



Research Article

Cobalt Iron-Metal Organic Framework Coordinated to CMC Aerogel by Solvothermal Method and Application to Tetracycline Antibiotics Adsorption

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Received: 27th October 2022; Revised: 20th December 2022; Accepted: 24th December 2022

Available online: 25th December 2022; Published regularly: December 2022



Abstract

In order to minimize the adverse impacts on the aquatic environment after treatment process, several attempts have been made to develop biodegradable, easy-to-recover, and environmentally friendly materials. The metal-organic framework material (CoFe-MOF) was developed in the CMC aerogel matrix by solvothermal method and applied in tetracycline antibiotic (TCC) adsorption. The morphological and structural properties of the materials were analyzed by scanning electron microscope (SEM), x-ray diffraction (XRD), Fourier Transform Infra Red (FT-IR), and (Brunauer-Emmett-Teller) (BET) to identify the crystals formed relative to the pristine MOF. The effects of various factors of the adsorption process such as time, pH, amount of adsorbent, and initial concentration of antibiotics were investigated. Results have shown that the adsorption capacity was 188.7 mg.g⁻¹ at pH 4, the initial TCC concentration of 80 g.L⁻¹ and equilibration time of 120 min. The experimental data describing the antibiotic adsorption process follows the Pseudo-second-order kinetic model and the Langmuir isothermal model. The CoFe-MOF aerogel material can recover and reuse all four cycles, thus it can be considered as a promising material for environmental remediation and other applications.

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Keywords: Aerogel; MOFs; Adsorption; Antibiotics; Solvothermal

How to Cite: T.K.N. Tran, V.P. Nguyen, A.C. Tran, T.H.N. Le, T.T.N. Tran (2022). Cobalt Iron-Metal Organic Framework Coordinated to CMC Aerogel by Solvothermal Method and Application to Tetracycline Antibiotics Adsorption. *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(4), 872-881 (doi: 10.9767/bcrec.17.4.16281.872-881)

Permalink/DOI: <https://doi.org/10.9767/bcrec.17.4.16281.872-881>

1. Introduction

To date, antibiotics pollution in water environment (e.g. ciprofloxacin, tetracycline, sulfa-

methoxazole, sulfadiazine) is at an alarming rate. As antibiotic compounds are often not metabolized well in humans and animals, and are not removed completely by wastewater treatment plants, thus the remaining are discharged into the aquatic environment, causing a serious

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impact on water quality. Therefore, global scientific and social concerns have been raised to develop effective and applicable methods for antibiotics removal from water sources [1–5].

Metal-organic frameworks (MOFs) are formed by binding organic ligands with metal-containing nodes through coordination bonds. These bridging properties play an important role in the formation of MOFs. Simultaneously, the shape of metal ions determined the structure of MOFs after synthesis. With their porous structure, large surface area, stability, and high functional group activity, MOFs are promising candidates for various applications such as gas storage, catalysis, adsorption, drug delivery, and sensing [6–9]. Therefore, MOFs are expected to become promising materials for many fields in the future. However, some applications of MOFs are hindered by their hardness and their high susceptibility to crumbling. In addition, some MOFs have poor aqueous stability, mainly in powder form, leading to agglomeration and complicating recycle. Therefore, the materials that can immobilize MOFs has been developed to effectively support the recovery and reuse of MOFs. In order to overcome these disadvantages, MOF materials are developed on different substrates, such as synthetic polymers, metal foams, and metal oxides. Specifically, Yang *et al.* generated Ni/Co–MOFs with support by a highly porous 3-dimensional (3D) carboxymethylcellulose sodium (CMC) aerogel as a substrate [10]. In 2021, Nuhaa Shaheed and colleagues successfully synthesized Cu-BTC/CNC (crystalline nanocellulose) and Cu-BTC/NFC (nanofibrillated cellulose) aerogel materials by direct mixing Cu-BTC powder with the pre-liquid solution, followed by gel formation and freeze-drying [11]. Liu *et al.* synthesized MOF(Fe)/HNTs material by adding HNTs by slightly increasing the specific surface area of the aerogel [12].

Aerogels are a special 3D material characterized by high porosity, open structure, and large specific surface area, with a density of about $0.004\text{--}0.005\text{ g}\cdot\text{cm}^{-3}$ [13]. Due to their distinct properties, aerogels are attractive for many applications, ranging from (1) energy insulation and storage, (2) drug delivery and packaging, (3) catalysis, to (4) adsorption and removal of contaminants in water and air. Aerogels are multifunctional materials with 3D bonded gel networks which can be prepared by either the drying method or the sol-gel method [14]. Various types of aerogels such as metal oxide aerogels, polymeric aerogels, silica aerogels, organic aerogels, protein-based aerogels, and carbon-based aerogels have been studied

[15–17]. Compared with other aerogels, aerogels based on MOFs have a high specific surface area and enhanced mechanical properties, due to the microporous and rigid structure of MOFs [18]. In the presence of aerogels as the matrix, the MOF crystals become more stable for growth and dispersion.

