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Use of hydroxypropyl β-cyclodextrin hybrid monolithic material as adsorbent for dispersive solid-phase extraction of fluoroquinolones from environmental water samples

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In this study, the hydroxypropyl β-cyclodextrin hybrid monolithic material was fabricated and firstly applied as an adsorbent for dispersive solid-phase extraction coupled with high-performance liquid chromatography to detect trace-level seven fluoroquinolones in water samples. The prepared hydroxypropyl β-cyclodextrin hybrid monolithic material was characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, and adsorption experiments, which showed excellent specific adsorption to the target fluoroquinolones. Under the optimized conditions, the extraction methodology showed satisfactory precision with relative standard deviations between 2.6% and 5.6%, good linearity ($R^2 \geq 0.9990$), and satisfactory recoveries (82.5–91.8%). The limits of detection and limits of quantification of the method were in the range of 0.4–1.2 and 1.4–4.0 ng/mL, respectively, which confirmed the possibility of quantifying trace levels. Furthermore, the material could be reused at least five times. These results demonstrated that the hydroxypropyl β-cyclodextrin hybrid monolithic material was a promising adsorbent for fluoroquinolones, and the established method combined dispersive solid-phase extraction with high-performance liquid chromatography was suitable for the determination of fluoroquinolones in aqueous samples.

KEYWORDS
adsorbent, cyclodextrin, dispersive solid-phase extraction, fluoroquinolones, high-performance liquid chromatography

1 | INTRODUCTION

Fluoroquinolones (FQs) are an important group of antibiotics that are widely used in human medicine and the field of animal breeding for inhibiting bacteria proliferation. However, the widespread usage of FQs antibiotics increases the possibility of residues appearing in environmental aqueous and food products [1]. Because of the hydrophilicity of FQs, water is mainly affected by its contamination [2]. Antibiotics in surface waters could negatively affect the key bacterial cycles/processes critical to aquatic ecology or agriculture and animal production [3]. In addition, they can also influence the evolution of microbial structure and thus may be harmful to ecological and human health. Due to the transmission of antibiotic

Article Related Abbreviations: AIBA, 2,2-azobis (2-methylpropionamidine) dihydrochloride; CDHM, hydroxypropyl β-cyclodextrin hybrid monolith; DSPE, dispersive solid-phase extraction; FQ, fluoroquinolone; GMA, glycidyl methacrylate; HP-β-CD, hydroxypropyl β-cyclodextrin; MPS, sodium 3-mercaptopropanesulphonate.

resistance through the food chain, the antibiotics that enter the environment can also be detected in food and drinking water resources [4, 5]. Therefore, the development of a feasible and effective method for the determination of FQs in water is of great importance to ensure the safety of human health.

Due to the complexity of sample matrices and low concentration levels of analytes, a preconcentration step is always required prior to FQs residues analysis. SPE is one of the widely used sample pretreatment techniques for FQs [6, 7]. However, the traditional SPE method needs a large amount of commercial adsorbent (>150 mg) and a long experimental time (>2 h). Therefore, to overcome these problems, solid phase-based extraction techniques including magnetic SPE [8, 9], stir bar sorptive extraction [10] SPME,[11, 12], and dispersive SPE (DSPE)[7, 13] were established. However, in magnetic SPE, the chromatographic column may be contaminated by nano-magnetic adsorbents when samples are transferred to subsequent instruments [14]. Stir bar sorptive extraction and SPME methods include shortcomings such as more complex instruments and a relatively long time to extract and reach equilibrium. For DSPE, adsorbents are added directly to the sample solution; the extensive interactions between the adsorbent and analytes can be facilitated by vortex stirring or ultrasound [15]. The adsorbent dispersed in solution increases the active surface area, which improves the kinetics of the extraction process. Compared to other pretreatment methods, DSPE has aroused great attention because of the advantages of no adsorbent conditioning, ease of operation, and high efficiency [16]. The extraction efficiency in the DSPE method depends primarily on the adsorbent properties, so finding a suitable adsorbent is of great importance.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of α-(1,4)-glycosidic linked D-glucopyranose units, which possess the hydrophobic central cavity and hydrophilic outer surface. Their particular cavity structures can offer a series of molecular interactions, such as van der Waals forces, hydrogen bonding, and hydrophobic interaction, then facilitate forming of host-guest inclusion complexes between CDs and analytes [17]. Up to now, many materials based on CDs have been widely used in adsorption and extraction fields [17–23]. For example, Wang et al. prepared a β-CD-based hypercrosslinked polymer (Bn-CD-HCP) through Friedel-Crafts reaction and applied it to enrich albendazole from aqueous media. The results proved that this adsorbent was efficient and recoverable [20]. Among these CDs-based adsorbents, crosslinked β-CD polymers have been reported extensively [18, 20, 21, 23]. Although CDs are safe for the environment, prolonged high-temperature reactions, large amounts of modifying reagents, and organic solvent are needed in the preparation of crosslinked β-CD polymers, which usually have a great impact on the environment.

