

RESEARCH ON CIPROFLOXACIN ADSORPTION CAPACITY OF HKUST-1 SYNTHESIZED BY ELECTROCHEMICAL METHOD

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Abstract: Cu₃(BTC)₂ (or HKUST-1) is a metal-organic framework (MOF) material that was synthesized by electrochemical method from Cu and benzene-1,3,5-tricarboxylic acid with large surface area and high porosity. The influence of some factors on the adsorption of ciprofloxacin (CIP) by Cu₃(BTC)₂ such as pH (4 - 11), initial concentration of CIP solution (10 - 80 mg/L), mass of adsorbent (1 - 5 mg) and adsorption time (10 - 60 minutes) has been studied. The results showed that the highest CIP adsorption capacity of Cu₃(BTC)₂ was achieved at pH 7. When the mass of Cu₃(BTC)₂ adsorbent increased (19.6 - 100.2 mg/L), the CIP adsorption capacity decreased, and the CIP removal efficiency increased. With 39.4 mg/L of the adsorbent and 20 mg/L of the CIP solution, the CIP adsorption capacity was 238.44 mg/g and the CIP removal efficiency was 46.53 %. The adsorption process took place rapidly in the first 20 minutes then reached equilibrium after about 30 minutes. The study of adsorption kinetics and isothermal adsorption showed that the CIP adsorption process on Cu₃(BTC)₂ material is consistent with the pseudo-second-order kinetic model and the Langmuir model. The CIP adsorption mechanism of Cu₃(BTC)₂ is also shown: π - π interaction, hydrogen bond, and electrostatic interaction.

Keywords: Ciprofloxacin, metal-organic framework, HKUST-1, adsorption, wastewater.

Classification numbers: 3.4.2; 3.6.1; 3.7.3;

1. INTRODUCTION

Ciprofloxacin (CIP) is a second generation fluoroquinolone and is widely used in the treatment of bacterial infectious diseases in humans and animals [1]. When released into the environment, CIP is quite stable in water and less biodegradable, so the concentration of CIP in

environmental water is relatively high compared to other antibiotics [2]. The concentrations of CIP in surface water have been reported at $\mu\text{g/L}$ [2 - 5] even mg/L in some wastewater samples [6]. The residue of antibiotics in the environmental water, in general, can affect the ecosystem and human health; it may contribute to increasing human allergies and the spread of resistant bacteria [7]. Therefore, the elimination of antibiotics in environmental water is increasingly concerned by scientists.

Recently, many different processes are used to remove contaminants from the aquatic environment. These effective technologies are advanced oxidation processes; phase-changing processes including adsorption in different solid matrices and membrane processes; and biological treatment [8]. Compared with other technologies, the adsorption method is a simple, economical, and effective method to remove antibiotics from the aquatic environment that does not produce toxic intermediates [9].

Metal-organic framework (MOF) is an innovative class of porous material including metal sites and organic ligands to form infinite crystalline networks. MOFs have typical properties such as high surface area, adjustable pore size; so that, they can be used for numerous applications in wastewater treatment, gas storage, energy conversion, drug delivery, and catalysis. In the world, some MOFs were applied as an effective adsorbent for the removal of antibiotics (sulfonamide [10]; ceftazidime [7]; quinolone groups [11]) from aqueous solution. $\text{Cu}_3(\text{BTC})_2$ is one type of MOFs that has a large surface area and high porosity. In Vietnam, scientists in Ho Chi Minh City have studied $\text{Cu}_3(\text{BTC})_2$ -derived porous carbon to remove chloramphenicol from wastewater [12]. At the Vietnam Academy of Science and Technology, scientists synthesized $\text{Cu}_3(\text{BTC})_2$ by electrochemical method and used it to remove two types of azo colorants in water [13]. To be able to expand the application of $\text{Cu}_3(\text{BTC})_2$ in the field of wastewater treatment, we study the CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ material in water. Various factors that affect the adsorption capacity such as pH, initial CIP concentration, the mass of adsorbent, and adsorption time were studied. Moreover, the adsorption kinetics and the adsorption isotherms were investigated.

2. MATERIALS AND METHODS

2.1. Materials and equipment

Solvents and chemicals including triethylamine (Scharlau), orthophosphoric acid (Scharlau), all of pure analytical standard, and acetonitrile of HPLC standard (Merck) were used. Deionized water (resistivity $\geq 18 \text{ M}\Omega\cdot\text{m}$) was produced by a water purification system (Merck Millipore, Germany).

Ciprofloxacin hydrochloride (RS) is a Vietnamese pharmacopoeia Reference substance (93.9 % $\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3\cdot\text{HCl}$ as basic) Lot: C0419029.04.

$\text{Cu}_3(\text{BTC})_2$ ($\text{Cu}_3(\text{C}_9\text{H}_3\text{O}_6)_2$) material synthesized by electrochemical method, has a large surface area ($906 \text{ m}^2/\text{g}$), high porosity (pore volume of $0.54 \text{ cm}^3/\text{g}$ and average pore size of 2.40 nm) [13].

A liquid chromatography system (Agilent 1260) with a diode-array detector was used in this study. Other types of equipment include analytical balance (Mettler Toledo AG 245), pH meter, horizontal shaker were used.

