well-known kinetic models were employed to fit the experimental kinetic data: pseudo-first-order (PO1), pseudo-second-order (PO2), and intraparticle diffusion models. These three models analyzed the rate-controlling step of Qt adsorption onto the Gd-MOFs. PO1 and PO2 in the linear forms are expressed as follows (eqs 2 and 3)\(^{41,45}\)

\[
\ln(q_e - q_t) = \ln(q_e) - K_1t
\]  

(2)

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]  

(3)

where \(q_t\) and \(q_e\) (mg/g) are the amounts of Qt adsorbed in the equilibrium state and at time \(t\), respectively. \(K_1\) (min\(^{-1}\)) and \(K_2\) [g (mg-min\(^{-1}\))] are rate constants of PO1 and PO2, respectively.

The intraparticle diffusion model is expressed as follows\(^{44}\)

\[
q_t = K_{id}t^{1/2} + C
\]  

(4)

where \(K_{id}\) (mg-g\(^{-1}\)-min\(^{-1/2}\)) is a rate constant and \(C\) is a constant which refers to boundary layer thickness.

2.4. Adsorption Isotherm. The adsorption isotherm proceeded in different Qt initial concentrations including 20, 40, 80, 100, 150, 200, 250, and 300 ppm. 1 mg of nanoparticles was mixed with 5 mL of Qt solutions at different concentrations. The solutions were stirred at a temperature of 25 °C for 1 h and then centrifuged, and finally, the supernatants were taken out to detect the equilibrium concentrations by UV−vis spectroscopy. The experiment for each concentration was repeated three times to get reliable data. The equilibrium adsorption capacity of Gd-MOFs was calculated using eq 1, in which \(C_t\) replaced \(C_e\).

Four known isotherm models were utilized to get deep insights into adsorption mechanisms: Langmuir, Freundlich, Dubinin−Radushkevich, and Temkin isotherms. The linear form of Langmuir, Freundlich, and Dubinin−Radushkevich is expressed using eqs 5−7, respectively.\(^{41}\)

\[
\frac{C_e}{q_e} = \frac{1}{K_1q_{max}} + \frac{C_e}{q_{max}}
\]  

(5)

\[
\ln q_e = \ln K_F + \frac{1}{n_F}\ln C_e
\]  

(6)

\[
\ln q_e = ln q_{max} - B\varepsilon^2
\]  

(7)

In eq 5, \(C_e\) is the equilibrium concentration of the drug, and \(K_1\) (mg/g) is the Langmuir constant related to adsorption capacity implying that large surface area and pore volume lead to higher adsorption capacity. \(q_{max}\) is the Langmuir monolayer adsorption capacity at the maximum level. For eq 6, \(K_F\) and \(n_F\) are Freundlich constants, referring to adsorption capacity and intensity, respectively. In eq 7, \(B\) (mol\(^2\)/kJ\(^2\)) is a constant related to the free energy of adsorption, and \(\varepsilon\) is the Polanyi potential that is defined below\(^{45}\)

\[
\varepsilon = RT \ln\left[1 + \frac{1}{C}\right]
\]  

(8)

where \(R\) and \(T\) are the universal gas constant (8.31 J/mol-K) and absolute temperature, respectively. The constant (\(B\)) of the Dubinin−Radushkevich model is also correlated with \(E\) (J/mol), which is the free energy change of adsorption of 1 mol of Qt onto the surface of the Gd-MOF, as follows.

\[
E = 1\sqrt{2B}
\]  

(9)

The linear form of the Temkin model is described as\(^{45,46}\)

\[
q_e = \frac{RT}{B_T}\ln(A_TC_e)
\]  

(10)

where \(B_T\) (kJ/mol) and \(A_T\) (L/g) are Temkin constants which demonstrate heat of adsorption and the binding constant of equilibrium, respectively.