Compared to the crosslinked β-CD polymers, the CD hybrid monolithic material based on sol-gel chemistry possesses better biocompatibility and lower toxicity, which can be prepared under mild conditions [24]. However, the research on CD-based monolithic material in DSPE was rare. All the CD-based monolithic materials in sample treatment were modified with native β-CD and then used as SPME adsorbents to extract only one or two drugs [25–28]. As mentioned, the procedure of SPME was time-consuming. Therefore, establishing an accurate and efficient DSPE method based on CD monolithic material adsorbent is desired. To the best of our knowledge, the application of CD hybrid monolithic material as the adsorbent for the analysis of FQs has not been explored. In this work, the hydroxypropyl β-cyclodextrin (HP-β-CD) hybrid monolithic material (CDHM) was prepared through a facile synthetic method and firstly used as a DSPE adsorbent to extract seven trace FQs including ofloxacin, ciprofloxacin, norfloxacin, enoxacin, lomefloxacin, gatifloxacin, and enrofloxacin in water samples. The effects of the experimental factors on the DSPE efficiency were investigated in detail. The adsorption mechanism of adsorbent toward FQs was comprehensively studied. The validation results showed the applicability of this method for the trace determination of FQs in environmental water.

2 | MATERIALS AND METHODS

2.1 | Materials

Glycidyl methacrylate (GMA), γ-methacryloxy propyltrimethoxysilane, and 1,8-diazabicyclo[5.4.0]undec-7-ene were purchased from Tokyo Chemical Industry (Tokyo, Japan). Poly(ethylene glycol) (Mn = 10,000) was obtained from Tianjin Bodi Chemical Holding (Tianjin, China). HP-β-CD was purchased from Shandong Binzhou Zhiyuan Biotechnology (Shandong, China). Tetramethoxysilane, 2,2-azobis (2-methylpropionamidine) dihydrochloride (AIBA), DMSO, sodium 3-mercaptopropanesulphonate were purchased from Energy Chemical (Shanghai, China). AIBA was recrystallized in methanol before use. Toluene, diethyl ether of analytical grade and ACN, methanol (MeOH), and formic acid of HPLC grade were obtained from Shandong Yuwang Industrial (Shandong, China). The studied seven FQs were all purchased from National Institutes for Food and Drug Control (Beijing, China), and their chemical structures are shown in Figure S1. Double distilled water was used throughout the study and

all the solutions were filtered through 0.22-μm pore size filters.

2.2 | Instrumental and HPLC conditions

The SEM image of the monolithic material was obtained using a Hitachi S4800 scanning electron microscope (Hitachi, Japan). Fourier-transform infrared spectroscopy (FT-IR) spectra of the samples were recorded with FT-IR Spectrometer Paragon 1000. Chromatographic analyses were performed on an LC-10A system (Shimadzu, Kyoto, Japan) consisting of an LC-10AT pump and SPD-10A UV-vis detector. The out signal was monitored and integrated using LC Solutions software (Shimadzu, Kyoto, Japan). A Phenomenex RP18 column (5 μm, 4.6 × 250 mm^2) was used for analytical separation. The column temperature was 25°C during the injection and the flow rate was 1 mL/min. UV detection was performed at 280 nm with 20 μL of injection volume. The mobile phase was a mixture of MeOH-ACN-water solution (10:8:82, v/v/v) containing 0.25% formic acid.

2.3 | Preparation of HP-β-CD hybrid monolith material

The monomer glycidyl methacrylate-bonded HP-β-CD (GMA-HP-β-CD) and CDHM adsorbents were synthesized according to our previous work with a minor modification [29]. A solution of HP-β-CD (2 g), GMA (0.73 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 g) in DMSO (5 g) was stirred for 30 min at 100°C. The resulting yellow solution was poured into a large amount of toluene, the oil-like precipitate was washed carefully with toluene and diethyl ether several times, then dried under vacuum at 70°C, GMA-HP-β-CD was finally obtained.

CDHM adsorbents were prepared as follows: a pre-polymerizable mixture was prepared by mixing and stirring 0.01 M acetic acid (6 mL), poly(ethylene glycol) (10000 MW, 648 mg), tetramethoxysilane (2280 μL), and γ-methacryloxy propyltrimethoxysilane (480 μL) for 2 h at 0°C to form a homogeneous solution. Then, GMA-HP-β-CD (200 mg), water (200 μL), sodium 3-mercaptopropanesulphonate (90 mg), and AIBA (10 mg) were added to 5 mL of the hydrolyzed mixture. The resulting mixture was mixed together and kept ultrasound for 5 min. Then, the mixture solution was maintained at 40°C for 20 h. The obtained polymerized monolithic material was Soxhlet extracted with methanol for 24 h and then dried under vacuum at 70°C.

