Copper metal-organic framework for selective detection of florfenicol based on fluorescence sensing in chicken meat

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ABSTRACT

Using a hydrothermal technique, a highly sensitive metal-organic Cu-MOFs sensor has been created to detect florfenicol (FFC) fluorescent in chicken meat. The sensor has demonstrated the ability to respond to the presence of FFC in an aqueous solution with accuracy and selectivity, as evidenced by an increase in fluorescence intensity. The interactions and adsorption mechanism based on hydrogen bonding, π- π, and n-π interactions demonstrate the high sensitivity and specificity of Cu-MOFs towards. FFC was detected quantitatively with a recovery of 96.48–98.79% in chicken meat samples. Within a broad linear range of 1–50 μM, the Cu-MOFs nanosensor exhibits a fast response time of 1 min, a low limit of detection (LOD) of 2.93 μM, and a limit of quantification (LOQ) of 8.80 μM. The potential applicability of the Cu-MOFs nanosensor for the detection of FFC in food matrices is confirmed by the results obtained with high-performance liquid chromatography (HPLC).

Chemical compounds: Copper (II) nitrate (PubChem CID: 18616); Terephthalic acid (PubChem CID: 7489); Polyvinyl pyrrolidone (PubChem CID: 486422059); N, N-dimethylformamide (PubChem CID: 6228); Ethyl alcohol (PubChem CID: 702); Hydrochloric acid (PubChem CID: 313); Sodium hydroxide (PubChem CID: 14798); Acetic acid (PubChem CID: 176); Trichloroacetic acid (PubChem CID: 6421); Florfenicol (PubChem CID: 114811).

1. Introduction

Antibiotics are one of the utmost important medical discoveries of the 20th century (Hutchings, Truman, & Wilkinson, 2019). The improper use of antibiotics as antipathogenic and growth promotion agent related to animal husbandry components can cause catastrophic contamination and accumulation of their residues in animal-derived food, water and soil resources. These residues can cause complications, including antibiotic resistance, allergic reactions, mutagenesis, aplastic anemia and visual impairment, carcinogenesis intestinal flora disorders and immunopathological disorders posing a threat to human health (Xie et al., 2021). Hence, to detect antibiotic residues, establishment of selective, efficient, rapid and sensitive techniques is important and necessary.

Currently, a number of techniques have been reported for the detection of antibiotic residues, including high performance liquid chromatography (HPLC), gas chromatography (GC), liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-tandem mass spectrometry (GC–MS), ion mobility spectrometry, Raman spectroscopy as well as ELISA and antibiogram (Alizadeh Sani et al., 2023; Marimuthu, Arumugam, Sabarinathan, Li, & Chen, 2021; Wang et al., 2019; Yue, Wu, Zhou, Fu, & Bai, 2022). These techniques are expensive technologies with high diagnostic costs, moderate sensitivity, accuracy and reliability. Their operation is complicated and difficult and requires skilled operators and takes time (Cao et al., 2023). Hence, it is crucial to develop a new detection method that can detect antibiotics in animal foods quickly and easily (Marimuthu et al., 2021).

Recently, sensors have comprehensive features that make them applicable in medicine, biomedicine, toxicology and environmental toxicology, engineering, technology and food safety monitoring. The design and choice of material sensing used in the sensor must consider cost, stability, sensitivity, and selectivity as the main attributes (Khezerlou, Tavassoli, Khalilzadeh, Ehsani, & Kazemian, 2023; Mansouri

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et al., 2020). Fluorescence probes get much attention among the optical sensors for detection antibiotics in water and food (Li et al., 2020).

MOFs are composed of polymers that have two parts: metal nuclei (metal clusters or ions) and monodentate or polydentate organic ligands that function as bridging molecules (Ali & Omer, 2022; Ameen, Mohammed, & Omer, 2023; Khezerlou, Tavassoli, Khalilzadeh, et al., 2023). Commonly, lanthanides such as Zn, Al, Fe, Zr, Tb, Eu are used metals as nodes of MOF-based sensors and the organic ligands of them are carboxylates, phosphates, sulfonates, azolates,and polyamines (Ahmadi et al., 2021; Jie et al., 2023; Yue et al., 2022). Metal organic frameworks (MOFs) materials as a promising new type of crystalline material are widely used in research fields such as detection of antibiotics, drug delivery, and other chemical sensing due to structural variability, controllable adsorption and synthesis sites in gas storage (Marimuthu et al., 2021; Yue et al., 2022). The interesting features of MOFs in chemical sensing, such as high porosity, high sensitivity and selectivity, rapid response, narrow fluorescence emission, structural and chemical stability, lower detection limits (micro, nano, pico, pheno-molar limits) and unlimited stability and surface modification has attracted great interests to applicate of them as sensors (Ahmadi et al., 2021; Ahmadijokani et al., 2022; Ameen et al., 2024; Mohammed Ameen, Qasim, Alhasan, Hama Aziz, & Omer, 2023; Yue et al., 2022). Fluorescent sensor based on Cu-MOFs is proposed for the detection of antibiotics in foods due to its potential for rapid detection, easy installation, low cost and optimal stability of markers.

Several studies have been conducted on the use of MOFs for the recovery of antibiotics such as sulfonamides, ciprofloxacin, chloramphenicol, and tetracycline from different food materials (Khezerlou, Tavassoli, Khalilzadeh, et al., 2023; Xia et al., 2020; Yue et al., 2022). Florfenicol (FFC) is a wonderful medicine belonged to amfenicol family in veterinary medicine versus infections caused by gram-positive and gram-negative bacteria which is used as an antibacterial agent for therapeutic objectives in livestock, poultry and aquaculture, instead of chloramphenicol (Sadeghi, Mohsenzadeh, Abnous, Taghdisi, & Ramezani, 2018). It is available as an antibiotic at a reasonable price, and its' quick detection in chicken meat will increase food safety in the consumption of this product. This is a great advantage for designing a MOF sensor to detect this antibiotic. So far there is no report for the detection of the FFC antibiotic in chicken meat using Cu-MOFs. In this study, we investigated the detection potential of FFC antibiotic in chicken meat using Cu-MOFs sensor probe as a fluorescence platform for the first time, and the fluorescence emission of Cu-MOFs, the recovery rate, accuracy and sensitivity of this sensor through the addition of FFC was evaluated.