Analytical column was Phenomenex Reversed-Phase (RP) 18 ($150 \times 4.6 \text{ mm}$; $3 \mu\text{m}$).

2.2. Method

2.2.1. HPLC method to determine ciprofloxacin concentration in water

The concentration of CIP was quantified using a high-performance liquid chromatography (HPLC) system (Agilent 1260) with a diode-array detector (DAD) at the wavelength of 278 nm. A Phenomenex C18 analytical column (150 × 4.6 mm, 3 μm) was used at 40 °C. The mobile phase consisted of 18 % (A) acetonitrile and 82 % (B) solution of 0.025 M orthophosphoric acid which was adjusted with triethylamine to pH 3.0; at a constant flow rate of 0.6 mL/min. A calibration curve was obtained for CIP at concentrations ranging from 2 to 50 mg/L.

The recovery (%) according to the calibration curve is calculated by:

$$\frac{C'}{C_0} \times 100$$

where, C' is the concentration of CIP solution (which is calculated based on the linear equation from y - the area of CIP peak); C₀ is the actual concentration of CIP solution.

Blank was deionized water.

Standard solution was a 20 ppm ciprofloxacin hydrochloride (RS) solution in deionized water.

Chromatograph the blank, standard solution, and record the responses.

The system suitability in the chromatogram obtained with the standard solution, the relative standard deviation (RSD) for replicate injections is not more than 2.0 %; the tailing factor (T) is not more than 2.0.

2.2.2. Validation of HPLC method to determine ciprofloxacin concentration in water

The analytical method is validated for specificity, system suitability, linearity, and accuracy according to the guidelines of the Association of Official Agricultural Chemists (AOAC) [14].

The relative standard deviation (RSD) is calculated according to:

$$RSD = \frac{100}{\bar{y}} \sqrt{\frac{\sum(y_i - \bar{y})^2}{n-1}}$$

where y_i is the individual area of CIP peak in the standard solution; \bar{y} is the average of the individual CIP area peaks; n is the number of replicate injections of the standard solution.

2.2.3. Adsorption test

The procedure of adsorption: Cu₃(BTC)₂ powder (from 1 to 5 mg) was added to 50 mL of 20 mg/L CIP solution (pH from 4 to 11, adjusted by 0.1 N NaOH and 0.1 N HCl solutions) and stirred (150 rpm) for a fixed time (from 10 to 60 mins) at room temperature (25 ± 2 °C). After a defined time, the solution was separated from the adsorbent by a syringe fitted with a 0.45 μm filter. The equilibrium concentration of CIP is determined by the HPLC method.

The adsorption capacity at equilibrium q_e (mg/g) is calculated according to:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \text{ (mg/g)}$$

The adsorption capacity at time t (min), q_t (mg/g) is calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \text{ (mg/g)}$$

The removal efficiency H (%) is calculated according to: $H (\%) = \frac{(C_0 - C_t)}{C_0} \times 100$

where C_0 , C_e are the initial and the equilibrium concentrations of CIP in solution (mg/L); C_t is the residual concentration of CIP at time t ; V is the volume of solution (L), and m is the mass of the adsorbent (g).

For adsorption kinetics studies, take different concentrations (10, 20, 40, 60, 80 mg/L) of 50 mL of CIP solutions (pH 7.0) and 2 mg of $\text{Cu}_3(\text{BTC})_2$ into conical flasks. The adsorption tests were carried out on a horizontal shaker at 150 rpm for a fixed times (from 10 to 60 minutes) at room temperature. The remaining concentrations of CIP after adsorption were measured by the HPLC method.

There are two kinetic models usually employed for adsorption, namely pseudo-first-order and pseudo-second-order.

The pseudo-first-order kinetic equation: $\ln(q_e - q_t) = \ln q_e - k_1 t$

The pseudo-second-order kinetic equation: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$

where: t is the adsorption time (min); k_1 (min^{-1}), k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the adsorption rate constants for pseudo-first-order and pseudo-second-order models, respectively.

For adsorption isotherm studies, batch adsorption experiments with 2 mg of $\text{Cu}_3(\text{BTC})_2$ at 25 °C were carried out at different initial CIP concentrations ranging from 10 to 80 mg/L (pH = 7.0). The final concentrations of CIP were measured by HPLC method.

The isothermal data were analyzed using two adsorption models, i.e. Langmuir and Freundlich isotherms.

Langmuir model: $\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m \cdot K_L}$

Freundlich model: $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$

where: q_m is the maximum adsorption capacity (mg/g); K_F [$\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$] and n are the adsorption constant and intensity constant of the Freundlich model, respectively.

K_L is the Langmuir adsorption constant (L/mg).

Additionally, the dimensionless separation factor (R_L) can also indicate the favorability of an adsorption process, and can be expressed by the following equation:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 is the maximum initial concentration of the adsorbate and the parameter suggests that the isotherm is either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), favorable (linear, $R_L = 1$) or unfavorable ($R_L > 1$ or $R_L < 0$) [11].