2.4 | Sample preparation

Two lake water samples were obtained from different sites of the lake (located in Shenyang Pharmaceutical University in Benxi, Liaoning). The third sample was collected from the river (located in Benxi county in Liaoning Province). These water samples were stored in the dark at 4°C and filtered through a 0.22 μm membrane before extraction.

2.5 | Dispersive SPE procedure

In a typical DSPE process, 10 mg CDHM was dispersed into 6 mL of the water sample. The mixture solution was ultrasonicated for 10 min. After centrifugation, the supernatant was discarded and the adsorbents were collected in a 4-mL tube. Then, 3 mL of methanol containing 20% ammonium hydroxide was added and sonicated for 10 min. Then the desorption solvent was concentrated and dried under a nitrogen stream at 35°C. The mobile phase (200 μL) was used to re-dissolve the residue. Finally, the solution was filtered through a 0.22-μm membrane and submitted to HPLC-UV analysis. The schematic diagram of the DSPE procedure is depicted in Figure 1.

2.6 | Adsorption experiments

The adsorption isotherm was performed by suspending 10 mg CDHM in 6 mL of a mixed solution of FQs with a series of different concentrations (5–100 mg/L). After ultrasound for 30 min, the two phases were separated by centrifugation and a syringe filter (0.22 μm). Then the residual concentrations of FQs in the supernatant were analyzed by HPLC-UV. The adsorption amount was calculated by the following Equation (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the adsorption amount of CDHM (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the seven analytes in solution, respectively, and V is the volume of solution (6 mL), m is the amount of adsorbent (10 mg).

For the adsorption kinetics experiment, 10 mg CDHM was suspended in a 6 ml solution with an initial concentration of 80 mg/L for each analyte. After ultrasonication for a different time at room temperature, the solution was centrifugated and filtered with a syringe filter (0.22 μm). Finally, the FQs concentrations in the supernatants were

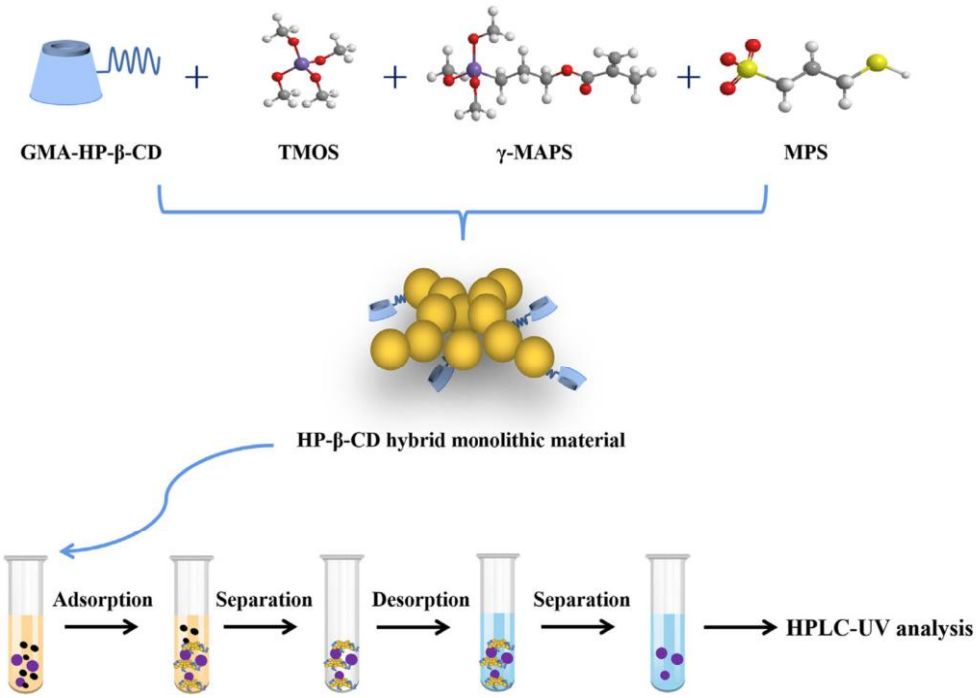

FIGURE 1 Schematic fabrication process of hydroxypropyl β-cyclodextrin hybrid monolith (CDHM) adsorbent and the dispersive SPE (DSPE) procedure for the determination of fluoroquinolones (FQs)