2. Materials and methods

2.1. Materials

Copper (II) nitrate $(Cu(NO_3)_2)$, terephthalic acid $C_6H_4(CO_2H)_2$ (TPA), polyvinyl pyrrolidone (PVP), N, N-dimethylformamide (DMF), Pure ethyl alcohol and Tris buffer, hydrochloric acid, sodium hydroxide, acetic acid, trichloroacetic acid were purchased from Merck (Darmstadt, Germany). Acetonitrile (chromatography grade), tetracycline (TET), chloramphenicol (CHL), florfenicol (FFC), enrofloxacin (ENR), erythromycin (ERY), penicillin (PEN), neomycin (NEO), have been purchased from Hirkani Sanat Company (Tehran, Iran). and chicken meat was obtained from local market of Tabriz (East Azerbaijan, Iran).

2.2. Synthesis of cu-MOFs

The Cu-MOFs has been prepared based on described method by (Huo, Li, Fan, & Pu, 2020), with some modification. First, in an Erlenmeyer flask, 2 g of PVP were dissolved in a solution containing 12 mL of DMF and 12 mL of ethanol. Then, 0.332 g of TPA and 0.724 g of Cu $(NO_3)_2$ were added to this solution. A blue colored solution was observed and due to the light sensitivity of the resulting solution, it was

completely covered with foil. In order to completely dissolve of the particles, the solution was placed and stirred on a magnetic stirrer at a temperature of 40 °C for 1 h. Then, the flask was placed in a Teflon-lined hydrothermal autoclave (250 mL) and heated at a temperature of 120 °C for 16 h. The solution was transferred to 50 mL tubes and centrifuged (4000 rpm, 5 min) after cooling at room temperature. The precipitate was washed with absolute ethanol three times. The remained blue precipitate (final product) poured onto Whatman paper and dried overnight in a vacuum oven at 50 °C.

2.3. Characterization of cu-MOFs

The morphology of the obtained Cu-MOFs was investigated using a field emission scanning electron microscope (FESEM) (Tescan, Czech Republic). The resolution of this device was up to 1 nm and it had a magnification power of up to 1 million times at a voltage of 30 kV. Also, Energy Dispersive X-ray Spectroscopy (EDS) was used to determine the type and quantity of elements on the surface of nanomaterials collected from (MIRA3 FEG-SEM) (Tescan, Czech Republic) equipped with energy dispersive X-ray (EDX). An X-diffractionometer (Tong Da TD-3700, China) was utilized to determine X-ray powder diffraction (XRD) and assess the crystallization and stability of the entire Cu-MOFs. The analysis accuracy of the device is 0.02 degrees in 0.5 s, and the voltage and current consumption are 30 kV and 20 mA, respectively. FT-IR spectra were taken between 500 and 3500 cm^{-1} on a Nicolet Fourier spectrophotometer (TENSOR 27, BRUKER, Germany), using a KBr beamsplitter. Thermogravimetric analysis (TGA) was performed using a (STA PT-1000 Linseis, Germany), with a heating rate of 10 °C min^{-1}. he Brunauer-Emmett-Teller (BET) technique was used to evaluate the specific surface area. The Belsorp model (MicrotracBel Corp, Japan) was utilized to obtain adsorption and desorption isotherms. Fluorescence spectra were obtained using a JASCO spectrometer (model FP-750, Japan) with the following experimental conditions: The optical voltage was 700 V, the emission and excitation split widths were both 10 nm, and the scanning speed was 8000 nm/min. A UV–Vis spectrometer (Shimadzu 2550, Japan) was used to obtain the absorption spectrum of the samples. A high-performance liquid chromatography device (KNAUER, Germany) was used to perform HPLC measurements (Amiripour, Ghasemi, & Azizi, 2021; Liu et al., 2019).

2.4. Optimization of experimental conditions

Analyte identification can be made more effective through the use of different parameters. Compositional parameters such as pH, solvent, molar ratio of raw materials and concentration of MOFs used, as well as process parameters such as temperature, pressure and time, and finally the interaction between the analyte and MOF. These parameters can vary depending on how the sensor is synthesized and designed (Seetharaj, Vandana, Arya, & Mathew, 2019).

Time and pH can also affect the performance of the probe (Amiripour et al., 2021). The effect of time on MOF is discussed in the article. The pH response of fluorescent MOFs is a result of their coordinated organic bonds. In cases where organic compounds are fluorescent, their protonation (or deprotonation) can directly affect their fluorescence intensity (Shamsipur, Barati, & Nematifar, 2019). Therefore, pH plays an essential role in MOFs. Therefore, the pH solution was made using 0.5% acetic acid, Tris buffer, and sodium hydroxide, then the pH was adjusted to 11–3, and each pH was applied with a volume of 100 μL with three repetitions in the spectrofluorometer (JASCO, FP-750, Japan).