In recent years, in order to improve biodegradability, easy reuse, low cost, and environmentally friendliness, cellulose aerogel is considered a potential substrate with aqueous stability, easy recycling and recovery, and a porous structure, hence the use in the adsorption process for environmental treatment. However, research on aerogel composites containing MOF-derived materials for antibiotic treatment have remained limited. Therefore, in the present study, the MOF aerogel material was synthesized on the carboxymethylcellulose sodium (CMC) substrate, followed by evaluation of the adsorption capacity of the material for tetracycline (TCC) antibiotic in the aquatic environment.

2. Materials and Methods

2.1 Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$), Terephthalic acid ($\text{HOOC}(\text{C}_6\text{H}_4)\text{COOH}$), N,N-Dimethylformamide ($(\text{CH}_3)_2\text{NCHO}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$) were obtained from Xilong Chemical Co., Ltd. (Shantou, China), Sodium Carboxymethyl Cellulose ($\text{C}_6\text{H}_9\text{OCH}_2\text{COONa}$), Tetracycline ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). All chemicals and reagents were of analytical grade and more than 99% of purity.

2.2 Preparation of CoFe-MOF Aerogel

Co-doped Fe-MOFs materials were synthesized by using the solvent heat method as described previously by Tran *et al.* [19]. Specifically, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (2.1 g), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.68 g), and 1,4-benzene dicarboxylic acid (0.83) were dissolved in 60 mL of DMF, then stirred homogeneously (solution A) [19]. Besides, 2 g of CMC was mixed homogeneously with 30 mL of deionized water until a clear solution was obtained, which was then transferred to a 96-well plate and incubated for 1 h for gel formation. Finally, the gel was subjected to freeze-drying to obtain CMC aerogel. Small cylinders of CMC aerogel were then inserted into a 100 mL stainless steel Teflon tube, added with solution A and heated at $120\text{ }^\circ\text{C}$ for 20 h. The material

samples were further cleaned with DMF and ethanol solvents. Finally, the product was dried at 120 °C for 12 h.

2.3 Adsorption of Tetracycline with CoFe-MOF Aerogel

The factors affecting the adsorption process such as initial concentration, adsorption time, pH, and amount of adsorbent were investigated to evaluate the effectiveness of antibiotic removal in an aqueous solution. The experimental procedure was carried out in an aqueous medium by evaluating the factors affecting the adsorption capacity. The specific adsorbent at the concentrations of 0.002–0.04 g.L⁻¹ was added into a conical flask (250 mL) containing 50 mL of TCC antibiotic solution (10 – 100 mg.L⁻¹). The pH of TCC solution was adjusted

at a range of 3–10 using HCl and NaOH (0.1 M). The experiments were carried out for 3 hours to reach equilibrium. The solid was removed from the solution after the adsorption process. The final solution concentration was determined at the maximum absorption wavelength on a UV-Vis instrument (Thermo, USA). All experiments were repeated three times and the data were represent as mean ± standard deviation (S.D.).

2.4 Characterizations

X-ray diffraction (XRD) method was performed using D8 Advanced - Hitachi (Germany) to analyze the structure and crystalline phase composition of the material at Cu K α radiation ($\lambda = 1.54188 \text{ \AA}$). Scanning electron microscope (SEM) was used to determine