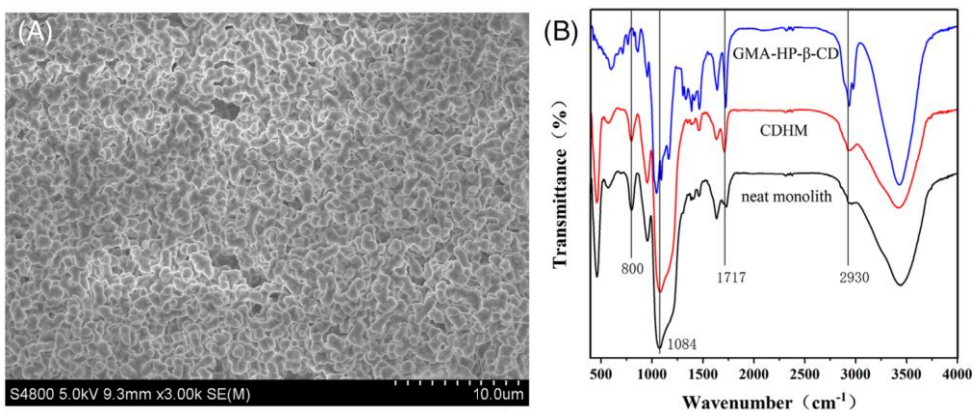

FIGURE 2 SEM image (A) and Fourier-transform infrared (FT-IR) spectra of GMA-HP-β-CD, hydroxypropyl β-cyclodextrin hybrid monolith (CDHM) adsorbent, and neat monolith (B)

calculated by HPLC-UV. The adsorption amount was determined by using Equation (1).

3 | RESULTS AND DISCUSSION

3.1 | Characterization of HP-β-CD hybrid monolithic adsorbent

The morphology of the CDHM adsorbent was observed by SEM. According to Figure 2A, the adsorbent exhibits large pores and a continuous skeleton. Mesopores are also found which is helpful for the adsorption of FQs onto the adsorbent. The FT-IR spectra of GMA-HP-β-CD, CDHM adsorbent, and neat monolith (without GMA-HP-β-CD modification) are shown in Figure 2B. In the spectra of CDHM adsorbent, the strong peaks at 1084 and 800 cm^{-1} are assigned to Si-O-Si vibrations. The peaks at 1717 and 2930 cm^{-1} correspond to the C=O vibration and the C-H vibration of GMA-HP-β-CD becomes stronger, these reveal the presence of GMA-HP-β-CD in the CDHM adsorbent.