3. RESULTS AND DISCUSSION

3.1. Validation of HPLC method to determine CIP in water

3.1.1. Specificity

Equal volumes (100 μl) of blank and standard solutions were injected into the analytical column, the retention times and the area of CIP peak were recorded. In the chromatogram of

standard solution, one peak with a retention time of about 6 min was designated as the CIP peak. No peak with the same retention time was observed in the chromatogram of the blank solution (Figure 1). The UV spectrum of the CIP peak in the sample solution corresponds to that in the standard solution, and the match factor is 999.621 (Figure 2). So that, this HPLC method is specific to assay ciprofloxacin in water.

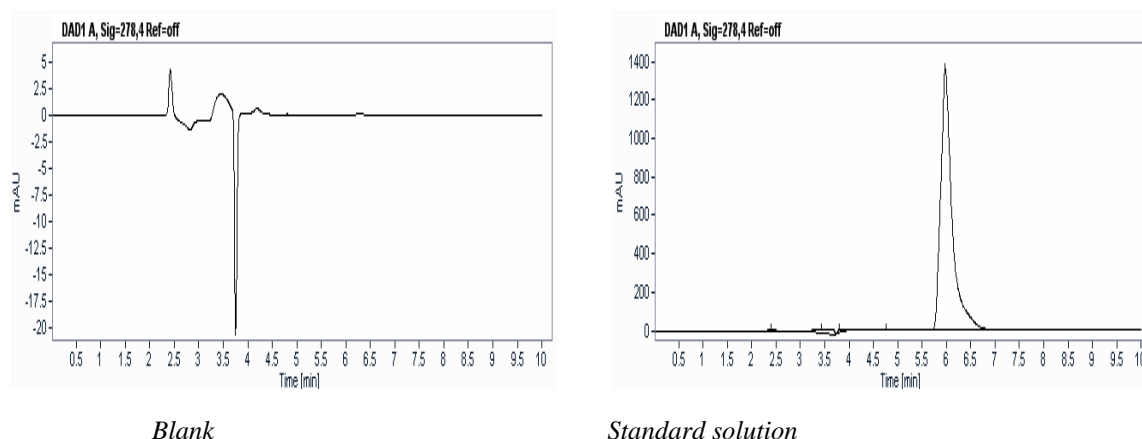


Figure 1. Chromatography of blank and standard solutions.

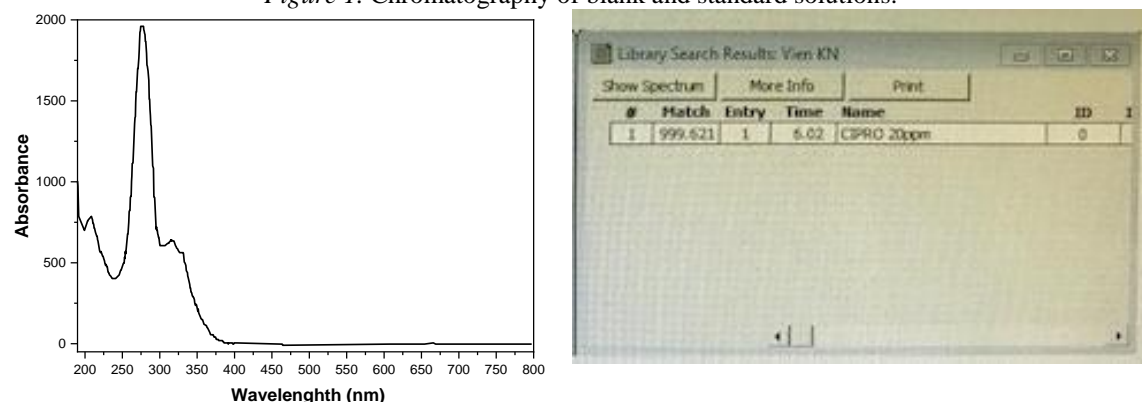


Figure 2. UV spectrum of CIP solution in water.

3.1.2. System suitability

Table 1. System suitability.

	1	2	3	4	5	6	Average	RSD %
Retention time (mins)	5.978	5.968	5.962	6.008	5.984	6.012	5.985	0.34
CIP peak area (mAU.s)	22229.3	22169.2	22157.0	22312.3	22245.2	22209.0	22220.33	0.25
RSD: Relative standard deviation ($RSD_{(peak\ area)} = 0.25\% < 2.0\%$ [14] and $RSD_{(retention\ times)} = 0.34\% < 1\%$; $T = 0.6 < 2.0$)								

The standard solution was chromatographed 6 times and the retention time, peak area, tailing factor were recorded. From the results shown in Table 1, we can conclude that the HPLC method meets the system suitability requirements.

3.1.3. Linearity

Standard solutions of ciprofloxacin in deionized water with concentrations ranging from 2 to 50 ppm were studied. Figure 3 shows a strong linear correlation between the CIP concentration in water (ppm) and the area of the CIP peak (mAU.s).