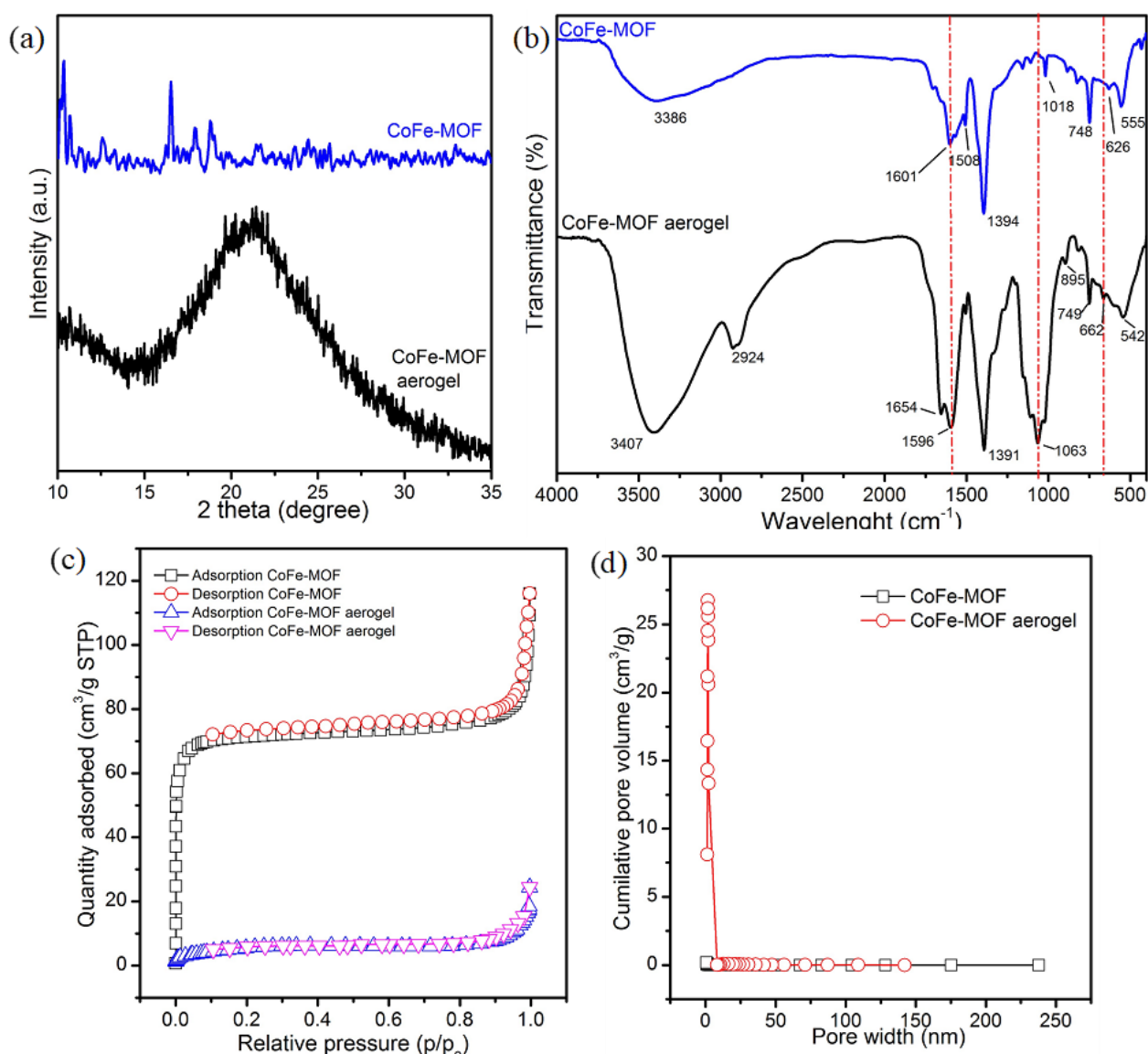


Figure 1. XRD patterns (a), FT-IR spectra (b), N₂ adsorption-desorption isotherms (c) and pore size distributions (d) of CoFe-MOF aerogel samples.

the surface morphology and particle size of the materials using S4800 - JEOL Japan. Fourier transform infrared spectroscopy (FTIR) determined the presence of functional groups in materials on a Nicolet 6700 (Thermo Fisher Scientific, USA) instrument with wave numbers ranging from 4000 to 400 cm^{-1} . Capillary characteristics and specific surface areas were analyzed on Micromeritics 2020 - Micromeritics (USA) equipment by N_2 desorption isotherm method (BET).

3. Results and Discussion

3.1 Characterization of CoFe-MOF Aerogel

The crystallinity of the prepared CoFe-MOF aerogel materials was characterized using XRD analysis. Figure 1(a) shows that the XRD results of the prepared materials exhibits a strong peak at $2\theta = 21^\circ - 22^\circ$, which is attributed to the cellulose II crystal structure, compared to a strong peak at $2\theta = 10.3^\circ, 16.6^\circ$, and 18.8° of CoFe-MOF. The high similarity between the XRD patterns of the CoFe-MOF aerogel diffraction patterns is due to the limited number of CoFe-MOF additions and the relatively low diffraction intensity. The study of Cong Huang *et al.* has successfully synthesized MOF material combined to the cellulose aerogel with crystal forms similar to that of the original MOF material based on a typical characteristic peak around 20° on an XRD sample [20].

To detect the functional groups in the CoFe-MOF aerogel structure, FT-IR spectroscopic analysis was shown in Figure 1(b). The peaks at 3386 and 3407 cm^{-1} show the covalent bond OH in the water molecule adsorbed on the surface of the material. The ranges from 7.48-1018 cm^{-1} (CoFe-MOF), and from 749-1063 cm^{-1} (CoFe-MOF aerogel) are assigned to the C-H

elongation of the benzene ring, respectively. The peaks at 1394-1598 cm^{-1} (CoFe-MOF) and 1391-1596 cm^{-1} (CoFe-MOF aerogel) are attributed to asymmetric ($\nu_{as}(\text{C}-\text{O})$) and symmetric ($\nu_s(\nu_s)$) oscillations. C-O)) of the carboxyl groups of BDC are coordinated to the central metal, indicating the formation of dicarboxylate group bonds in the sample [21]. In addition, the CoFe-MOF aerogel has a sharp peak at 1654 cm^{-1} (very strong) and the vibrational characteristics of the C=O asymmetric bond, which have been shifted slightly to a higher wavelength than that of CoFe-MOF [22]. The peaks at 555 and 542 cm^{-1} represent Fe-O, and the peaks at 626 and 662 cm^{-1} represent Co-O bending fluctuations in CoFe-MOF and CoFe-MOF aerogel samples, respectively.