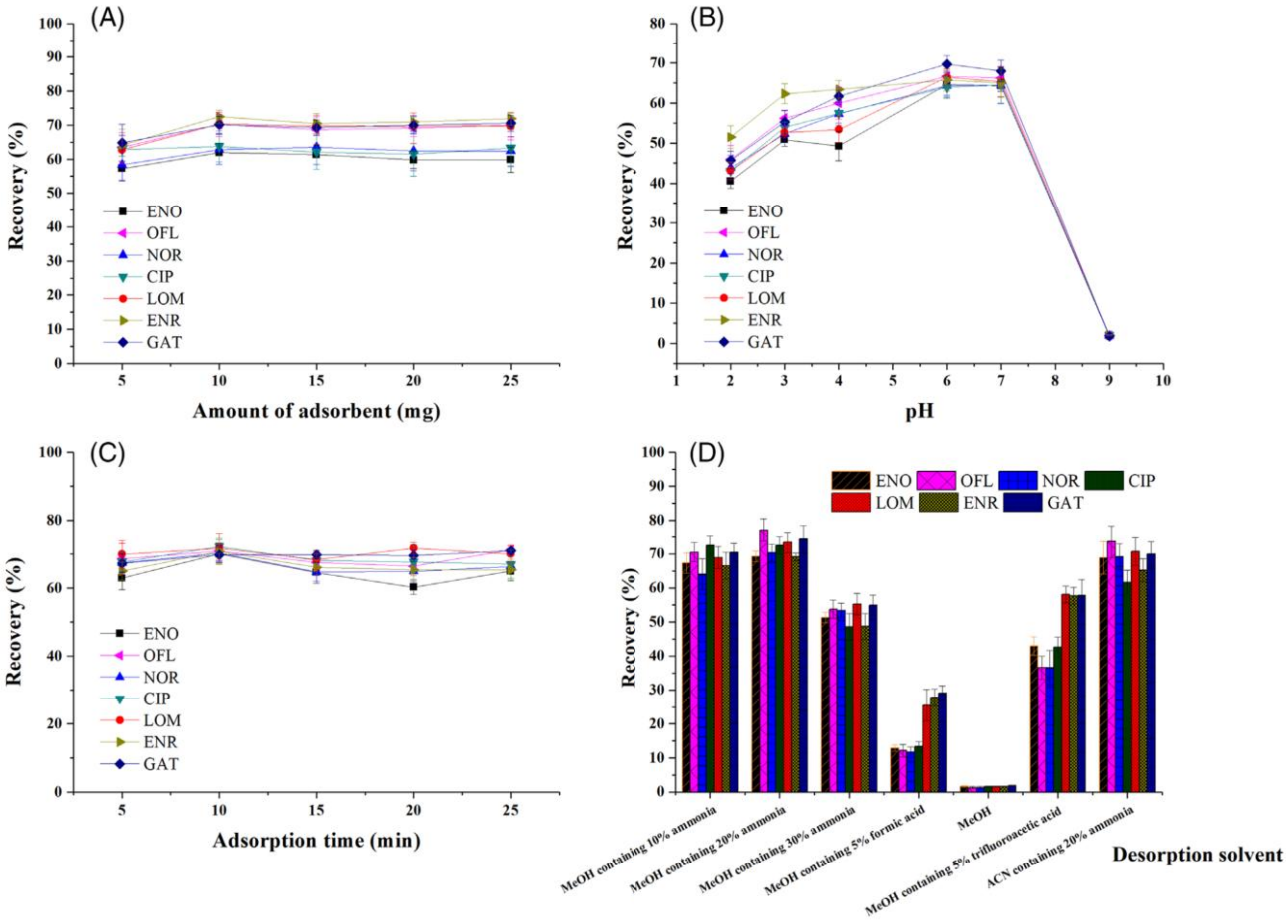

FIGURE 3 Effects of amount of adsorbent (A), pH of sample solution (B), adsorption time (C), and the type of desorption solvent (D) on extraction performance of dispersive SPE (DSPE) for fluoroquinolones (FQs)

3.2 | Optimization of extraction conditions

In order to obtain high extraction efficiency towards seven FQs, several key experimental parameters, including adsorbent amount, pH of sample solution, extraction time, type and volume of desorption solution, desorption time, and sample volume were investigated. All the experiments were performed in triplicate. The extraction recovery was used to evaluate the extraction efficiency.

3.2.1 | Effect of adsorbent amount

The adsorbent amount was optimized by varying its weight in the range of 5–25 mg. The extraction efficiency of FQs was lower when the less adsorbents were applied. With the adsorbent amount increasing from 5 to 10 mg, the recoveries of most FQs were increased. Continuously increasing the adsorbent amount from 10 to 25 mg, the recoveries of FQs were revealed almost constant (Figure 3A). Thus, the adsorbent amount of 10 mg was selected in this work.

3.2.2 | Effect of pH of sample solution

The pH value of the sample solution can affect the existing forms of analytes and the interactions between adsorbent and analytes, which, in turn, influence their extraction efficiencies. In this study, the effect of pH value on the extraction recoveries was investigated in the range of 2–9 (Figure 3B). The studied FQs are amphoteric compounds that possess pK_a1 (5.8–6.8) and pK_a2 (7.8–9.3) values [30–32]. In acidic pH conditions, FQs exist in protonated forms, and their electrostatic interaction with the negatively charged sulfonic acid groups of CDHM would occur. With the rise of pH from 2 to 6, the electrostatic interaction was decreased, while the extraction recoveries were increased. This might indicate that the electrostatic interaction is not the dominant mechanism in the extraction process. At pH 6–7, we obtained the highest extraction recoveries. The possible reason can be explained that at pH 6–7, FQs are in the molecular state, and HP-β-CD in CDHM can form host-guest inclusion complexes with FQs. On the other hand, hydrogen-bonding interaction between FQs and CDHM also contributes to adsorption. When the

pH further increased to alkaline, FQs tended to be negatively charged, the electrostatic repulsion between CDHM and FQs inhibits adsorption, and too many OH^- groups in the solution can weaken the hydrogen-bonding interaction. Accordingly, it results in low extraction recovery. Since the sample pH is in the range of 6–7, pH adjustment is not needed in later studies.

3.2.3 | Effect of extraction time

Extraction time is also an important factor that has an effect on extraction efficiency. In this study, the extraction time was optimized in the range of 5–25 min. In Figure 3C, when the adsorption time at 5 min, there was inadequate contact between CDHM and FQs, which resulted in incomplete adsorption. With the increasing extraction time from 5 to 10 min, the recoveries of FQs were increased, while further increasing the extraction time can not improve the extraction efficiency. The possible reason was that the distribution of the target between FQs and the absorbent sites on CDHM has reached equilibrium as the extraction time increased from 10 to 25 min. Therefore, 10 min was selected as the optimized extraction time.