2.4.1. Thermodynamics Studies. Thermodynamics of adsorption can give further insights into the adsorption mechanisms. Therefore, to investigate the thermodynamics of adsorption of Qt onto the Gd-MOF nanoparticles, adsorption experiments were performed at three different temperatures of 25, 35, and 45 °C for a Qt concentration of 20 ppm. Thermodynamic parameters such as standard entropy (\(\Delta S^0\), J/mol K), standard enthalpy (\(\Delta H^0\), kJ/mol), and standard Gibbs free energy (\(\Delta G^0\), kJ/mol) were achieved using the following equations\(^{47}\)

\[
\ln\frac{q_e}{C_e} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(11)

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]  

(12)

where \(R\) (J/mol K) and \(T\) (K) are the gas constant and the absolute temperature, respectively.
2.5. **pH Effects.** The adsorption behavior of the 3d-E MOF was investigated at various pH values other than the natural pH of the 3d-E MOF in 20 ppm Qt solution, that is, pH = 5. The pH of solutions was adjusted using NaOH and HCl solutions. The experiment for each pH was performed three times to get validated data.

2.6. **Characterizations.** The crystalline structure of Gd-MOF nanoparticles activated under various conditions was analyzed using an X-ray diffractometer (D/Max-3A, Rigaku Co.) at room temperature. The test was performed with a copper anode and a graphite monochromator to select Cu Kα radiation (λ = 1.54060 Å), with an accelerating voltage of 40 kV and a current of 40 mA. To study and compare the specific surface area of synthesized nanoparticles, a N₂ gas adsorption—desorption analyzer instrument at 70 K was used by a BELSORP-miniII gas adsorption. The ζ potential of nanoparticles was also studied using a Zeta-Sizer Nano-ZS (Malvern, UK). The morphology of nanoparticles was observed by field-emission scanning electron microscopy (FESEM) with a FESEM-MIRA3 TESCAN. The thermal decomposition behavior of the nanoparticles was investigated using a PerkinElmer Pyris thermogravimetric analyzer at a heating rate of 10 °C/min from room temperature up to 800 °C under a nitrogen atmosphere. The concentration of Qt was inspected by an ultraviolet–visible (UV–vis) spectrum at λ = 370 nm using a Philips PU9400 atomic adsorption spectrophotometer. The amount of Gd ions leaching from the 3d-E MOF during Qt adsorption was measured using an inductively coupled plasma-optical emission spectrometer (Spectro Arcos) equipped with a charge coupled device.

3. **RESULTS AND DISCUSSION**

3.1. **Characterization of Gd-MOFs.** X-ray diffraction (XRD) spectra of synthesized Gd-MOFs are depicted in Figure 1. The prominent peak observed around 2θ = 10° shows the Gd metal in the MOF structure. As can be inferred from Figure 1, the main peaks of Gd-MOFs with different activation conditions agree with the simulated XRD pattern; however, some differences in their XRD patterns suggest the different crystalline structures of various Gd-MOFs synthesized in this investigation. Remarkably, the prominent peak at around 2θ = 10° may be one or split into two or three smaller peaks for different Gd-MOF particles. The microstructure is actually affected by the number of solvent molecules remaining in the pores of MOFs.

Meanwhile, the number of DMF molecules in the synthesized Gd-MOFs depends on the activation solvent type and the activation duration. Furthermore, a reduction in peak intensity of 5d-A and 5d-E can be seen, which indicates that the crystalline structure of the acetone- and ethanol-activated MOF starts to degrade on day 5. Among Gd-MOFs synthesized in this investigation, the MOF activated by ethanol...
shows the best agreement with XRD patterns reported in the literature. Additionally, the XRD pattern of 0d-DMF does not show all the characteristic peaks because the guest solvent resides inside the pores of MOFs, and its crystalline structure does not appear ideally.