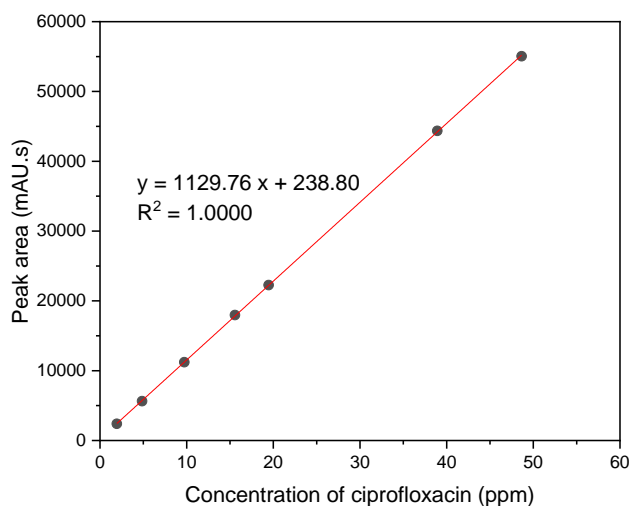


Figure 3. The linear correlation between the CIP concentration and the area of the CIP peak.

3.1.4. Accuracy

Table 2. Results obtained from the study of accuracy.

No	Concentration of CIP added (ppm)	The area of CIP peak (mAU.s)	Concentration of CIP recovered (ppm)	Recovery (%)
1.	4.865	5844.7	4.962	101.99
2.	4.865	5716.2	4.848	99.66
3.	4.865	5790.7	4.914	101.01
Average %				100.89
RSD %				1.16
4.	19.460	22403.0	19.618	100.81
5.	19.460	22356.5	19.577	100.60
6.	19.460	21985.5	19.249	98.92
Average %				100.11
RSD %				0.93
7.	38.920	44592.2	39.259	100.87
8.	38.920	44598.0	39.264	100.88
9.	38.920	44592.8	39.260	100.87
Average %				100.88
RSD %				0.01

The accuracy of the method was assessed by analyzing samples spiked at three different concentrations of 5, 20, and 40 ppm in triplicate at each concentration. Based on the area of the CIP peak and the calibration curve, the CIP concentration in these samples was determined. The results (Table 2) showed that the recovery of each level concentration is from 98.92 % to 101.99 % (within the limited range 98.0 % - 102.0 %). RSDs (%) of recoveries at each concentration level are less than 2.0 %, therefore, the method was satisfactory for accuracy.

3.1.5. Limit of detection (LOD) and limit of quantification (LOQ)

LOD and LOQ of this method are 1 ppm and 2 ppm, respectively.

3.1.6. Precision

Repeatability should be assessed using the results of 9 determinations in accuracy. Average precision was defined as repeatability but different dates, different analysts, different equipment. The results are shown in Table 3. The RSD of the results of 9 determinations in accuracy is 0.87 % (< 2.0 %) and the RSD of the results of 18 determinations is 1.0 % (< 3.0 %). Thus, this method was satisfactory in terms of precision.

Table 3. Results of intermediate precision.

No	Repeatability			Average precision		
	Concentration of CIP added (ppm)	Concentration of CIP recoved (ppm)	Recovery (%)	Concentration of CIP added (ppm)	Concentration of CIP recoved (ppm)	Recovery (%)
1.	4.865	4.962	101.99	4.665	4.693	100.59
2.	4.865	4.848	99.66	4.665	4.601	98.63
3.	4.865	4.914	101.01	4.665	4.622	99.07
4.	19.460	19.618	100.81	18.660	18.946	101.53
5.	19.460	19.577	100.60	18.660	18.980	101.71
6.	19.460	19.249	98.92	18.660	18.807	100.79
7.	38.920	39.259	100.87	37.320	37.777	101.22
8.	38.920	39.264	100.88	37.320	37.515	100.52
9.	38.920	39.260	100.87	37.320	36.930	98.96
	Average		100.62	Average		100.34
	RSD (n = 9) %		0.87	RSD (n = 9) %		1.16
RSD (n = 18) = 1.0 % < 3.0 %						

Therefore, this HPLC method has been fully validated according to the AOAC guidelines. The range of this method is from 2 to 50 mg/L. The method has advantages that include: simple sample handling, common chemicals, short analysis time (8 - 10 mins).

3.2. Research on the CIP adsorption capacity of Cu₃(BTC)₂ in aqueous solutions

3.2.1. The effect of pH

The effect of pH (in the range from 4 to 11) on the CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ material was presented in Figure 4.

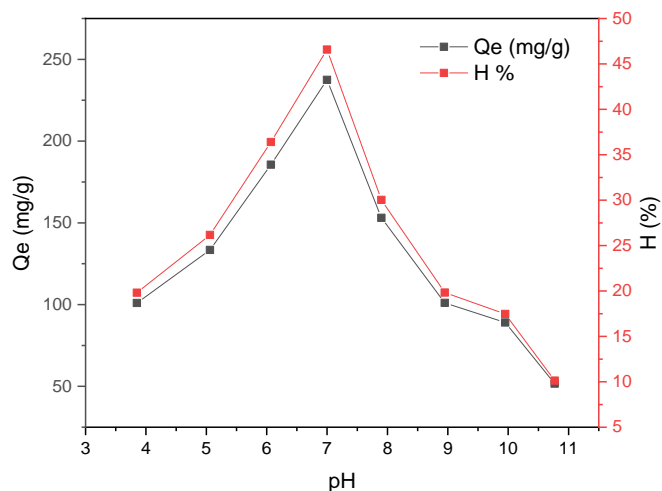


Figure 4. The effect of initial solution pH on adsorption capacity Q_e of $\text{Cu}_3(\text{BTC})_2$ and the CIP removal efficiency $H\%$ ($C_0 = 20.19$ ppm and 39.4 mg/L of the adsorbent).

