

ROOM-TEMPERATURE AQUEOUS CO-PRECIIPITATION SYNTHESIS OF
MAGNETIC Fe_3O_4 @ZIF-8 CORE-SHELL NANOCOMPOSITE FOR MAGNETIC
SOLID-PHASE EXTRACTION AND COLORIMETRIC DETERMINATION OF
FLUOROQUINOLONE POLLUTANTS IN WATER SAMPLES

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DOI: <https://doi.org/10.5281/zenodo.23031260>

Keywords

Fe_3O_4 @ZIF-8; Magnetic solid-phase extraction; Fluoroquinolones; Colorimetric determination; Water analysis.

Article History

Received: 01 June 2026

Accepted: 23 August 2026

Published: 29 September 2026

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Abstract

Fluoroquinolone residues in aquatic environments require analytical methods that combine efficient extraction with simple and sensitive detection. In this study, an aqueous Fe_3O_4 @ZIF-8 core-shell-type magnetic nanocomposite was prepared for magnetic solid-phase extraction (MSPE) and colorimetric detection of the ciprofloxacin (CIP), levofloxacin (LEV), and ofloxacin (OFX) in water samples at room temperature. The Fe_3O_4 magnetic nanoparticles were initially synthesized by aqueous precipitation and then coated with a ZIF-8 shell at room temperature. FTIR, XRD, SEM and TEM characterization confirmed the formation of the composite and its core-shell structure. The optimization of the MSPE conditions was conducted in terms of pH, adsorbent dose, extraction time, initial concentration, ionic strength and desorption volume. For maximum extraction performance, the pH of the solution was optimized at 6–7 and the contact time was optimized at 20–30 min, with about 20–30 mg of adsorbent. Initial adsorption was fast and reached nearly to the equilibrium after a while and the kinetic and equilibrium studies showed pseudo-second-order adsorption and saturation-type adsorption. The linear calibration response (R²) for the integrated analytical procedure was 0.9987, 0.9984, and 0.9986 for CIP, LEV and OFX, respectively. Mean extraction recoveries reached 95.1%, 94.3%, and 94.7%, with mean RSD values of 2.18%, 2.31%, and 2.24%. A sample of 50 mL was taken, and 5 mL of elution was used, which gave a nine-fold enrichment. Recoveries were generally over 90% for both spiked tap and

surface waters, which indicated a low matrix influence. The composite also showed good extractability in repeated extractions. The developed $\text{Fe}_3\text{O}_4/\text{ZIF-8-MSPE}$ /colorimetric method was thus an integrated magnetic separation method for the determination of CIP, LEV and OFX in aqueous samples. The integration made sample handling much easier.

INTRODUCTION

Fluoroquinolones (FQs) are broad-spectrum antibacterial agents that have been widely used in human and veterinary medicine due to their activity against a variety of pathogenic microorganisms. Examples of common members of this class are ciprofloxacin, norfloxacin, ofloxacin, levofloxacin and enrofloxacin[1]. The widespread use, inadequate metabolism and ongoing discharge from domestic, hospital, agricultural and pharmaceutical use have led to their presence in aquatic environments [2]. The environmental concern of FQs is due to their chemical stability, persistence and biological effects at relatively low concentrations. They have been detected in surface water, wastewater, ground water, sediments and in aquatic organisms in various geographical areas[3]. The detection and control of FQs is difficult in water, as is protecting the environment. These compounds may bind to natural organic matter, metal ions, minerals or other dissolved constituents present in the sample, and thus affect their mobility, persistence, and bioavailability, as well as their recovery in the laboratory analysis. They are also found in the environment and have concerns with environmental persistence and effects on non-target organisms[4].