The average capillary structure of the CoFe-MOF aerogel material was determined based on the set point of the N_2 adsorption-desorption isotherm (BET) showing the type II hysteresis ring (according to IUPAC classification) (Figure 1(c)-(d)). Compared to CoFe-MOF, the surface area and the pore volume of the experimentally synthesized CoFe-MOF aerogel decreased from 280.9 to 11.7 $\text{m}^2\cdot\text{g}^{-1}$ and from 2.2 to 0.02 $\text{cm}^3\cdot\text{g}^{-1}$, respectively. The surface area depletion can be attributed to the presence of CMC in the aerogel structure which is significantly less porous in nature than that of CoFe-MOF, depending on the MOF particles anchored on the aerogel matrix. On the other hand, the large pore size can facilitate the diffusion of antibiotic molecules to the surface of the material, whereas the adsorption efficiency decreases when the pore size is too small, even though the surface area is high [23].

The morphology and structure of CoFe-MOF and CoFe-MOF aerogel are shown in Figure 2 according to the optical image, the CoFe-MOF aerogel material grows and has the color of the

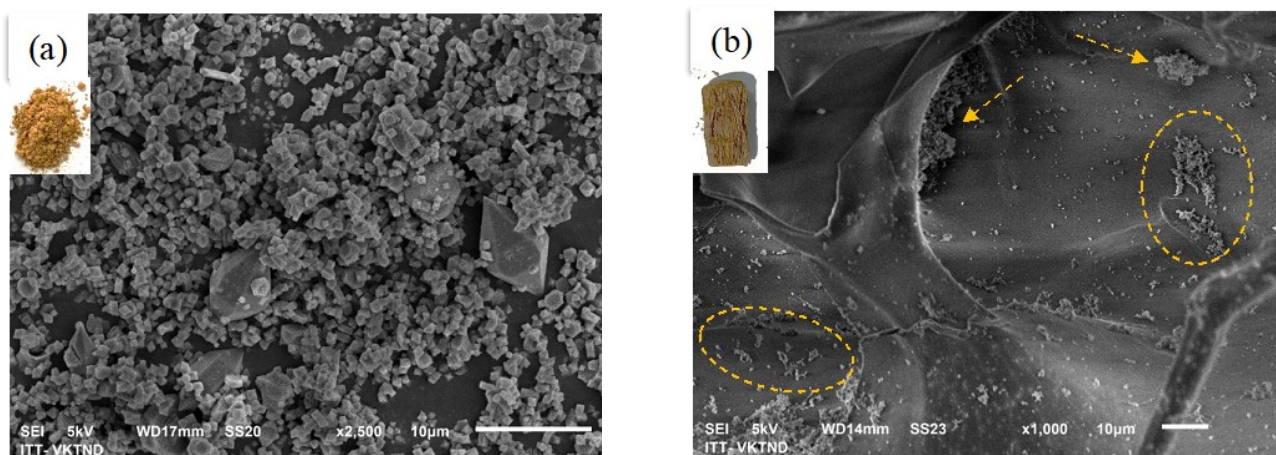


Figure 2. SEM image of CoFe-MOF aerogel.

synthetic hybrid material as light brown. CoFe-MOF aerogel presents an interconnected three-dimensional lattice structure and the MOFs contained therein exhibit good dispersion, which further proves that the three-dimensional lattice structure can effectively limit the growth and agglomeration of MOF particles. The different CMC contents in the aerogel lead to different morphology and structure of CoFe-MOF aerogels with MOF particles grown in a different lattice framework. CoFe-MOF aerogel has an uneven surface due to the growth of MOFs and the distribution of CoFe-MOFs in all locations on the flat aerogel surface of the CoFe-MOF aerogel sample.

3.2 Effect of Operating Parameters on Antibiotic Adsorption Capacity

The surface properties of the CoFe-MOF aerogel and the state of existence of the TCC molecule are both affected by the solution pH. Therefore, the batch adsorption was carried out at different pH levels from 3 to 10. As shown in Figure 3(a), after a period of 120 min, it can be seen that the adsorption capacity increases sharply. When the pH value increased from 3 to 4 and above 5, the maximum adsorption capacity ($32.2 \text{ mg}\cdot\text{g}^{-1}$) was achieved at pH 4. The pH affects the absorption and dissociation of compounds. The charge distribution on the adsorbent surface and the oxidizing capacity of the adsorbent valences. Changes in Ph level can affect the adsorption of TCC molecules to the material surface. Specifically, the isoelectric point (pzc) of CoFe-MOF aerogel in an aqueous medium is 4.2 (Figure 3(b)). When the solution has a $\text{pH} < \text{pH}_{\text{pzc}}$, the material surface