3.2.4 | Effect of desorption conditions

The desorption step plays an important role in the extraction procedure. A proper desorption solvent can provide effective desorption of targeted analytes from the adsorbent. In our preliminary experiment, pure MeOH and ACN were tested as desorption solvents. However, the adsorptive FQs could not elute from the adsorbent. Considering that the hydrogen-bonding and electrostatic interactions may involve the extraction, along with acid and alkaline conditions breaking the hydrogen-bonding and electrostatic interactions between the adsorbent and target FQs, three kinds of additives including ammonia, formic acid, and trifluoroacetic acid were added in the eluting reagent in order to obtain optimum desorption conditions. Compared with ACN-ammonia solvent, MeOH-ammonia solvent provided higher recoveries, which might be attributed to the fact that MeOH has a strong hydrogen bonding capacity to compete for the CDHM binding sites. Therefore, extraction efficiencies of different kinds of MeOH solutions were further investigated. The results in Figure 3D clearly revealed that the MeOH/ammonia solvent can significantly improve the extraction efficiency, and MeOH with 20% (v/v) ammonia solvent exhibited the best desorption performance among the solvents. This is attributed to the fact that under alkaline conditions, FQs were negatively charged, leading to a decrease in the interaction between the analytes and adsorbent. Consequently, MeOH with 20% (v/v) ammonia was chosen as the desorption solvent.

Next, the effect of the desorption solvent volume in the range of 1–4 mL was studied (Figure S2A). For norfloxacin, lomefloxacin, enrofloxacin, and gatifloxacin, there was no obvious change in their recoveries when the desorption solvent volume increased from 1 to 4 mL. And enoxacin, ofloxacin, and ciprofloxacin obtained the highest extraction efficiencies when the desorption solvent volume was 3 mL. Thus, 3 mL desorption solvent was used for further study.

Desorption time is a significant factor affecting recovery. The desorption time ranging from 5 to 25 min was also examined and the results were shown in Figure S2B. It was observed that the best extraction recovery was obtained when the desorption time was 10 min. Therefore, the desorption time was set at 10 min for the following experiments.

3.2.5 | Effect of the sample volume

In order to achieve good recovery, the sample volume was also studied in the range from 3 to 15 mL. Figure S2C demonstrated the recoveries increased with the increase of the sample volume from 3 to 6 mL, however, further increasing the sample volume gave no obvious improvement for the extraction recoveries. Therefore, 6 mL of the sample volume was used to perform all experiments.

3.3 | Reusability and repeatability

The reusability of adsorbents is of great importance from both environmental and economic standpoints and is a reference factor for the stability of materials. To study the reusability of the CDHM adsorbent, the regeneration of CDHM was performed by washing two times with desorption solvent and one time with MeOH before the next extraction. Then, the adsorbent was repeatedly used for the extraction of FQs. As shown in Figure S2D, the CDHM adsorbent can be reused at least five times without a significant change in extraction capacity, indicating that the CDHM adsorbent exhibited good reusability.

3.4 | Adsorption behavior of adsorbent

For a better understanding of the adsorption process, the kinetic adsorption and isothermal adsorption experiments of the studied FQs were carried out, as shown in Figures S3 and S4, respectively.

3.4.1 | Kinetic adsorption analysis

The kinetic adsorption experiments of seven FQs were carried out at the various time and their adsorption curves are shown in Figure S3. From Figure S3, we can see that the adsorption amounts of seven FQs onto the adsorbent increase rapidly with the increment of adsorption time from 2 to 10 min, then reach the adsorption equilibrium. Furthermore, the pseudo-first-order rate equation and pseudo-second-order rate equation were used to analyze the kinetics data and explore the binding mechanism, as expressed in Equations (2) and (3):

$$Ln\,(Q_e - Q_t) = LnQ_e - k_1 t \tag{2}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{3}$$

where Q_e and Q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively; k_1 and k_2 are the equilibrium rate constants of pseudo-first-order and pseudo-second-order; and t is adsorption time.

The experimental results using two models are shown in Table S1. Compared with the pseudo-first-order model, the calculated values of Q_e from the pseudo-second-order model are closer to the actual experimental values, and the coefficient of determination (R^2) values are higher than those of the pseudo-first-order model. Thus, the pseudo-second-order model is more fitted to the adsorption kinetic behavior of CDHM. These findings implied that the adsorption process favors chemical adsorption.

3.4.2 | Isothermal adsorption analysis

Next, we investigated the adsorption capacity of CDHM adsorbent toward seven FQs under a broad initial concentration range (5–100 mg/L). In this study, two typical isothermal models (Langmuir and Freundlich) were chosen to describe the adsorption behavior [18]. The linear equations for Langmuir and Freundlich isotherms are illustrated below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{4}$$

$$LnQ_e = LnK_F + \frac{1}{n} LnC_e \tag{5}$$

where Q_e and Q_m are the equilibrium and maximum adsorption amount, respectively; C_e is the concentration of analytes at equilibrium; K_L is the Langmuir adsorption isotherm model constant; and K_F and n are the Freundlich adsorption isotherm model constants.