There have been recent reports on measurable effects on freshwater organisms for a number of FQs, highlighting the need for sensitive monitoring and reliable detection of these contaminants in water. The analysis of water is an integral part of the environmental assessment of contaminants, and the development of analytical methods that are both efficient and suitable for the enrichment and detection of trace FQs in water is therefore important[5]. Chromatographic methods are the most sensitive and selective

methods for the determination of FQs, and in particular, high-performance liquid chromatography and liquid chromatography-mass spectrometry (LC-MS) are powerful tools for FQ determination[6]. These methods are, however, quite costly and require specialized instrumentation, operation and extensive sample preparation, and relatively high amounts of solvent use[7]. Recent developments in FQ analysis have therefore focused on combination of target enrichment, molecular recognition and signal transduction to enhance the analytical performance, while decreasing the complexity of the procedure. In this respect solid-phase extraction (SPE) can be very useful to isolate target components from complex aqueous matrices while at the same time concentrating the sample prior to instrumental or spectroscopic analysis[8]. An added benefit of magnetic solid phase extraction (MSPE) is that it is an extraction method that incorporates a magnetic component into the sorbent. After adsorption, the sorbent may be easily retrieved from the sample by means of an external magnetic field, which eliminates the necessity of using traditional filtration and/or centrifugation[9]. Therefore, the development of magnetic porous material has received great attention, particularly for the pharmaceutical and environmental analysis [10]. Metal-organic frameworks (MOFs) are particularly appealing because of their chemically tunable pore structures, their high surface areas, and their chemically tunable interaction sites, making them appear to be particularly attractive as extraction materials [11]. ZIF-8 is a zeolitic imidazolate framework material with a porous structure and chemical properties that can promote the interactions with the organic contaminants[12]. Hydrogen bonding, electrostatic interaction, π - π

interaction, pore filling and surface complexation have all been studied and suggested to be mechanisms that can contribute to the adsorption of FQ. The ZIF-8 and magnetite (Fe_3O_4) make a complementary material architecture, with the porous MOF part offering adsorption functionality and the Fe_3O_4 part magnetic manipulation[13]. In recent years, magnetic ZIF-based materials have been shown to have potential as fast extractor of FQ, such as the one, which comprises Fe_3O_4 and ZIF-8 in more complex composite structures[14]. As the designs become more and more complex, however, there might be several synthesis steps and other functional parts. In the case of simple extraction, efficient separation, efficient analyte enrichment, and simple analytical application, a simpler Fe_3O_4 @ZIF-8 core-shell system made under mild aqueous conditions might be a good alternative[15].

Metal-organic frameworks (MOFs) have emerged as versatile porous materials with considerable potential in environmental analysis and separation science because of their high specific surface areas, tunable pore structures, diverse surface functionalities, and adjustable chemical compositions [16, 17]. Their porous architectures provide abundant active sites for the adsorption and preconcentration of a wide range of organic and inorganic pollutants from aqueous matrices [18]. In recent years, the integration of MOFs with magnetic nanoparticles has attracted particular attention for developing multifunctional nanocomposites that combine the high adsorption capacity of MOFs with the rapid magnetic separation capability of magnetic materials [19]. Such MOF-based magnetic nanocomposites can facilitate efficient extraction of target contaminants while eliminating conventional filtration or centrifugation steps, thereby improving analytical efficiency and reducing sample-processing time [20]. Among various MOFs, zeolitic imidazolate framework-8 (ZIF-8), composed of Zn^{2+} ions and 2-methylimidazole linkers, is especially attractive owing to its high porosity, chemical stability, and surface

characteristics suitable for interactions with pharmaceutical contaminants. Incorporation of magnetite (Fe_3O_4) into ZIF-8 further provides magnetic responsiveness and enables convenient recovery of the adsorbent from aqueous samples. Therefore, magnetic MOF-based core-shell nanocomposites represent promising platforms for the selective preconcentration and subsequent sensitive determination of emerging pharmaceutical pollutants in environmental water samples [21].

In this study, the Fe_3O_4 @ZIF-8 core-shell nanocomposite is investigated to be an adsorbent for the extraction of fluoroquinolone pollutants from water samples using magnetic solid phase extraction. The developed approach involves magnetic enrichment followed by colorimetric determination, which offers a pathway where the FQs are first enriched on the porous magnetic nanocomposite, and are then quantified by a spectrophotometric color response. The study of the structural and physicochemical characteristics of the material produced, optimization of the main extraction conditions, adsorption behavior studies, analytical performance of the colorimetric method and its applicability to water samples. The project combines material synthesis, magnetic extraction and colorimetric detection, in order to develop a feasible analytical approach to determine FQ contaminants in water.