is positively charged and reversely when the solution has a $\text{pH} > \text{pH}_{\text{pzc}}$, the surface of the material is negatively charged. Under different pH conditions, TCC exists as the cation TC^+ ($\text{pH} < 3.3$), the zwitterion form TCC^0 ($3.3 < \text{pH} < 7.69$) and TCC exists as the anion TCC^- ($7.69 < \text{pH} < 9.69$) and TCC^{2-} ($\text{pH} > 9.69$) [24]. The surface of CoFe-MOF aerogel is positively charged at $\text{pH} < 4.2$. In an acidic environment, it is difficult for TCC molecules to be adsorbed on the surface of the material because of the electrostatic interaction between the positively-charged surface of CoFe-MOF aerogel and the TCC cation. TCC molecules exist in a quasi-neutral zwitterion form, which is electrostatically attracted by the positively charged mixture, leading to a significant increase in the adsorption capacity of TCC. On the other hand, in alkaline environments with antibiotics, TCC carries a negative charge. Therefore, the surface of CoFe-MOF aerogel accumulates a lot of negative charge, and the positive charge on the surface of the adsorbent decreases gradually, while the negative charge of TCC gradually increases. Furthermore, at higher pH, the residual OH^- competes with TCC^{2-} for binding to the adsorbent [20]. As a result, a dominant electrostatic repulsion between CoFe-MOF aerogel and TCC occurs and results in a low amount of TCC adsorption.

The adsorption process occurred from 10 to 240 minutes, while other experimental conditions were maintained constant, including adsorbent of 0.01 mg pH 4, and the initial concentration of TCC of $20 \text{ mg}\cdot\text{L}^{-1}$. As shown in Figure 4(a), at the early stage (0–120 min), the adsorption capacity rapidly increased the contact time

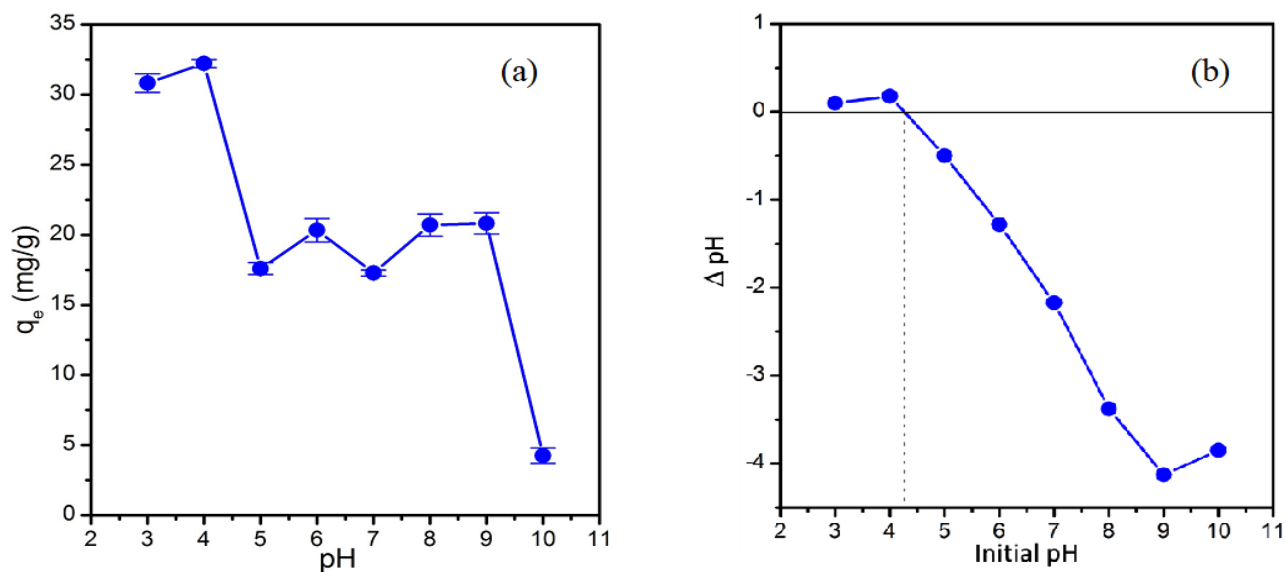


Figure 3. Effect of initial pH (a) and zero charge point (b) of CoFe-MOF aerogel.

was prolonged. The adsorption equilibrium was observed at nearly 120 min with a maximum adsorption capacity of 33.95 mg.g^{-1} . The results indicate that the removal efficiency is enhanced by increasing contact time due to the presence of empty active sites that are capable of capturing TCC molecules. However, after about 120 min of the process, due to the saturation of the active sites, the removal efficiency was remained almost constant.

After 120 min, the content of the material increased from 0.002 to 0.01 g.L^{-1} , the adsorption efficiency of the TCC solution of the material increased rapidly from 26.96 to 73.42% and the adsorption capacity decreased gradually from 115 to 62.65 mg.g^{-1} (Figure 4(b)). The increase in antibiotic removal efficiency with increasing dose may be due to an increase in the total surface area and adsorption sites of the

adsorbent, similar to the study Seyed Mohammad *et al.* [24]. This forms more space for antibiotic molecules to be adsorbed on the surface of the material. Under the condition of a small amount of adsorbent, the number of reactant molecules is higher than that of reaction centers. Thus, when increasing the amount of adsorbent, the reaction rate and adsorption efficiency increase. However, if the amount of adsorbent continues to increase, the adsorption center would decrease due to the collision and contact between the particles, thus leading to a decrease in the adsorption capacity.