2.5. Fluorescence detection of FFC

All fluorescence recognition studies of Cu-MOF were performed based on the method described by Huo et al., 2020 with some modification. In a typical test procedure, different concentrations of FFC standard solution (10, 25 and 50 μM) were added to separate tubes and
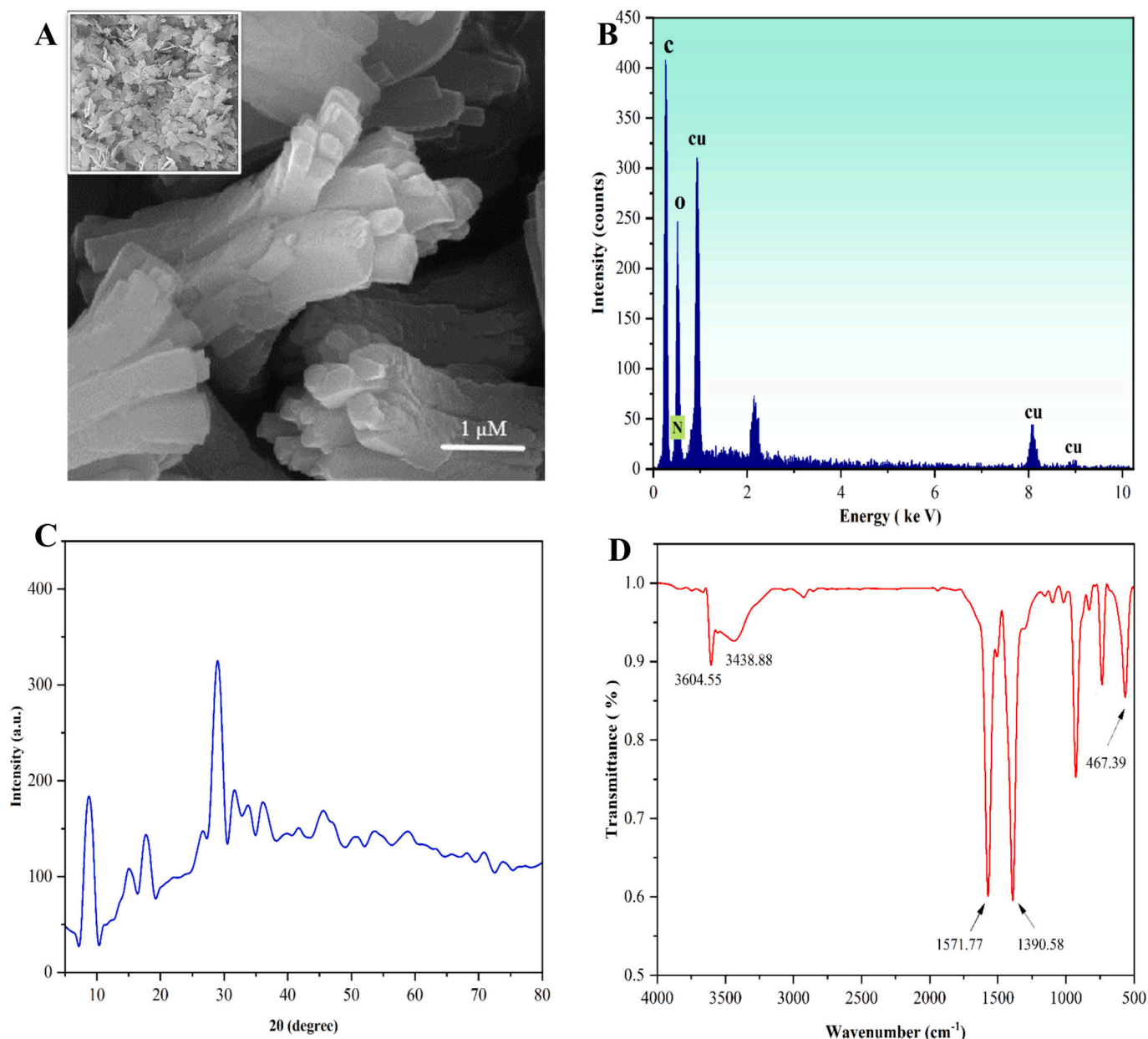
Fig. 1. (A) SEM image of Cu-MOFs, (B) EDS elemental analysis of Cu-MOFs, (C) XRD patterns of Cu-MOFs, (D) FT-IR spectra of Cu-MOFs.

then diluted with Tris buffer (pH = 8.0) to 2 mL and incubated at room temperature for 30 s. Each mixture was then added to a quartz cuvette (10 × 10 mm), and the fluorescence intensity of the solutions was measured from 400 to 530 nm upon excitation at 380 nm. TET, CHL, ERY, PEN, ENR and NEO antibiotics were mixed in equal concentrations (100 μL) with 500 μL of Cu-MOFs solution and volume to 1400 μL with Tris buffer (pH = 8.0) to measure the selectivity of the Cu-MOFs probe to FFC. All samples were run in triplicate for FFC measurement for statistical purposes.

2.6. Fluorescence assay of FFC in chicken meat

First, to remove lipids, proteins and other organic compounds, 5 g of the meat sample (Spiked with different concentrations of standard FFC solution (10, 25 and 50 μM)) were mixed in a solution containing 35 mL of trichloroacetic acid 7.5% and 10 mL of chloroform and homogenized for 5 min using a vortex. After that the samples were subjected to sonication for 30 min. The homogenized mixture was centrifuged for 2 min