N$_2$ adsorption–desorption behavior and pore distribution graphs of activated Gd-MOFs are shown in Figure 2. Further information of Brunauer–Emmett–Teller (BET) analysis, like specific surface area and average pore diameter, is presented in Table 2. BET analysis of all Gd-MOFs shows that adsorption of N$_2$ gas on the Gd-MOFs is a type-3 isotherm which means that this adsorbent is macroporous nanoparticles and has weak interactions with the adsorbed gas molecules. Concerning the specific surface area of Gd-MOFs (Table 2), for methanol-activated MOFs, as the duration of activation increases, the surface area increases as well. However, since the specific surface area and pore diameter of 3d-M and 5d-M are almost the same, extending the duration time to more than 3 days for methanol-activated MOFs is inessential. Nevertheless, the opposite is true for acetone, which means that the surface area decreases steadily by increasing BET surface area. Moreover, the highest adsorption capacity (i.e., 45 mg/g) belongs to the 3d-E MOF, whose BET surface area was found to be the highest among all Gd-MOFs investigated in this research.

Three kinetic models were employed to fit the experimental adsorption data for all Gd-MOFs to explore the rate-controlling step during Qt adsorption on Gd-MOFs; the relevant model constants are given in Table 3. According to the correlation coefficients (R$^2$) of kinetic models and good correlation of experimental and theoretical maximum adsorption capacity (q$_{\text{max}}$), it can be suggested that PO2 fits best experimental data. As a result, it can be concluded that the rate-controlling step of Qt adsorption is chemisorption.

### 3.3. Characterization of 3d-MOFs

Since the 3d-E MOF has the highest adsorption capacity compared to Gd-MOFs activated by other solvents (methanol and acetone) at the same activation time of 3 days, it is chosen for deep analysis. FESEM, $\zeta$ potential, and thermogravimetric analysis (TGA) of N$_2$ gas on the Gd-MOFs is a type-3 isotherm which means that this adsorbent is macroporous nanoparticles and has weak interactions with the adsorbed gas molecules. Concerning the specific surface area of Gd-MOFs (Table 2), for methanol-activated MOFs, as the duration of activation increases, the surface area increases as well. However, since the specific surface area and pore diameter of 3d-M and 5d-M are almost the same, extending the duration time to more than 3 days for methanol-activated MOFs is inessential. Nevertheless, the opposite is true for acetone, which means that the surface area decreases steadily by increasing BET surface area. Moreover, the highest adsorption capacity (i.e., 45 mg/g) belongs to the 3d-E MOF, whose BET surface area was found to be the highest among all Gd-MOFs investigated in this research.

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were carried out to further examine the morphology and physical properties of 3d-E. Figure 4 exhibits the FESEM microphotographs of 3d-MOFs. MOFs activated by methanol and acetone show larger agglomerates, while the 3d-E MOF exhibits a separated rod-shape morphology. As it is obvious, different activation solvents significantly affect the morphology and size of activated Gd-MOFs.

As it is evident in Figure 5a, the surface charge of every three activated MOFs is positive. The surface charge of 3d-M and 3d-A is almost the same (5.4 and 2.5 mV, respectively), but 3d-E owns the biggest charge value (13.6 mV). As a result, it can be suggested that the high drug adsorption capacity of 3d-E is ascribed to its higher surface charge value.

Figure 5b exhibits TGA thermograms of 3d-MOFs and 0d-DMF. As shown, a two-stage mass loss is observed. The first mass loss step occurred at temperatures between 145 and 186 °C, which is attributed to the evaporation of guest DMF molecules remaining in the pores of nanoparticles. It is clear that the weight loss of the 0d-DMF sample is relatively higher than that of other activated samples. This observation indicates the presence of more DMF molecules in the porous structure of the MOF.

Moreover, the 3d-E MOF thermogram is slightly above that of the two other Gd-MOFs, suggesting its better activation and exchanging of DMF molecules with ethanol molecules. Additionally, 3d-E decomposes at 518 °C, which is higher than 3d-A (500 °C) and 3d-M (505 °C) degradation temperature, unveiling higher stability of the 3d-E MOF. Furthermore, it can be observed that the ash content of the 0d-DMF sample is significantly higher than that of samples activated with volatile solvents, further indicating the presence of more DMF molecules.