Figure 4(c) shows the effect of initial TCC antibiotic concentration on the ability to eliminate TCC antibiotics. For CoFe-MOF aerogel, when increasing the initial concentration at equilibrium for 120 min of TCC solution (low concentration $10\text{-}80 \text{ mg.L}^{-1}$), the adsorption ca-

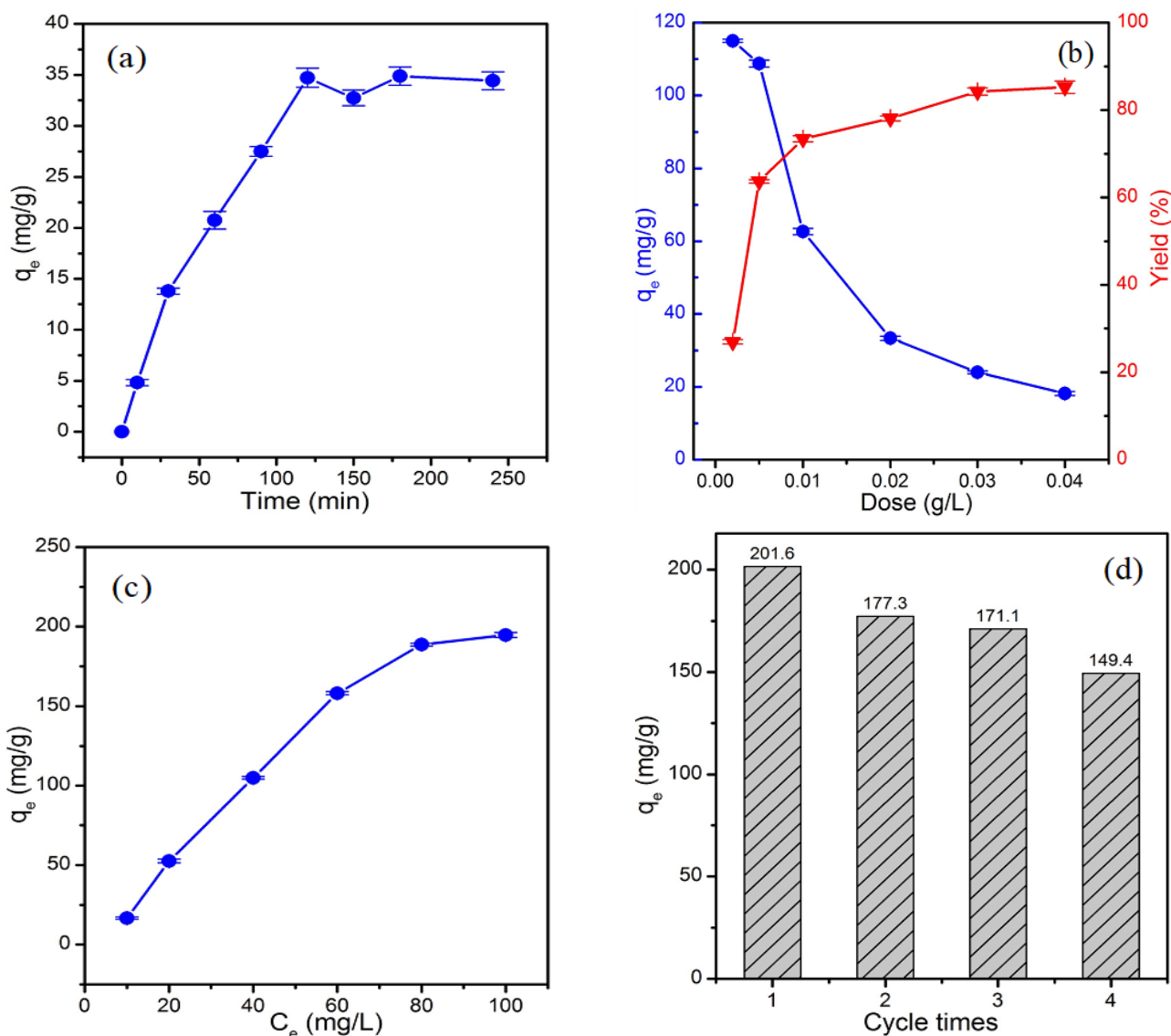


Figure 4. Effect of time (a), dose (b) and TCC initial concentration (c), and recycle (d) on the adsorption capacity of CoFe-MOF aerogel.

capacity was linearly increased from 16.6 to 188.7 mg.g⁻¹. However, continuing to increase the concentration to more than 100 mg.L⁻¹ would result in increasing the adsorption capacity (196.7 mg.g⁻¹). At low TCC concentration, there are many more positions on the surface of CoFe-MOF, leading to gradual increase in the capacity. In contrast, when the initial concentration of TCC is high, many TCC molecules are adsorbed on the surface of CoFe-MOF aerogel, which hinders the diffusion of TCC molecules and their effect with photogenic holes or hydroxyl radicals.