at 3000 rpm and the supernatant was filtered through a 0.22 μM membrane filter. Then 500 μL of the Cu-MOFs solution and 500 μL of the sample solution were filtered and combined with FFC standard solution (10, 25 and 50 μM) and diluted to a volume of 2 mL with Tris buffer (pH = 8). A spectrofluorometer (FP-750, JASCO, Japan) was used to calculate the FFC concentrations in the chicken meet samples according to the fluorescence spectrum. The efficacy of the present method was evaluated in the specified samples by calculating the limit of detection (LOD), limit of quantification (LOQ) and recovery percentage. Additionally, the outcomes of the MOF sensor were compared with HPLC results. HPLC analysis of antibiotic FFC was performed under the following conditions: reverse-phase HPLC column M05CLA25 (Kromasil, Nouryon, Sweden) 100–5-C18 series, (250 mm, 4.6 mm, 5 μm), column temperature 25 °C detector Ultraviolet wavelength was 304 nm, mobile phase consisted of water/acetonitrile with volume ratio (65,35 *v*/v) and flow rate was 1.0 mL/min and injection volume was 100 μL. To evaluate the application, a standard method of addition to meat samples was performed (Alizadeh Sani et al., 2023; Khezerlou et al., 2023).
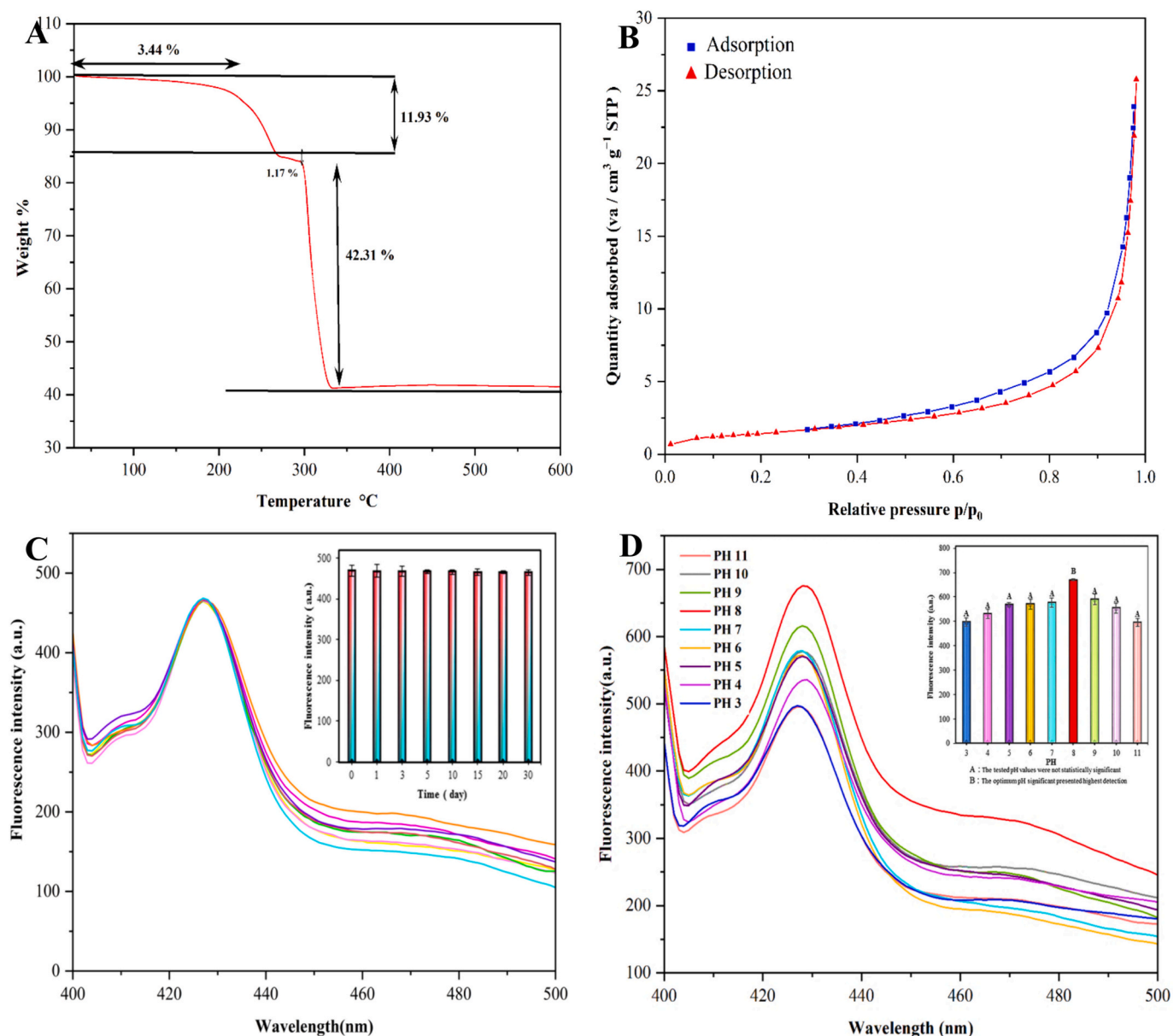
Fig. 2. (A) The TGA curve of Cu-MOFs, (B) The result of the BET chart, (C) Fluorescence stableness of the Cu-MOFs, (D) The effect of PH on the fluorescence performance of Cu-MOFs.

2.7. Statistical analysis

All experiments were performed in three replicates and the results are presented as Mean ± standard deviation, and. The statistical analysis of the obtained results was done using Excel software Microsoft 2016 and the drawing of spectrum diagrams was conducted using the Origin Pro 2022 software (V9.9.0.225 (SR1)) (EA, USA).

3. Results

3.1. Characterization

Antibiotic detection has shown significant promise for fluorescent nanomaterials, including metal nanoclusters (MNC), carbon .s (CD), quantum .s (QDs), and fluorescent metal-organic frameworks (FMOFs). All materials, however, have intrinsic shortcomings that prevent their widespread application. For example, the presence of heavy metals in conventional QDs can be a threat to food safety. While CDs are too small

for isolation and purification, MNCs are prone to aggregation because of their low stability. MOFs are currently the most widely investigated fluorescent material for chemical sensing, thanks to their attractive spectral properties, infinite stability, excellent thermal stability, pore capability, and external surface modification. These properties make them highly effective in detecting various targets such as metal ions, small molecules, gases, biomarkers, pH values, and temperature. The fluorescent properties of MOFs are strongly influenced by the crystal structures and coordination environment of the metal centers, as well as their interactions with guest species (e.g., coordination and hydrogen bonds, π–π interactions). This provides a solid rationale for their use in fluorescent sensing. At present, MOFs are synthesized mainly in organic solvents to preserve their topological structure (Li et al., 2020).