The results showed that the adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ increased when the solution pH increased from 4 to 7. When the solution pH was higher than 7.0, the adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ decreased. This can be explained as follows: Ciprofloxacin has $\text{pK}_{a1} = 6.09$ and $\text{pK}_{a2} = 8.74$. With $\text{pH} < 6.09$, CIP existed mainly in the form of cations ($-\text{NH}$ is protonated to $-\text{N}^+\text{H}_2$). In the range of $6.09 < \text{pH} < 8.74$, CIP existed mainly in zwitter-ions with a fraction of cations. When pH was higher than 8.74, CIP existed mainly in the form of anions. The pH of the isoelectric point of $\text{Cu}_3(\text{BTC})_2$ is 5.0, therefore when pH was higher than 5.0, the surface of $\text{Cu}_3(\text{BTC})_2$ was negatively charged. So, at pH 7.0, the CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ was highest due to electrostatic interactions between part of anions on $\text{Cu}_3(\text{BTC})_2$ surface and part of cations on CIP, as well as π - π interaction between benzene rings of $\text{Cu}_3(\text{BTC})_2$ and CIP, and hydrogen bond between Cu-O-Cu in $\text{Cu}_3(\text{BTC})_2$ and $-\text{NH}$ group in CIP. At $\text{pH} < 7$, $-\text{NH}$ was protonated to $-\text{N}^+\text{H}_2$, so the hydrogen bonds weren't formed, the adsorption capacity was lower. At $\text{pH} > 7$, an anionic fraction on CIP exerted an electrostatic repulsion with a part of anions on the $\text{Cu}_3(\text{BTC})_2$ surface [11]. Thus, pH 7.0 was chosen for the next experiments.

3.2.2. The effect of adsorbent dosage

The effect of adsorbent dosage on the CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ material was shown in Figure 5.

The results showed that when the mass of $\text{Cu}_3(\text{BTC})_2$ increased in the range from 19.6 to 100.2 mg/L, the amount of adsorption sites increased while the number of CIP molecules remained unchanged, the CIP adsorption capacity decreased and the CIP removal efficiency increased. When the mass of $\text{Cu}_3(\text{BTC})_2$ was smaller, the adsorption sites on $\text{Cu}_3(\text{BTC})_2$ were completely exposed in solution. So, the adsorption can reach an equilibrium state in a short time and the adsorption capacity was high. However, as the mass of $\text{Cu}_3(\text{BTC})_2$ increased, the number of adsorption sites was more than the number of CIP molecules, leading to a decrease in the

adsorption capacity. To obtain a reasonable adsorption capacity and removal efficiency, we chose 39.4 mg/L of $\text{Cu}_3(\text{BTC})_2$ ($Q_e = 238.44$ mg/g and $H = 46.53$ %) for the next experiments.

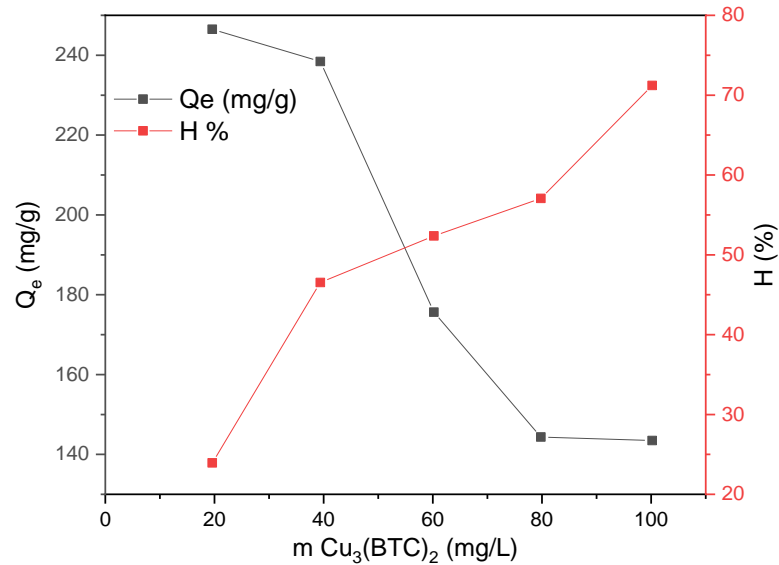


Figure 5. The effect of adsorbent dosage on the CIP adsorption capacity and the CIP removal efficiency of $\text{Cu}_3(\text{BTC})_2$ ($C_0 = 20.19$ ppm and $\text{pH} = 7.0$).