As shown in Table S2, the maximum adsorption amount calculated by Langmuir isothermal model is close to the actual experimental values. In addition, the coefficient of determination (R^2) values in the Langmuir isothermal model are higher than those of the Freundlich isothermal model, which suggested that the Langmuir isothermal model is more suitable to describe the adsorption equilibrium. However, it can be found that the adsorption of CDHM to seven FQs also has a well-fitting degree to the Freundlich isothermal model ($R^2 > 0.97$), which indicates the adsorption process may be identified as the incorporation of both chemisorption and physisorption. Figure S5 shows the FQs adsorption mechanism of CDHM. We supposed that the following adsorption interactions which can influence the adsorption of FQs on CDHM: the host-guest inclusion hydrophobic interaction effect of HP-β-CD hydrophobic cavity to FQs; the hydrogen-bonding forces among the hydroxy groups of HP-β-CD (and polymer backbone) and the carboxyl groups and nitrogen-atoms of FQs; electrostatic interaction between the sulfonic acid groups in CDHM and the amphoteric FQs. Therefore, the adsorption of FQs with CDHM can be regarded as a complicated process that combined several factors.

3.5 | Analytical performance

To evaluate the practicality of the proposed DSPE-HPLC method for the analysis of FQs, analytical performances including specificity, linearity, LOD, LOQ, and extraction recovery were examined under the optimum experimental conditions. The results are shown in Table 1. Chromatograms of the spiked water sample, standard solution, and blank water sample are shown in Figure 4. There was no interfering signal at the retention of the targeted analytes, indicating that no matrix interference existed. Good linearity was observed within the concentration range with R^2 values higher than 0.9990. The LOD and LOQ were estimated as the minimum detectable concentration corresponding to S/N values of 3 and 10, and their values were in the ranges of 0.4–1.2 and 1.4–4.0 ng/mL, respectively. The repeatability of the method was evaluated by the intra-day and inter-day precisions at three concentration levels (20, 200, and 500 ng/mL). The intra-day and inter-day RSDs were in the ranges of 2.6–4.5 and 3.8–5.6%, respectively. The ranges of extraction recovery and enrichment factor were 82.5–91.8 and 26.8–28.8%, respectively.

3.6 | Application to real samples

To evaluate the practical reliability, the method was applied to the analysis of FQs in three kinds of water

TABLE 1 Parameters of analytical performance

Analyte	Linearity range (ng/mL)	R^2	LOD (ng/mL)	LOQ (ng/mL)	Repeatability (RSD%) Intra-day ($n = 9$)	Repeatability (RSD%) Inter-day ($n = 27$)	Extraction recovery (%)	Enrichment factor[a]
Enoxacin	1.4–500	0.9992	0.4	1.4	2.6	4.2	85.6	26.8
Ofloxacin	1.9–500	0.9990	0.6	1.9	4.5	5.6	89.1	28.8
Norfloxacin	1.4–500	0.9992	0.4	1.4	3.0	5.2	85.4	28.2
Ciprofloxacin	1.6–500	0.9994	0.5	1.6	2.9	4.1	82.5	28.4
Lomefloxacin	2.8–500	0.9995	0.8	2.8	2.9	4.5	87.6	27.6
Enrofloxacin	1.5–500	0.9996	0.4	1.5	2.6	3.8	91.8	27.8
Gatifloxacin	4.0–500	0.9995	1.2	4.0	3.1	4.2	84.8	27.2

[a]The enrichment factor (EF) was calculated using the following equation: $EF = C_1/C_2$, where C_1 and C_2 are the analyte concentration in the final extract and the initial analyte concentration in the water sample solution, respectively.