Cu-MOFs were made by hydrothermally combining Cu^{2+} as the metal ion node, TPA as a ligand, and PVP as an adhesive and complex agent. This synthesis was performed using a reliable source and making some changes. According to the mentioned reference, we have used copper nitrate instead of amino-functionalized copper as the central core
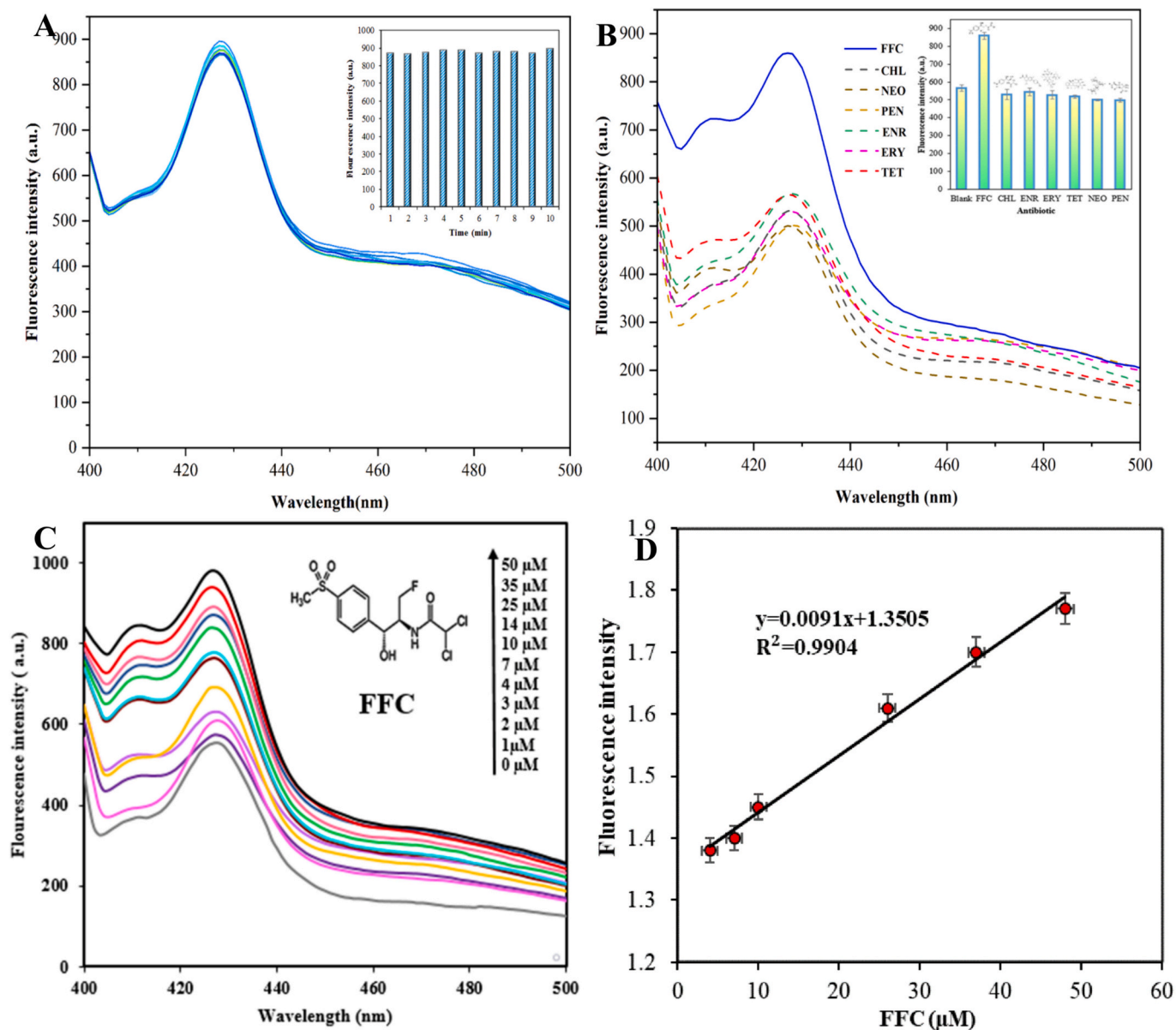
Fig. 3. (A) 0 to 10 min time interval stability for Cu-MOFs fluorescence intensity, (B) Fluorescence increase of Cu-MOFs compared to different types of antibiotics (100 μL),(C) Fluorescence spectra intensity of Cu-MOFs addition several concentrations of FFC (0–50 μM), (D) Standard curve of Cu-MOFs with different concentrations for FFC detection.

and terephthalic acid instead of aminoterephthalic acid as a ligand, as a result, modification has occurred in the synthesis (Huo et al., 2020).

As shown in Fig. 1A, the morphology of Cu-MOFs was investigated using SEM. The synthesized material has a nanostructure with a particle size of 2.23 ± 0.2 μM. Cu-MOFs' elemental composition was examined using EDS to display their chemical composition, as seen in Fig. 1B. Cu-MOFs' crystal structure was examined using XRD. Fig. 1C, showed that 8.82, 14.42, 15.42, 17.72, 29.06, 31.64, 33.74, and 36.14 degrees are consistent with the simulated single crystal XRD results reported by Huo et al. (2020), which included peaks at 9.28, 17.84, 24.7, 33.02 degrees (Huo et al., 2020).

These outcomes demonstrate that the success of the synthesis of Cu-MOFs. Moreover, FT-IR was used to characterize the Cu-MOFs (Fig. 1D) in order to disclose their functional groups and molecular structures. (Fig. 1D). The symmetric and asymmetric carboxylate stretching vibrations, which show the carboxylate groups' final coordination state, are responsible for the peaks at 3604.55 and 3438.88 cm^{-1}. The distinguished peak located at 1390.58 cm^{-1} can be attributed to the