3.2.3. The effect of adsorption time

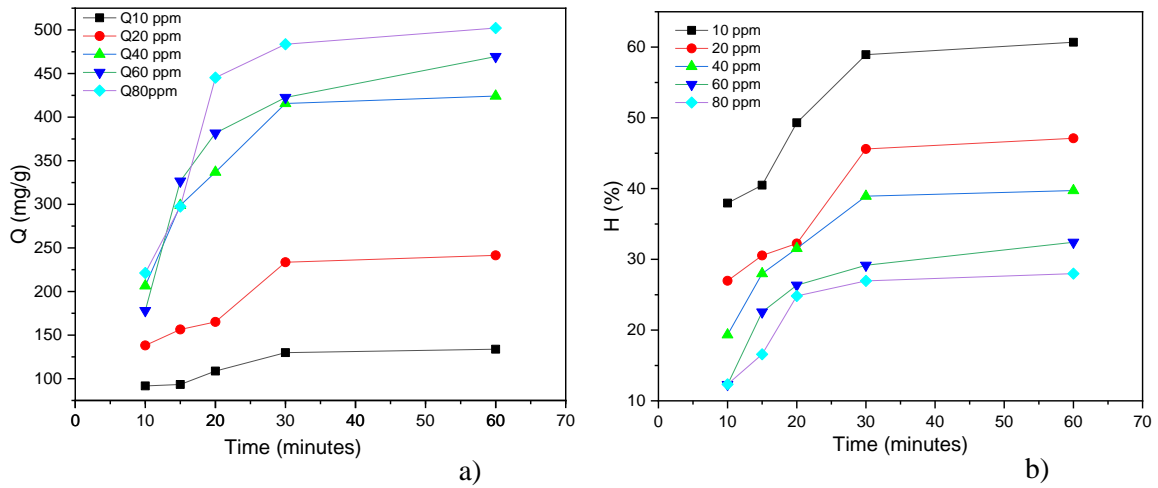


Figure 6. Variation of adsorption capacity (a) and CIP removal efficiency (b) over time at different initial concentrations of CIP solution ($\text{pH} = 7.0$ and 39.4 mg/L of the adsorbent).

Adsorption experiments with 39.4 mg/L $\text{Cu}_3(\text{BTC})_2$ in 50 mL of CIP-containing solution (with concentrations from 10 ppm to 80 ppm, $\text{pH} = 7.0$) for different contact durations (from 10 mins to 60 mins) were conducted. The CIP adsorption capacity and the CIP removal efficiency of $\text{Cu}_3(\text{BTC})_2$ at each corresponding time were shown in Figure 6. The adsorption took place

rapidly in the first 20 minutes and reached equilibrium after 30 minutes. When the initial concentration of CIP solution was higher, the CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ increased.

3.2.4. Adsorption kinetics

The adsorption of CIP on $\text{Cu}_3(\text{BTC})_2$ was very complicated and it is difficult to determine the real kinetics of the adsorption process. The adsorption kinetics of CIP adsorption on $\text{Cu}_3(\text{BTC})_2$ samples was estimated using two common kinetic models: pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order kinetic model

Table 4. Parameters of the pseudo-first-order kinetic model.

Co (ppm)	Linear equation	Qe.exp (mg/g)	Qe.cal (mg/g)	k_1 (min^{-1})	R^2
10 ppm	$y = -0.0802x + 4.6327$	133.75	102.79	0.0802	0.9449
20 ppm	$y = -0.0990x + 5.7956$	241.40	328.86	0.0989	0.9522
40 ppm	$y = -0.1103x + 6.370$	424.22	584.12	0.1103	0.9577
60 ppm	$y = -0.1114x + 6.808$	469.57	905.22	0.1114	0.9891
80 ppm	$y = -0.1135x + 6.664$	502.16	783.91	0.1135	0.9825

Where: Qe.exp: The experimental equilibrium adsorption capacity (mg/g);

Qe.cal: The equilibrium adsorption capacity calculated from the pseudo-first-order kinetic model (mg/g)

The pseudo-second-order kinetic model

From the experimental data, by representing the relationship between t/q_t vs t , kinetic parameters of the adsorption process were presented in Table 5.

Table 5. Parameters of the pseudo-second-order kinetic model.

C_o (ppm)	R^2	k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	Qe.cal (mg/g)	Qe.exp (mg/g)
10	0.9931	0.0009	151.57	133.75
20	0.9789	0.0003	294.84	241.40
40	0.9789	0.0002	519.33	424.22
60	0.9368	0.0001	617.84	469.57
80	0.9468	0.0001	647.26	502.16

The results showed that with the pseudo-first-order model, the correlation coefficient (R^2) was in the range of 0.9449 - 0.9891 (Table 4). The equilibrium adsorption capacity calculated from the pseudo-first-order kinetic model (Qe.cal) was much different from the experimental equilibrium adsorption capacity (Qe.exp).

In the pseudo-second-order model, the correlation coefficient R^2 was in the range from 0.9368 to 0.9931, which was higher than that obtained from the pseudo-first-order model. The

difference between the equilibrium adsorption capacity calculated from the kinetic equation ($Q_{e.cal}$) and the experimental value ($Q_{e.exp}$) of the pseudo-second-order model was lower than that of the pseudo-first-order model. The value of k_2 was not constant, but it decreased with increasing initial CIP concentration.