The important factor when assessing the actual usability of the material is based on the reuse of the adsorbent in four consecutive uses, at constant conditions (Figure 4(d)). Before use, the CoFe-MOF aerogel adsorbent was washed

with ethanol and dried at 120 °C for 20 h. TCC adsorption capacity after four cycles did not change significantly from 201.6 mg/g to 149.4 mg/g. The decreasing adsorption capacity may be due to the elution process that has not completely removed the TCC molecules, the adsorption sites are covered. Overall, the results show that the antibiotic removal efficiency of the material decreases after each reuse cycle. This phenomenon may be due to the masking of adsorption sites on the surface of CoFe-MOF aerogel materials, thus reducing the capture of antibiotic molecules by the adsorbent. Similarly, Cong Huang *et al.* indicated that the antibiotic removal capacity decreased over the cycles due to the loss of adsorbent after each experiment [20].

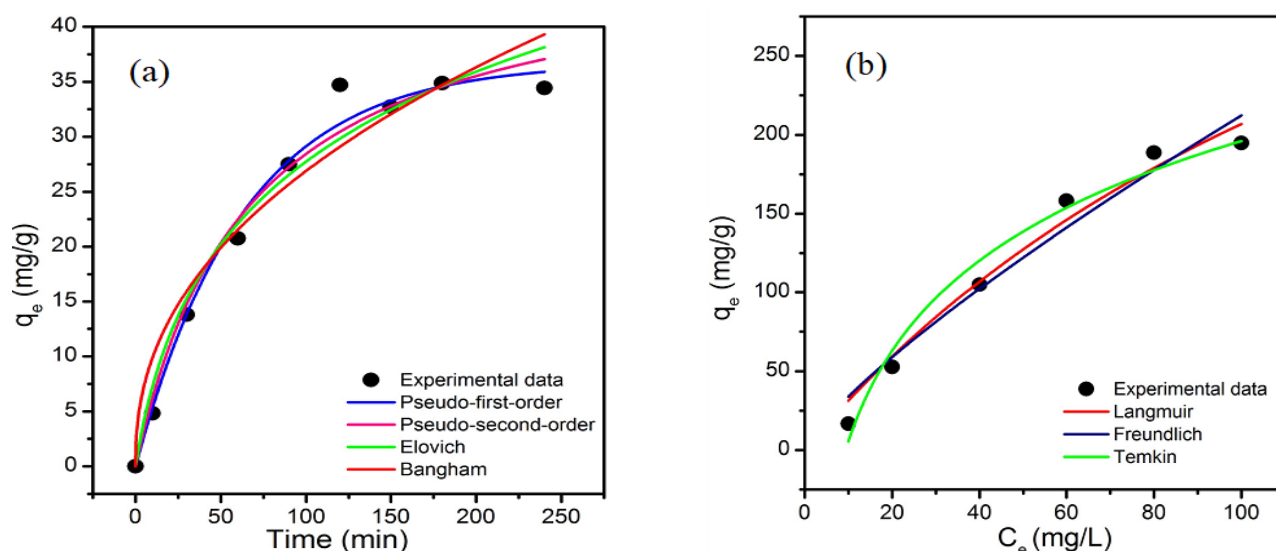


Figure 5. Kinetic (a) and isothermal (b) model of TCC adsorption on to CoFe-MOF aerogel.

Table 1. The adsorption kinetic constants.

Kinetic models	Equation	Parameters	Value
Pseudo-first-order	$Q_t = Q_1 (1 - \exp(-k_1 t))$	$k_1 (\text{min}^{-1}/(\text{mg/L})^{1/n})$	0.0157
		$Q_1 (\text{mg.g}^{-1})$	36.75
		R^2	0.9857
Pseudo-second-order	$Q_t = \frac{t}{\frac{1}{k_2 Q_2^2} + \frac{t}{Q_2}}$	$k_2 \times 10^4 (\text{g}/(\text{mg.min}))$	3.1877
		$Q_2 (\text{mg.g}^{-1})$	47.29
		R^2	0.9958
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	$\alpha \text{ mg}/(\text{g.min})$	0.974
		$\beta (\text{g.mg}^{-1})$	0.0773
		R^2	0.9843
Bangham	$\log \left(\log \left(\frac{C_m}{C_m - q_t \cdot \frac{m}{V}} \right) \right) = \log \left(\frac{k_B}{2.303V} \right) + \alpha_B \log t$	$k_B \text{ mL}/(\text{g.L})$	3.6417
		α_B	0.434
		R^2	0.9732