symmetric stretching vibration of the carboxyl category, and the distinct peak located at 1571.77 cm^{-1} can be attributed to the asymmetric stretching vibration of the carboxyl group. Also, the Cu—O bond was visible at 467.39 cm^{-1}, indicating their coordination with the carboxyl group, further demonstrating the success of the synthesis of Cu-MOFs. These findings are also in line with the results reported by Huo et al. (2020), based on the similarity of symmetric and asymmetric stretching vibrations of the carboxyl group (Huo et al., 2020). Using TGA, the thermal stability of Cu-MOFs was investigated at temperatures between 30 and 600 °C and a heating rate of 10 km in air. As shown in Fig. 2A, 16.54% weight loss is caused by solvent evaporation in pores at lower temperatures (between 50 and 310 °C). Cu-MOFs exhibited thermal stability up to 320 °C, at which point they started to decompose. The results of TGA analysis reported by Huo et al. (2020) on NH2-Cu-MOFs revealed that, although they were thermally stable up to 240 °C, but a weight loss of more than 44.1% occurred. Considering the weight reduction (16.54%) of our synthesized materials (Cu-MOFs) compared to the weight reduction of NH2-Cu-MOFs, it can be concluded that our
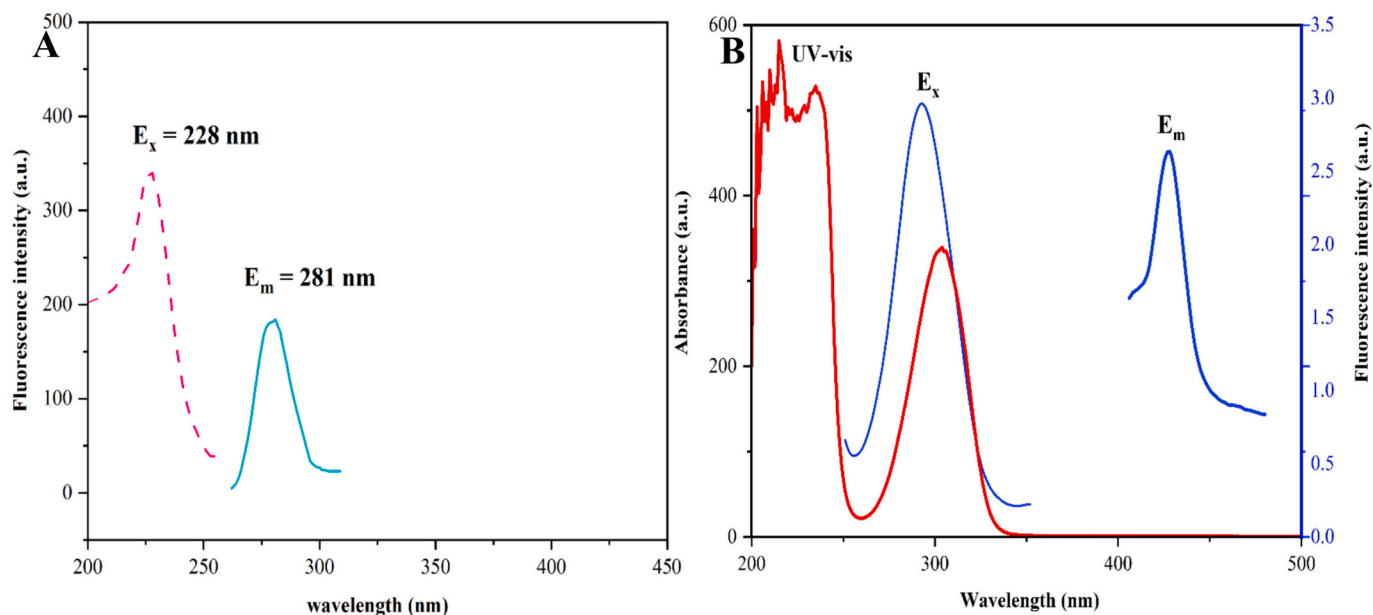
Fig. 4. (A) Excitation (E$_x$) and emission (E$_m$) spectra of FFC, (B) UV–Vis absorption spectrum of FFC (red line) and fluorescence emission spectrum of Cu-MOFs (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

designed Cu-MOFs have superior thermal stability. Based on characterization results, Cu-MOFs exhibit good thermic stability. The presence of mesoporous material is confirmed by the adsorption and desorption isotherms, and the specific surface area value obtained from the BET diagram showed 5.2052 m^2/g (Fig. 2B). Given this, Wang, Xie, et al. (2019) confirmed the presence of microporous and mesoporous in this structure and reported the specific surface area as 9.81 m^2/g (Wang, Ye, An, Wang, & Li, 2019). The synthesis of Cu-MOF using various techniques and substances is the reason for the difference in the value of the specific surface between our study and Wang, Ye, et al. (2019).

3.2. Time stability

The effects of pH and incubation time on fluorescence intensity were examined in order to maximize sensitivity. As shown in Fig. 2C, the fluorescence emission remained mostly unchanged from day 0 to day 30, and the structure of Cu-MOFs showed good temporal stability and the storage stability of Cu-MOFs both demonstrated good temporal stability over a period of 30 days.

3.3. Florfenicol sensing based on cu-MOFs

Respond time and pH play a significant role in FFC recognition. By measuring the fluorescence intensity at variable pH = 3–11, the impact of pH on Cu-MOFs' ability to function as fluorescent materials was further explored. As depicted in Fig. 2D. In fact, the fluorescence intensity of Cu-MOFs rises in the pH range of 3–8 and falls in the pH range of 9–11. It was discovered as a result that pH = 8 is perfect for this structure. Furthermore, in Fig. 3A, it was demonstrated that the fluorescence intensity of Cu-MOF did not change noticeably for the reaction time assay between 0 and 10 min. Cu-MOFs have the potential to serve as a "high-speed" fluorescent probe in FFC reconnaissance, as evidenced by the high response time observed in the first min (all measurements and fluorescence assays were carried out at room temperature (25 °C)). A measurement of FFC's fluorescence spectrum revealed that it had two peaks: an emission peak at 281 nm and an excitation peak at 228 nm (Fig. 4A). The analyses demonstrate that the addition of FFC significantly boosts Cu-MOFs' fluorescence; in fact, the porous structure of MOFs permits the analyte to enter the MOFs' space selectively and manifest as a fluorescence peak. By means of the accumulation of Pi (π–π