Table 3. Kinetics Constants for Q<sub>t</sub> Adsorption onto the Gd-MOF

| samples | pseudo-1st order | pseudo-2nd order | intraparticle diffusion | q<sub>e,exp</sub> (mg/g) | q<sub>e,cal</sub> (mg/g) | pseudo-1st order | pseudo-2nd order |
|---------|------------------|------------------|-------------------------|------------------------|----------------------|------------------|------------------|
| 1d-M    | 0.725            | 0.9999           | 0.9580                  | 48.800                 | 2.315                | 48.780           |                  |
| 3d-M    | 0.779            | 0.9998           | 0.8892                  | 28.801                 | 2.360                | 27.855           |                  |
| 5d-M    | 0.379            | 0.9992           | 0.9368                  | 14.857                 | 1.534                | 15.015           |                  |
| 1d-A    | 0.280            | 1                | 0.8329                  | 42.151                 | 1.284                | 42.373           |                  |
| 3d-A    | 0.689            | 0.9998           | 0.8916                  | 37.137                 | 2.713                | 37.313           |                  |
| 5d-A    | 0.200            | 1                | 0.7619                  | 31.611                 | 1.131                | 31.746           |                  |
| 1d-E    | 0.389            | 0.9999           | 0.770                   | 39.586                 | 1.621                | 39.682           |                  |
| 3d-E    | 0.175            | 1                | 0.899                   | 50.668                 | 1.550                | 50.761           |                  |
| 5d-E    | 0.579            | 0.9999           | 0.9566                  | 39.146                 | 1.946                | 39.216           |                  |
| 0d-DMF  | 0.788            | 0.9997           | 0.9628                  | 37.977                 | 2.701                | 38.168           |                  |
of more DMF molecules in the pores of the MOF without the activation step.

3.4. Drug-Loaded Gd-MOFs. Due to higher adsorption capacity, only 3d-E is used for further analysis in drug loading experiments. To prove loading of Qt onto 3d-E, Fourier-transform infrared (FTIR) spectra before and after drug adsorption are illustrated in Figure 6. The similarity of FTIR spectra for 3d-E and 3d-E/Qt indicates that no new covalent functional groups are formed. According to Figure 6, for the pristine 3d-E MOF, the two peaks at 1400–1550 cm$^{-1}$ indicate stretching vibrations of C=C and C=O bonds. The characteristic sharp peak of Qt at 3400 cm$^{-1}$ refers to the hydroxyl (O–H) group of the Qt phenol ring, which after drug loading into 3d-E (3d-E/Qt) gets smaller. This indicates that the hydroxyl group of Qt interacts via a hydrogen bond with the carboxyl group of 3d-E. Moreover, for the spectrum of 3d-E/Qt, a weak peak at 2830–2940 cm$^{-1}$ has appeared, attributed to the aromatic C–H Qt group, in which the peak intensity increases by increasing the amount of drug adsorption (Figure 9c). As a result, the FTIR spectra confirmed Qt adsorption into the 3d-E MOF by possible π−π stacking and hydrogen bond interactions between the hydroxyl group of the Qt phenol ring and the carboxyl group of 3d-E. In addition to the interactions mentioned above, electrostatic attractions can be essential in adsorption. Since the Qt structure contains positive and negative polar regions, electrostatic attractions exist between negative polar regions of Qt and positively charged 3d-E MOFs.

3.5. Isotherm Adsorption. Among different activated Gd-MOFs, 3d-E is selected to perform isotherm adsorption analysis because 3d-E has the highest specific surface area, capacity to adsorb Qt, and high crystalline structure. Figure 7 depicts the isotherm behavior of Qt adsorption on the 3d-E MOF. By increasing the initial concentration of Qt solution, the equilibrium adsorption capacity of Qt increases until it reaches an equilibrium where the diagram becomes a plateau and remains unaffected by increase in the initial concentration of Qt solution. Therefore, the maximum drug loading capacity of 3d-E is found to be 370 mg/g. As presented in Table 4, this loading capacity is compared to that of other adsorbents reported in the literature. As can be deduced, the loading capacity of this MOF is one of the highest adsorbent capacities among the reported ones. Four well-known isotherm models, Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin models, fitted to the experimental data. According to these models, the best fit is obtained for the Langmuir model, indicating monolayer adsorption onto a homogeneous surface. As a result, the adsorption of Qt on the 3d-E MOF is mainly due to the high crystalline structure, high specific surface area, and the capability of holding more Qt molecules within the pores of the MOF.
isotherm data (Figure 8), and relevant data are collected in Table 5. Accordingly, it is realized that the Temkin model, with a slight difference compared to the Freundlich model, has the highest $R^2$ and fits the experimental data better than other models. According to this model, binding energy and heat of adsorption of molecules in the layer decrease linearly by increasing adsorbing molecules on the surface.