3.3 Adsorption Kinetics and Isotherm

The mechanism and rate of TCC adsorption can be determined through kinetic modeling (Figure 5(a)). The CoFe-MOF aerogel was studied with four models (Pseudo first-order, Pseudo second-order, Elovich, and Bangham). The fit curves of Pseudo first-order, Pseudo second-order, Elovich and Bangham are shown in Figure 5(a) and the corresponding parameter values are shown in Table 1. The correlation coefficient (R^2) of the kinetic model of CoFe-MOF aerogel is 0.9857, 0.9958, 0.9843, and 0.9732, respectively. It can be seen that the correlation coefficient R^2 of the PSO model is the highest ($R^2 = 0.99857$), indicating that the PSO model describes the TCC adsorption undergoing chemisorption on the surface of the PSO. The Elovich model has prominently demonstrated the adsorption and desorption rates of antibiotics on the surface of the material. According to Table 1, the adsorption and desorption rates are $0.974 \text{ mg} \cdot (\text{g}^{-1} \cdot \text{min}^{-1})$ and $0.0773 \text{ g} \cdot \text{mg}^{-1}$, respectively, indicating high TCC adsorption by the material. In addition, the Bangham model with a correlation coefficient $R^2 > 0.97$ shows that the model is suitable for the diffusion of TCC into the pores of CoFe-MOF aerogel materials.

The adsorption isotherm values are determined by Freundlich, Langmuir, and Temkin adsorption isotherm models in non-linear form, the adsorption isotherm parameters and correlation coefficient R^2 (Table 2 and Figure 5(b)). The adsorption isotherms of TCC on CoFe-MOF aerogel show the fit of the Langmuir model with correlation coefficient R^2 which is more suitable than the Temkin and Freundlich model, and Langmuir and Temkin isotherm model can better analyze the adsorption process of aerogel, with the corresponding correlation coefficients of Langmuir ($R^2 = 0.9752$),

Temkin ($R^2 = 0.9721$) and Freundlich ($R^2 = 0.915$). The results have shown that the uneven surface of the aerogel can form adsorption active sites with different energies. Furthermore, using the Langmuir equation, the maximum adsorption capacity was calculated as 550 mg/g , which is insignificantly high as compared to previous studies. However, the time to reach equilibrium (or maximum adsorption) for CoFe-MOF-aerogel (120 min) is much lower than other studies [24,25]. Finally, the adsorption of antibiotics on CoFe-MOF aerogel materials can be best explained by the Langmuir model with the highest R^2 value of 0.9709. Based on the results, the predominance of the monolayer adsorption mechanism can be applied to this case.

4. Conclusions

CoFe-MOF aerogel material on CMC substrate was successfully synthesized based on the solvothermal method. The CoFe-MOF aerogel material has a relatively high TCC adsorption capacity with an adsorption capacity of $188.7 \text{ mg} \cdot \text{g}^{-1}$ at pH 4, and an initial TCC concentration of $80 \text{ mg} \cdot \text{L}^{-1}$ in 120 minutes. Durability tests have demonstrated that the material has high strength after 4 reuse cycles (from $201.6 \text{ mg} \cdot \text{g}^{-1}$ to $149.4 \text{ mg} \cdot \text{g}^{-1}$). According to the isotherm adsorption model Langmuir, the maximum adsorption capacity of CoFe-MOF aerogel for TCC is $550.37 \text{ mg} \cdot \text{g}^{-1}$, and follows the Pseudo-second adsorption kinetic model. The electrostatic interaction between the surface of the adsorbent and the specific structure of the antibiotic TCC molecule is a factor that directly affects the adsorption capacity. This can be considered as a successful platform to improve the effectiveness of antibiotic adsorption in the water pollution treatment in recent years.

Table 2. The adsorption isotherm constant.

Kinetic models	Equation	Parameters	Value
Langmuir	$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$k_L (\text{L} \cdot \text{mg}^{-1})$	0.006
		$Q_m (\text{mg} \cdot \text{g}^{-1})$	550.37
	$R_L = \frac{1}{1 + K_L C_0}$	R^2	0.9752
Freundlich	$Q_e = K_F C_e^{1/n}$	$k_F (\text{mg/g})/(\text{mg/L})^{1/n}$	5.3897
		$1/n$	0.7976
		R^2	0.9514
Tempkin	$q_e = B_T \ln K_T + B_T \ln C_e$	$k_T (\text{L} \cdot \text{mg}^{-1})$	0.1068
		B_T	82.7517
		R^2	0.9621

Acknowledgements

This research is funded by Foundation for Science and Technology Development Nguyen Tat Thanh University under grant No. 2022.01.69/HD-KHCN.

Credit Author Statement

Author Contributions: Van Phuoc Nguyen: Conceptualization, Methodology; A Chau Tran: Formal Analysis; Thi Thanh Ngan Tran: Data Curation; Thi Kim Ngan Tran: Writting Draft Preparation, Visualization, Software, Project Administration; Thi Hong Nhan Le: Validation, Writing, Review and Editing.

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