stacking), FFC can bind to the ligand terephthalic acid (PTA), which has the chemical formula $C_8H_6O_4$. On the other hand, when FFC binds to Cu$^+$ ion through their interaction, the Cu-MOF sensing platform's fluorescence intensity increases. This is because the Cu-MOF structure contains numerous chemical bonds of main functional groups, including O—H bonds and CO bonds of carboxyl groups, among others. Consequently, interactions such as n–π and π–π interactions, as well as hydrogen interactions between Cu-MOF and functional groups of FFC (such as OH, NH of amide, etc.), may be crucial in enhancing the adsorption of FFC to MOFs. Interestingly, our designed sensor exhibits the same response to other antibiotics; and no discernible variations in fluorescence intensity were noticed (Fig. 3B). (van Tran et al., 2020). Fig. 3C displays the fluorescence spectra of Cu-MOFs at various concentrations. In terms of (F0—F)/F0, the fluorescence intensity of Cu-MOFs increased with FFC concentration in the range of 0 to 50 μM which were reported using the calibration equation, (y = 0.0091× + 1.3505), at the coefficient of determination (R2 = 0.9904) (Fig. 3D). Based on computations, 2.93 μM is the limit of detection (LOD) for (n = 7) FFC. For FFC detection, this method has a lower LOD than traditional fluorescent probes, indicating the higher sensitivity of Cu-MOFs. Compared to the results of the study conducted by Sadeghi, Jahani, and Belador (2016) on a designed aptasensor based on ZnS composite with manganese to detect FFC in meat, a higher LOD value of 24 μM was obtained than in the Cu-MOFs sensor (Sadeghi et al., 2016). The comparison of our method with other antibiotic detection methods using different designed MOFs is shown in the Table 2.

3.4. Mechanism of FFC detection

The mechanism of fluorescence quenching includes both static and dynamic quenching. Three methods can be used to quench fluorescence: inner filter effect (Chou & Dennis, 2015), photo-induced electron transfer (PET), and Förster resonance energy transfer (FRET). IFE and FRET are common among them. Resonant energy transfer (FRET) is the non-radiative process in which an excited donor molecule uses a dipole-dipole interaction to transfer energy to a ground state acceptor molecule (Chou & Dennis, 2015; Kaur, Kaur, & Ahuja, 2020). The efficiency of energy transfer is dependent on the degree of spectral overlap between the acceptor and donor emission spectra as well as the relative positions of the two dipoles (Feng et al., 2021). On the other hand, when FRET
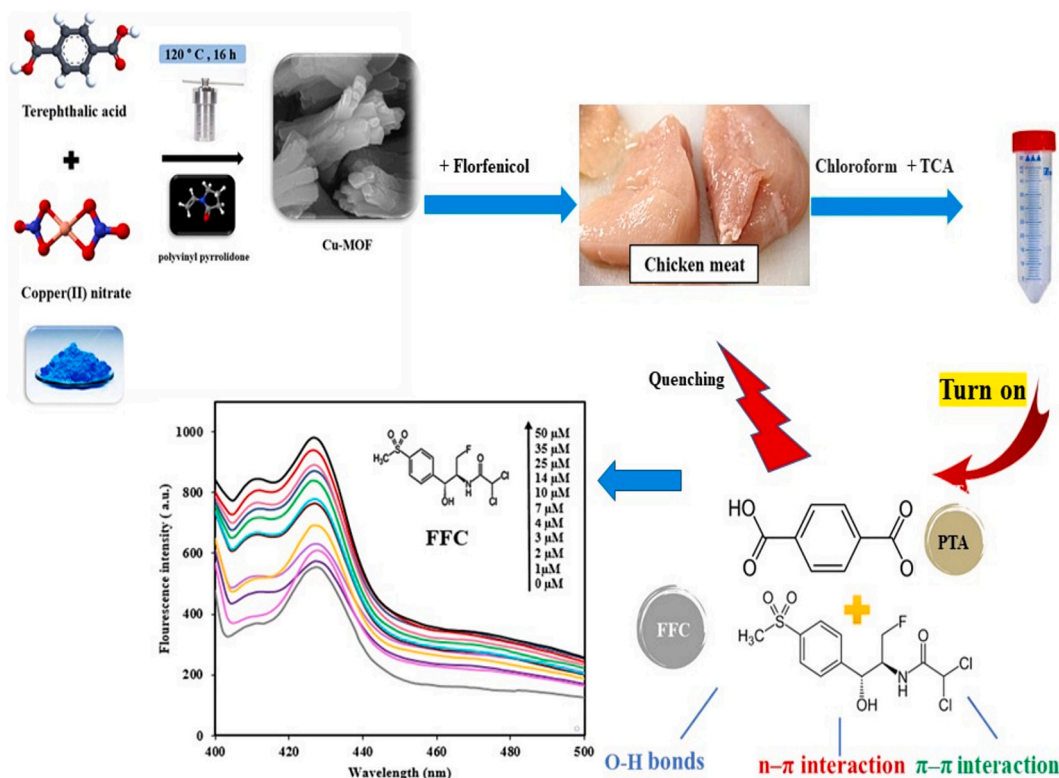
Fig. 5. A schematic diagram of the Cu-MOF achieving selective fluorescence detection of florfenicol in chicken.

Table 1
Comarison the accuracy and reproducibility of Cu-MOFs sensor with HPLC method to detect of spiked concentrations of florefenicol in chicken meat.

Spiked (μM)	Founded of Cu-MOFs (μM)	Founded of HPLC (μM)	Recoveries (%)	RSD(n = 3)
10	9.83 ± 0.012	7.45 ± 0.347	98.35	0.53
25	24.12 ± 0.016	22.22 ± 0.673	96.48	0.62
50	49.39 ± 0.047	48.60 ± 0.062	98.79	0.16

takes place, the organic ligand's (the energy donor's) fluorescence typically decreases rather than increases. On the other hand, the overlap between the analyte's absorption spectrum and its emission excitation spectrum is what causes the IFE process (Al-Hashimi, Omer, & Rahman, 2020). Measurements were made of the antibiotic's UV–Vis spectrum and the Cu-MOFs' excitation spectrum to validate the absorption by UV–Vis and to support such a mechanism, as illustrated in Fig. 4B shows a good overlap between the FFC absorption spectrum and the Cu-MOFs excitation spectrum. This suggests that because of the high selectivity of Cu-MOFs, IFE, which can effectively block the excitation light for Cu-MOFs and alter the energy transfer from organic ligands to Cu^{2+} ions and the fluorescence spectrum, may be useful for the detection of FFC. The FFC display exhibits a visible UV absorption peak at 304 nm (red line) and absorption at 200–700 nm in its UV–Vis absorption spectrum. It was discovered that 380 nm was the ideal wavelength for excitation of Cu-MOFs. On the other hand, at 427 nm, a notable fluorescence emission peak was observed at an excitation wavelength of 380 nm. Additionally, it was demonstrated by the evidence gathered that there is a significant overlap between the UV–Vis absorption spectrum and the emission and fluorescence excitation spectra of Cu-MOFs. Consequently, the results demonstrated that the internal filter effect, or IFE mode, is applied between the UV–Vis absorption spectrum and the Cu-MOFs.