Therefore, the CIP adsorption on $Cu_3(BTC)_2$ matched the pseudo-second-order kinetic model better than the pseudo-first-order model. This result is similar to the study result of CIP adsorption by $Fe_3O_4/HKUST-1$ [11]. The adsorption rate (at time t) depended on the square of the adsorption capacity of the adsorbent.

3.2.5. Isotherm adsorption

Table 6 presents isotherm parameters of CIP adsorption onto $Cu_3(BTC)_2$ according to Langmuir and Freundlich models.

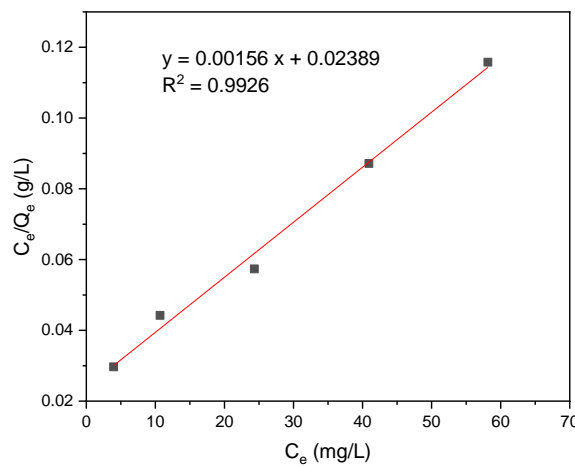


Figure 7. The dependence of C_e/Q_e on C_e .

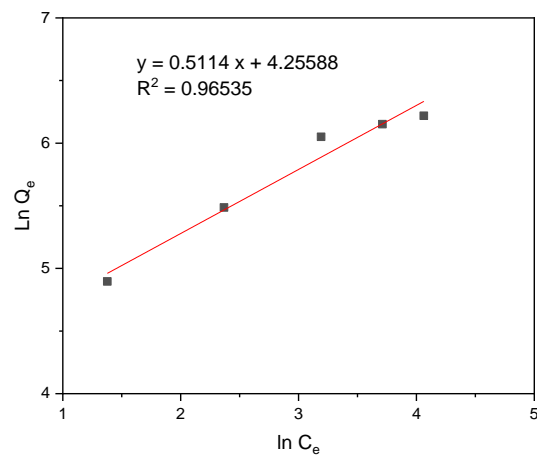


Figure 8. The dependence of $\ln(q_e)$ on $\ln(C_e)$.

The Langmuir equation is $C_e/Q_e = 0.0016 C_e + 0.0239$ with the correlation efficient $R^2 = 0.9926$ (Figure 7) and the Langmuir adsorption constant $K_L = 0.065$ (L/mg).

The Freundlich equation is $\ln(q_e) = 4.2295 + 0.5114 \ln(C_e)$ with the correlation efficient $R^2 = 0.9654$ (Figure 8); the Freundlich adsorption constant $K_F = 70.52$ [$mg \cdot g^{-1} (L \cdot mg^{-1})^{1/n}$] and $n = 2$.

Table 6. Isotherm parameters of CIP adsorption onto $Cu_3(BTC)_2$

Langmuir			Freundlich		
Q_m (mg/g)	K_L (L/mg)	R^2	$K_F [mg \cdot g^{-1} (L \cdot mg^{-1})^{1/n}]$	n	R^2
642.90	0.065	0.9926	70.52	2	0.9654

The agreement between theoretical and experimental isotherm adsorption models of CIP on $Cu_3(BTC)_2$ was determined based on 3 factors: R^2 , n , and R_L . In the Freundlich model, with n values between 1 and 10, and in the Langmuir model, R_L values from 0 to 1, the adsorption conditions were favorable.

The results showed that with the Langmuir isotherm model, R_L is in the range from 0.16 to 0.60, between 0 and 1. In the case of the Freundlich isotherm model, the n value was 2, between

1 and 10; both Langmuir and Freundlich models exhibited high correlation coefficients ($R^2 > 0.96$). So, both monomolecular layer adsorption and multilayer adsorption contributed to the CIP adsorption onto $\text{Cu}_3(\text{BTC})_2$. But the linear correlation coefficient of the Langmuir model was higher than that of the Freundlich model ($R^2 = 0.9926 > 0.9654$), therefore in the process of CIP adsorption on $\text{Cu}_3(\text{BTC})_2$, monomolecular layer adsorption was predominant. The maximum CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ (q_m) was 642.90 mg/g at 25 °C. This result shows that the $\text{Cu}_3(\text{BTC})_2$ material has a higher maximum CIP adsorption capacity than the magnetic copper-based metal organic framework material ($q_m = 538$ mg/g) [11].