Research Gap and Study Rationale

It has been recently confirmed that MOFs, ZIF-8, and magnetic MOF-based composites are good platforms for the adsorption and enrichment of fluoroquinolones. Most of the previous research has been conducted on adsorptive removal of FQs or highly complex magnetic composites and chromatographic detection. In recent years, for instance, magnetic ZIF materials containing other materials like multiwalled carbon nanotubes or silica have been developed, and ZIF-8-based molecularly imprinted materials have been used in combination with HPLC for the highly selective determination of FQ materials. This affords a chance to explore a simpler magnetic

extraction/core-shell ZIF-8/Fe₃O₄ contrast agent combination that is relatively easy to access and also employs a colorimetric method for detection. The idea behind the present study is thus to combine the complementary properties of Fe₃O₄ and ZIF-8 in one magnetic adsorbent. Fe₃O₄ has been found to have fast magnetic separation while ZIF-8 has a porous surface that allows multiple adsorption processes to occur between the zeolite and FQs. The aqueous, room-temperature synthesis is designed to result in a relatively mild preparation route and to avoid the unnecessary complexity. When combined with MSPE, this material can focus trace FQs prior to colorimetric measurement, which may provide enhanced analytical response and minimize sample-preparation needs. The study, therefore, aims to fill the gap of a simple, enrichment-based, magnetically assisted analytical method for the determination of FQs in water and to assess its performance by its optimization, validation, reusability and real sample analysis.

Materials and Methods

Chemicals, Reagents, Materials and Instruments

The magnetic nanocomposite was prepared and processed using analytical grade Ferric chloride hexahydrate (FeCl₃·6H₂O), Ferrous chloride tetrahydrate (FeCl₂·4H₂O), Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O], 2-methylimidazole, Sodium hydroxide (NaOH), Methanol, Hydrochloric acid, and Ethanol. Throughout the experimental work, de-ionized water having resistivity of about 18.2 MΩ cm was utilized. Fluoroquinolones analytical standards of Ciprofloxacin, Norfloxacin and Levofloxacin were used as representative analytes. Standard solutions were prepared in 1000 mg L⁻¹ in the stock bottles (amber glass bottles) and stored at 4 °C and then prepared into working solutions just before use. With magnetic stirrer controlled by the magnetic stirring rate, analytical balance, pH meter, centrifuge, ultrasonic bath, vacuum drying system and neodymium magnetic separator, the synthesis was conducted under controlled conditions. Powder X-ray diffraction (XRD), scanning electron

microscopy (SEM) and transmission electron microscopy (TEM) were used for structural and morphological characterization. Subsequent analytical measurements were made using UV-visible spectrophotometry. Laboratory detergent was used to clean all glassware followed by a thorough tap and deionized water wash before drying. Unless otherwise indicated, all solutions used were freshly prepared.

Synthesis of Fe₃O₄@ZIF-8 Core-Shell Nanocomposite

Preparation of Fe₃O₄ Magnetic Nanoparticles

Aqueous co-precipitation was used for the preparation of magnetite nanoparticles. FeCl₃·6H₂O (5.40g, 20mmol) and FeCl₂·4H₂O (3.98g, 20mmol) were each dissolved in 50mL of deionized water and mixed together under continuous magnetic stirring, N₂ free. The solution of Fe³⁺/Fe²⁺ was heated up to 60 °C and stirred at 600 rpm for 20 min. A 2.0 M NaOH solution was then added dropwise until a pH of ~10.0 was reached. The solution quickly turned from yellowish brown to black, which meant that magnetite had formed. Stirring continued for 45 min, at 60 °C. The black precipitate was magnetically collected, washed several times with deionized water until the washings were close to neutral pH and then washed twice with ethanol. Fe₃O₄ nanoparticles obtained were dried under vacuum at 60 °C for 12 h and kept in a sealed glass vial[22].