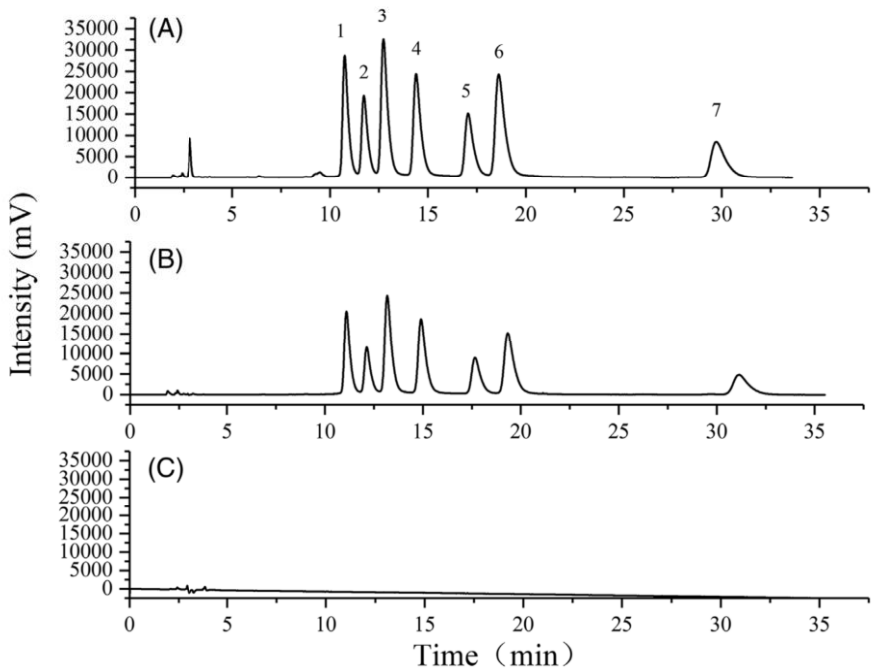

FIGURE 4 Typical HPLC chromatograms of (A) spiked water sample (200 ng/mL), (B) standard solution (5 μg/mL), and (C) blank water sample. Peaks: (1) Enoxacin (ENO); (2) ofloxacin (OFL); (3) norfloxacin (NOR); (4) ciprofloxacin (CIP); (5) lomefloxacin (LOM); (6) enrofloxacin (ENR); (7) gatifloxacin (GAT)

samples. The recoveries were determined by adding a mixture of quinolone standard solutions with three concentrations of 20, 200, and 500 ng/mL to the real samples. From Table S3, we can see that FQs were not detected in these samples. Recoveries of FQs are between 85.8 and 102.6%, and the RSDs are in the range of 1.6–5.8%. The chromatograms of the spiked water sample, standard solution, and blank water sample are shown in Figure 4.

3.7 | Comparison of the method with other reported methods

The proposed method was compared with other analytical approaches for the determination of FQs in water, and the results are shown in Table 2. Although lower LODs and LOQs were obtained when using LC-MS/MS method [6, 7, 33], also had disadvantages of the complicated operation and high cost. It is worth noting that the adsorbent amount, sample amount, and extraction time of the proposed method are superior to those of most outlined methods, indicating the good extraction efficiency of the proposed adsorbent [6, 7, 18, 33–35]. The low RSDs (≤5.6%) of the developed method show its good precision. And the CDHM adsorbent can be reused for five cycles which reduces the analysis costs (Figure S2D). In addition, we also evaluated the cost to produce CDHM adsorbents. It costs approximately US$0.90 to produce a batch of 100 adsorbents (Table S4). If the material is scaled up for production, the cost will be reduced significantly. The above results demonstrated that the method has the advantages of simple operation, low cost, acceptable linear range, and

TABLE 2 Comparison of the proposed method with other techniques for the determination of quinolone in water samples

Adsorbents	Methods	Sample amount (ml)	Extraction time (min)	Linearity (ng/ml)	LODs (ng/ml)	LOQs (ng/ml)	RSD (%)	Enrichment factors	Ref.
500 mg/3 ml Strata-X cartridge	SPE-HPLC-DAD-FLD	100	>30	0.025–10	0.001–0.05	0.005–0.1	0.7–7.3	-	[34]
8 mg porous cyclodextrin polymers	SPE-HPLC-DAD	20	>80	25–5000	2.67–5.50	8.95–18.9	1.88–4.4	-	[18]
3 ml GO@NH@Fe_3O_4	MSPE-MALDI-TOF MS	12	45	-	10	-	-	80–100	[35]
30 mg microporous polymeric microspheres	DSPE-LC-MS/MS	20	>35	0.02–10	0.005–0.0067	0.012–0.02	4.8–7.8	183–194	[7]
500 mg/6 ml Oasis HLB cartridge	SPE-UPLC-MS/MS	100	60	LOQ–4	0.02–0.04	0.07–0.15	0.2–2.4	-	[6]
20 mg of IRMOF-3 coated SiO_2/Fe_3O_4 MPs	MSPE-LC-MS/MS	25	20	0.01–5	0.001–0.003	0.005–0.01	6.58–10.6	21.0–23.8	[33]
10 mg CDHM	DSPE-HPLC-UV	6	30	LOQ–500	0.4–1.2	1.4–4.0	2.6–5.6	26.8–28.8	This work

comparable detection limit. Therefore, the method is considered to be a promising strategy for the analysis of FQs in environmental water.

4 | CONCLUDING REMARKS

In this work, a method of detecting seven FQs in environmental water samples was built, using HP-β-CD hybrid monolithic material as dispersive solid-phase extractant. The proposed adsorbent exhibited good adsorption performance to target FQs, due to multiple interactions including host-guest inclusion hydrophobic interaction, hydrogen-bonding force, and electrostatic interaction. Meanwhile, the developed analytical method provided analytical advantages in terms of simple operation, low cost, comparable detection limit, and accuracy. Based on the obtained results, it can be indicated that the described method might be a tool for the determination of FQs residues in the real samples, as well as providing useful information on the application of cyclodextrin-based hybrid materials in the separation field.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

The author elects to not share data.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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