This model further validates that Qt adsorption onto 3d-E is a chemisorption process. Furthermore, the positive value achieved for $B_T$ (19.96 kJ/mol) from the Temkin model emphasizes that the adsorption process is a spontaneous exothermic reaction.

### 3.6. Thermodynamic Study

According to Table 6, the free energy of Qt adsorption onto 3d-E is negative, so the adsorption of Qt onto the 3d-E MOF is spontaneous. However, according to eq 12 and the negative value of $\Delta S^0$, it is clear that a more ordered arrangement of Qt molecules on the surface of 3d-E is formed during the adsorption process. Accordingly, the randomness at the solid–solution interface is decreased. Moreover, the Qt adsorption process onto 3d-E is spontaneous ($\Delta G^0$ remains negative) only at low temperatures, which means that the adsorption process is thermodynamically controlled by enthalpy change. Since the $\Delta H^0$ value is negative, the adsorption reaction is exothermic, coinciding with the Temkin isotherm model as well, and as a result, the adsorption capacity decreases with the rising temperature.

#### Table 5. Isotherm Parameters of Qt Adsorption for Four Isotherm Models

| Adsorbent | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ (mg/g) | $n$ | $R^2$ | $q_{max}$ (mg/g) | $B$ (mol$^2$·kJ$^{-2}$) | $E$ (J/mol) | $R^2$ | $B_T$ (kJ/mol) | $A_T$ (L/g) | $R^2$ |
|-----------|-------------------|--------------|-------|--------------|----|-------|------------------|------------------|-----------|-------|---------------|------------|-------|
| 3d-E      | 625               | 0.008        | 0.887 | 8.848        | 1.35 | 0.924 | 303.87           | $5 \times 10^{-5}$ | 1 $\times 10^2$ | 0.855 | 19.96         | 0.11       | 0.970 |

#### Table 6. Thermodynamic Parameters of the 3d-E MOF and Other Adsorbents Reported in the Literature

| Adsorbent           | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/mol K) | references |
|---------------------|-----------------------|-----------------------|------------------------|------------|
| 3d-E                | $-3.112$              | $-4.923$              | $-6.0784$              | this work  |
| PS/PAM IPN          | $-4.28$               | $-27.08$              | $-76.51$               | 72         |
| Fe$_3$O$_4$@PAA@UiO-66-NH$_2$ | $-4.43$           | $-23.54$              | $-65.21$               | 42         |
| SHA-PS/SiO$_2$      | $-26.37$              | $-20.27$              | $20.46$                | 61         |
are also collected. Upon comparing the parameters with those of 3d-E, it is shown that $\Delta G^0$ of Qt adsorption onto 3d-E has the lowest amount among other adsorbents.

### 3.7. pH Effect

As shown in Figure 9a, the adsorption capacity rises by increasing or decreasing the pH value relative to 5. This change in adsorption capacity can be due to variation in the $\zeta$ potential of the 3d-E MOF, ionization degree, and chemical stability and structure of Qt. Furthermore, XRD and FTIR analyses were performed to determine the stability of the 3d-E MOF and Qt at different pH after the adsorption process (Figure 9b,c). According to XRD analysis (Figure 9b), after the adsorption mechanism, the 3d-E MOF was found to be stable at basic pH values (7.6 and 9.1). However, as pH decreased to an acidic value ($\text{pH} = 2$), the crystalline structure of 3d-E started to collapse. It may be stated that at acidic pH (2.1−1.5), some ligands of the crystalline structure of 3d-E began to be separated from the Gd nodes. Consecutively, the pores inside the framework started to grow so that 3d-E could adsorb more drug into the pores than the pristine one; this mechanism is known as the pore filling mechanism.\(^{76}\)