Room-Temperature Aqueous Formation of ZIF-8 Shell

The prepared Fe₃O₄ nanoparticles were ultrasonicated in 50 mL of deionized water for 20 min and the Zn(NO₃)₂·6H₂O (1.49 g, 5 mmol) was dissolved in 50 mL of deionized water, while 2-methylimidazole (1.64 g, 20 mmol) was dissolved in 50 mL of water. Fe₃O₄ suspension was then added to the zinc nitrate solution and stirred for 15 min at 500 rpm. This was done by introducing the 2-methylimidazole solution slowly, while stirring. The reaction mixture was allowed to react at room temperature (25 ± 2 °C) for 6 h to allow nucleation and growth of ZIF-8 on the magnetic

cores. The dark composite material suspension was then separated by magnetic separation and washed three times with deionized water and twice with ethanol to wash away unreacted precursors and loosely bound surface species[4].

Formation of Fe_3O_4 @ZIF-8 Core-Shell Nanocomposite

The purified Fe_3O_4 @ZIF-8 material was subsequently redispersed in ethanol and sonicated for 10 min to eliminate the weakly attached particles and enhance core-shell structure

dispersion. It was then recovered by an external neodymium magnet, and dried at a vacuum of 60 °C for 12 h. The dried product was ground to give a uniform powder with a gentle grinding of the agate mortar. The Fe_3O_4 @ZIF-8 nanocomposite was kept in an air tight amber bottle for further characterization and adsorption experiments. No hydro or solvothermal treatment was made during synthesis, and the synthesis was carried out in room-temperature aqueous solutions to obtain a relatively gentle synthesis method for the porous magnetic composite.

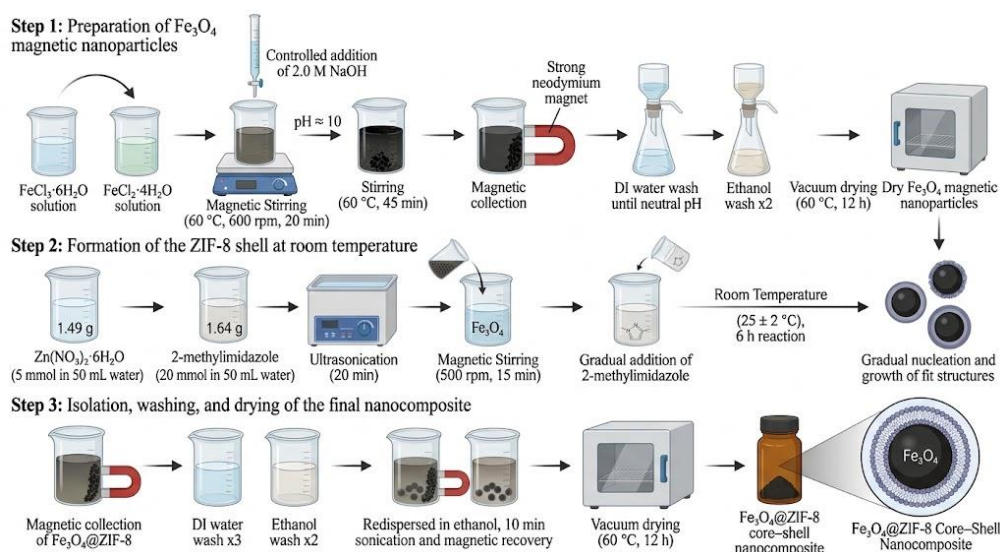


Figure 2. 1 Graphical Abstract of Synthesis of Fe_3O_4 @ZIF-8 Core-Shell Nanocomposite

Characterization of the Synthesized Nanocomposite

Fourier Transform Infrared Spectroscopy

The characteristic functional groups and chemical bonds of Fe_3O_4 , ZIF-8 and Fe_3O_4 @ZIF-8 nanocomposite were identified using Fourier transform infrared (FTIR) spectroscopy. Finely ground samples were analyzed in the range 4000–400 cm^{-1} , with the appropriate sampling configuration. The spectra of individual Fe_3O_4 and ZIF-8 and the final composite were compared to identify characteristic Fe–O, Zn–N, C–N, C=N and imidazolate-related vibrational bands. Successful integration of the magnetic core and ZIF-8 framework was assessed by changes in the

position and intensity of the bands after the formation of the composite.