3.5. Detection of FFC s in chicken meat

The Cu-MOFs sensor was utilized to measure the FFC concentration in order to examine the use of the nanosensor in a real sample of chicken meat (Fig. 5). As demonstrated in Table 1, the recovery rate acquired ranged from 96.48% to 98.79% at different concentrations (10, 25 and 50 μM), with corresponding relative standard deviation (RSD, $n = 3$) of 0.53 and 0.62%, respectively. The LOD and LOQ for this work were 2.93 μM and 8.80 μM, respectively. The analytical results indicate the complex components in chicken samples did not cause considerable interference on the sensing potency of the Cu-MOFs. Furthermore, the results were in agreement with the HPLC results, suggesting that the Cu-MOF probe can be reliable for the detection of FFC in actual samples due to its appropriate reproducibility and acceptable accuracy (Table 1).

This study explores fluorescence detection of FFC in chicken meat using Cu metal-organic framework (MOF) materials. So far, Cu-MOFs have not been used for the detection of FFC. Florfenicol is available as an antibiotic at a reasonable price, and its quick detection in chicken meat will increase food safety in the consumption of this product. Chicken meat is a complex food item that Cu-MOFs show the ability to detect in this research. In this study, we have precipitated and removed disturbing and soothing factors such as lipids and proteins as much as possible as a practical method that is used in most studies using chloroform and trichloroacetic acid solutions. To ensure the selectivity the result of this measurement can be confirmed by using different concentrations of FFC on the sensor, and it has proven the high ability and extraordinary sensitivity of this sensor in detection. We understand the sensitivity of Cu-MOFs by comparing the fluorescence peak from a standard concentration of 50 μM FFC solution with the fluorescence result from a 50 μM spike on chicken meat, but the fluorescence results in the spike show that the interfering substances anyway, have been effective in the final result. Of course, with more experiments, the results will be clearer, but due to device limitations, our analysis was limited.

This is a great advantage for designing the above sensor to detect this

Table 2

Comparison of Cu-MOF sensing method with other methods to identify the residual antibiotics in different food samples.

Antibiotics	Sensing materials	Detection Method	Linearity range	LOD	Sample	Ref
Florfenicol	Cu-MOF	Fluorescence	2.5–50 μM	10.46 μM	Chicken	Present study
Florfenicol	Mn:ZnS QDs	Fluorescence	30–700 μmol L^{-1}	24 μM	Chicken	(Sadeghi et al., 2016)
Tetracycline	Al-MOF@Mo/Zn-MOF	Fluorescence	0.001–53.33 μM	0.53 nM	Water	(Li et al., 2020)
	Ln-MOF (Tb-L1)	Fluorescence	0.06–10 μg mL^{-1}	8 ng mL^{-1}	Water	(Li et al., 2021)
	Cr(III)-MOF	Fluorescence	5–45 ng/mL	0.78 ng/mL	Chicken Egg	(Khezerlou, Tavassoli, Sani, et al., 2023)
Chloramphenicol	MIP/Zr-LMOF	luminescent	0.16_161.56 μg.L^{-1}	0.013 μg.L^{-1}	Milk Honey	(Amiripour et al., 2021)
	zirconium-porphyrin MOF (PCN-222)	Fluorescence	0.1 pg mL^{-1} 10 ng/mL	0.08 pg mL^{-1}	Milk shrimp	(Liu et al., 2020)
Ciprofloxacin	Eu-MOF	Fluorescence	0.1–18 μM	0.0136 μM	Milk	(Yue et al., 2022)

antibiotic. As is shown in Table 2, several studies conducted on other antibiotics, not reported in the diagnosis of FFC. In this study, by performing various analyzes on Cu-MOFs, according to the study conducted by Huo et al., the results of our research showed that Cu-MOFs have higher thermal stability. In terms of the sensitivity and accuracy of the designed Cu-MOFs sensor has the ability to detect antibiotics specifically in with the lowest LOD, and also in terms of the stability time of the designed sensor, this sensor has shown its stability for 30 days.

4. Conclusions

A novel Cu-MOF probe with excellent selectivity, high thermal stability, and chemical stability has been developed and synthesized in this work. The findings demonstrated that the addition of FFC results in an increase in fluorescence intensity. Additionally, Cu-MOF can successfully distinguish FFC from TET, CHL, ENR, ERY, PEN, and NEO. The results demonstrate that this sensor's low LOD and quick response time are its special qualities, making it appropriate for Cu-MOFs that are designed to match high performance liquid chromatography results. Cu-MOFs with amine functionality can form hydrogen bonds with FFC, and Cu-MOFs' fluorescence intensity can be increased by electron transfer between Cu-MOFs and FFC. The Cu-MOFs sensor responds quickly and has a broad pH and temperature detection range. These findings demonstrate that Cu-MOFs is a very helpful and inspiring ideology for the development of fluorescent probes that detect antibiotics with notable selectivity. Moreover, Cu-MOFs serves as a practical fluorescence probe that can be used for practical purposes such as detecting FFC in chicken meat.

CRediT authorship contribution statement

Roshanak Hasani: Writing – review & editing, Writing – original draft, Resources, Project administration, Investigation. **Ali Ehsani:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Hassan Hassanzadazar:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Majid Aminzare:** Writing – review & editing, Visualization, Methodology. **Arezou Khezerlou:** Writing – review & editing, Resources, Project administration, Investigation.

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.

Data availability

Data will be made available on request.

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