4. CONCLUSIONS

This study has developed and validated a method for the quantitative determination of ciprofloxacin in water by HPLC according to the guidelines of the Association of Official Agricultural Chemists (AOAC) for specificity, system suitability, linearity, accuracy, and precision. This HPLC method has LOD, LOQ of 1 mg/L and 2 mg/L, respectively, and ranges from 2 to 50 mg/L. The advantages of this method are low LOQ (2 mg/L), high accuracy (from 98.9 % to 102.0 %), simple sample handling, and short analysis time. The influence of different factors on the CIP adsorption of $\text{Cu}_3(\text{BTC})_2$ was investigated, including: solution pH, amount of adsorbent, adsorption time, and initial CIP concentration. The adsorption process reached equilibrium within 30 minutes. The kinetic data of the adsorption process fitted the pseudo-second-order model better than the pseudo-first-order model. On the other hand, the adsorption isotherm studies showed that the Langmuir model was more in agreement with the experimental data. The maximum CIP adsorption capacity of $\text{Cu}_3(\text{BTC})_2$ calculated from the Langmuir model was 642.90 mg/g.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

1. Ministry of Health - Vietnamese National Drug Formulary, Science and Technics publishing house, 2018.
2. Dilanka N. D. S., Xin L., Guangcai Z., Tilak P., Riffat N. M., Gan Z., Mahdi S. K, Zewen Z. and Xianzhi P. - Antibiotics in two municipal sewage treatment plants in Sri Lanka: Occurrence, consumption and removal efficiency, *Emerg. Contam.* **5** (2019) 272-278. <https://doi.org/10.1016/j.emcon.2019.08.001>.
3. Vishal D., Ashok J. T., Rakesh K.K., Shanta S. Manjeet A., Yogyata M., Rama V.I., Karin S-T. and Cecilia S-L. - Antibiotics and antibiotic-resistant bacteria in waters associated with a hospital in Ujjain, India, *BMC Public Health* **10** (2010) 414-421. <https://doi.org/10.1186/1471-2458-10-414>.

4. Hong A. D., Ngoc H. P., Hoang T. N., Thi T. H., Hung V. P., Van C. P., Michael B., Walter G. and Alfredo C. A.- Occurrence, Fate and Antibiotic Resistance of Fluoroquinolone Antibacterials in Hospital Wastewaters in Hanoi, Vietnam, *Chemosphere* **72** (2008) 968-973. <https://doi.org/10.1016/j.chemosphere.2008.03.009>.
5. Won-Jim S., Ji-Woo L., Eung-Sun L., Sun-Kyoung S., Seung-Ryul H. and Jeong-Eun O.- Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures, *Chemosphere* **82** (2) (2011) 179-186. <https://doi.org/10.1016/j.chemosphere.2010.10.026>
6. Jerker F., Hana S., Richard H. L, Chau P., Mats T. and Joakim L. - Contamination of surface, ground, and drinking water from pharmaceutical production, *Environ.Toxicol. Chem.* **28** (12) (2009) 2522-2527. <https://doi.org/10.1897/09-073.1>.
7. Ge W., Tingting S., Zhirong S. and Xiang H. - Preparation of copper based metal organic framework materials and its effective adsorptive removal of ceftazidime from aqueous solutions, *Appl. Surf. Sci.* **532** (2020) 147411. <https://doi.org/https://doi.org/10.1016/j.apsusc.2020.147411>.
8. Vincenzo R., Maryam H., Francesco B., Maria R. I., Ok-Sang J. and Martino D. S. - Applications of Metal Organic Frameworks in Wastewater Treatment: A Review on Adsorption and Photodegradation, *Front. Chem. Eng.* **2** (15) (2020) 581487. <https://doi.org/10.3389/fceng.2020.581487>.
9. Fei Y., Sainan S., Sheng H., Jie Z. and Jie M. - Adsorption Removal of Ciprofloxacin by Multi-walled Carbon Nanotubes with Different Oxygen Contents from Aqueous Solutions, *Chem. Eng. J.* **285** (2016) 585-589. <https://doi.org/10.1016/j.cej.2015.10.039>.
10. Muhammad R. A., Hussein R. A., Hongqi S., Vijay P., Moses O. T. and Shaobin W. - Excellent performance of copper based metal organic framework in adsorptive removal of toxic sulfonamide antibiotics from wastewater, *J. Colloid Interface Sci.* **478** (2016) 344-352. <https://doi.org/10.1016/j.jcis.2016.06.032>.
11. Gege W., Jiping M., Shuang L., Jing G., Bo J., Liyan W., Jinhua L., Xiaoyan W. and Lingxin C. - Magnetic copper-based metal organic framework as an effective and recyclable adsorbent for removal of two fluoroquinolone antibiotics from aqueous solutions, *J. Colloid Interface Sci.* **528** (2018) 360-371. <https://doi.org/10.1016/j.jcis.2018.05.105>.
12. Thuan V.T., Duyen T. C.N., Hanh T. N.L., Huu L.H., Trung T. N., Van-Dat D., Trinh D. N. and Long G.B. - Response surface methodology-optimized removal of chloramphenicol pharmaceutical from wastewater using Cu₃(BTC)₂-derived porous carbon as an efficient adsorbent, *C. R. Chim.* **22** (11) (2019) 794-803. <https://doi.org/10.1016/j.crci.2019.09.004>.
13. Phuong. T. N. – Electrochemical synthesis of copper frameworks from trimesic acid and sodium dicyanamide, thesis, Free University of Brussels, 2018.
14. The Association of Official Agricultural Chemists (AOAC) - Appendix F: Guidelines for Standard Method Performance Requirements, 2016.