FTIR spectra (Figure 9c) at different pH values show no changes in the stability of the 3d-E MOF structure. However, it signifies that by increasing the amount of Qt adsorption into the 3d-E MOF at pH values of 2, 7.6, and 9.1, the characteristic peak in the range of 2830−2940 increases compared with that at a natural pH of 5. Therefore, the safe pH range for the 3d-E MOF is 5−9, which agrees with the literature.\(^{35}\) Regarding the stability of the 3d-E structure under alkaline conditions, it can be stated that the rise in Qt adsorption capacity by increasing the pH value is due to the more electrostatic interactions between the Qt and the 3d-E MOF. Because at basic pH values, the surface charge of Qt molecules becomes more negative than that at normal pH values,\(^{55,77}\) more Qt molecules are adsorbed by the surface of the 3d-E MOF.

### 3.8. ICP Analysis

To study the stability of the 3d-E MOF during the Qt adsorption process, inductively coupled plasma (ICP) analysis was done to measure the amount of released Gd$^{3+}$ ions. Accordingly, the Qt adsorption test was done with 200 mg/L 3d-E poured into 25 mL of 20 ppm Qt solution. After specified intervals (20, 40, and 60 min), 8 mL of the solution was taken out. The separated solution was centrifuged and then investigated by ICP analysis. Regarding Figure 10a, the leaching of Gd$^{3+}$ ions after 20 min of the drug adsorption process was 0.15 mg/L, and then, after 40 min, it increased subtly (0.22 mg/L). Moreover, the release of Gd$^{3+}$ ions after 40 min was almost unchanged, indicating that the structure of a few MOFs at the first interval collapses. However, after 40 min, the amount of released Gd$^{3+}$ ions does not change, and the crystalline structure of other existent MOFs remains intact.

### 3.9. Regeneration and Cycle Study

In order to evaluate the structural stability and reusability of 3d-E, adsorption−desorption cycles were studied. After each adsorption cycle, the adsorbents were washed with NaOH solution ($\text{pH} \approx 8$) and ethanol under sonication for 20 min and dried in an oven at 50 °C under vacuum. The results (Figure 10b) show that 3d-E almost maintains its adsorption capacity after four cycles, and its adsorption efficiency reduces by about 14% after four Qt adsorption−desorption cycles. From the above-mentioned result, it can be stated that the reusability of 3d-E is at an acceptable level.

### 4. CONCLUSIONS

In this work, a simple activation method was presented to increase the specific surface area of synthesized Gd-MOFs. Accordingly, different conditions as various solvents over different durations were applied to activate the MOFs after synthesis. In the following, the crystalline structure, morphology, specific surface area, and drug adsorption behavior of activated MOFs were studied. After this, the best MOF in terms of the crystalline structure, specific surface area, and highest adsorption capacity was selected which was 3d-E for
further analysis, including the isotherm, thermodynamics, and pH effect on Qt adsorption. The results show that the mechanism of drug adsorption by the 3d-E MOF can be interpreted by possible π−π stacking between aromatic rings of Qt and 3d-E and hydrogen bond interactions.

Furthermore, the role of electrostatic interactions between Qt molecules and 3d-E cannot be ignored. As reported in the literature, the pore diameter of MOFs plays a vital role in adsorption. However, in this work, maximum adsorption capacity belongs to the 3d-E MOF, which has the smallest pore diameter (7.79 nm) compared to other activated MOFs. Therefore, the interactions mentioned above have a more critical role than pore diameter in Qt adsorption onto the 3d-E MOF. The adsorption process of Qt onto the 3d-E MOF is spontaneous at low temperatures and is an exothermic reaction. The adsorption capacity of the 3d-E MOF increases with the change in the pH value, and its maximum adsorption capacity is approximately 370 mg/g. The results of this work indicate that by applying a simple activation method, adsorption capacity of the Gd-MOF can increase dramatically, which is an optimistic point for this MOF to be used as a drug carrier and MRI CA.

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Notes
The authors declare no competing financial interest.

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