X-Ray Diffraction

Structure characterization of the prepared Fe_3O_4 @ZIF-8 nanocomposite was performed by Powder X-ray diffraction (XRD). $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) was used over 2θ angle range of 5–80° with suitable scanning rate for the analysis of dried samples. The diffraction pattern of the composite was compared with the diffraction pattern of the separately prepared Fe_3O_4 and ZIF-8 materials. To confirm the retention of the magnetite phase, as well as the formation of the

crystalline ZIF-8 framework, characteristic reflections were examined.

Scanning Electron Microscopy

The surface morphology, particle aggregation and approximate particle-size characteristics of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ were studied by scanning electron microscopy. A small amount of each of these dry samples was spread on conductive carbon tape on an aluminum stub and then dried completely before examination. The samples were investigated at a voltage that is suitable for imaging morphological nanostructures. Changes in morphology were assessed by comparing the SEM images of Fe_3O_4 and the composite, which were obtained before and after the growth of ZIF-8 around the Fe_3O_4 particles.

Transmission Electron Microscopy

The core-shell architecture of the synthesized material has been directly confirmed at the nanoscale by using TEM. The $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ powder was ultrasonically dispersed in ethanol and a drop of the dilute dispersion was placed on a carbon coated copper grid and left to dry at ambient temperature. TEM images were recorded at well-chosen accelerating voltage and magnification to achieve the resolution of the magnetic Fe_3O_4 core and ZIF-8 shell. The dimensions of the particles and their shell morphology were determined by taking representative micrographs.

Preparation of Fluoroquinolone Standards and Water Samples

Preparation of Standard Solutions

The following fluoroquinolones were chosen as model compounds: Ciprofloxacin (CIP), ofloxacin (OFL), and levofloxacin (LEV). The stock solutions for individual stocks were accurately dissolved in an appropriate volume of deionized water to give a stock solution of 1000 mg L^{-1} . Where necessary the dilute hydrochloric acid was added as it was used to aid in complete dissolution, fluoroquinolones being pH dependent. Amber glass bottles were used for the

stock solutions, which were stored at 4°C . Mixed working standard solutions were made up by serial dilution of the individual stocks in deionized water. The calibration and extraction experiments were performed with concentrations which fall within the analytical range of the method developed.

Preparation of Spiked and Real Water Samples

Optimization experiments were carried out using deionized water to reduce matrix related interference. Aliquots of the tap and surface-water samples were spiked with known amounts of CIP, OFL and LEV for recovery experiments. The water samples were collected in clean polyethylene bottles and brought to the laboratory for analysis and stored at 4°C . After sampling was carried out at room temperature and suspended particulate matter was removed by using the membrane filters with $0.45 \mu\text{m}$ pore size. 50 mL of the water sample was placed into a clean glass vessel for each experiment, adjusted to the pH required for the experiment and then passed through the magnetic solid phase extraction. Samples were analyzed in parallel without the use of spikes to evaluate background contributions[23].

Magnetic Solid-Phase Extraction Procedure

Adsorption of Fluoroquinolones

50 mL aliquot of FQ-contained water was placed in a glass extraction vessel and a fixed mass of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was placed in it. The extraction time was determined and the suspension was shaken at 500 rpm. In this step, FQ molecules interacted with porous ZIF-8 shell, and concentration of these molecules on the magnetic adsorbent was achieved.

Magnetic Separation

The extraction vessel was then positioned next to a neodymium permanent magnet after it was adsorbed. The $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particles attracted quickly to the wall of the vessel and the aqueous phase was carefully decanted. In order to reduce the loss of adsorbent during removal of the sample

matrix, magnetic separation was performed until the solution was visually clear.

Washing and Desorption

Then, 5 mL of DI water was used to wash the $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ for the purpose of removing matrix components that could be easily washed away. The selected desorption solvent was then added to the adsorbent (2 mL) and vortex-mixed for 2 min. The eluate obtained after magnetic separation was collected for colorimetric determination of FQs.

Extraction Recovery

The extraction recovery was determined by calculating the concentration recovered from MSPE with the known concentration added into the aqueous sample. Recovery was calculated as the percentage of the relationship $C_e/C_0 \times 100$, where C_e is the concentration found after the addition of the spike and C_0 is the initial concentration of the spike added[24].

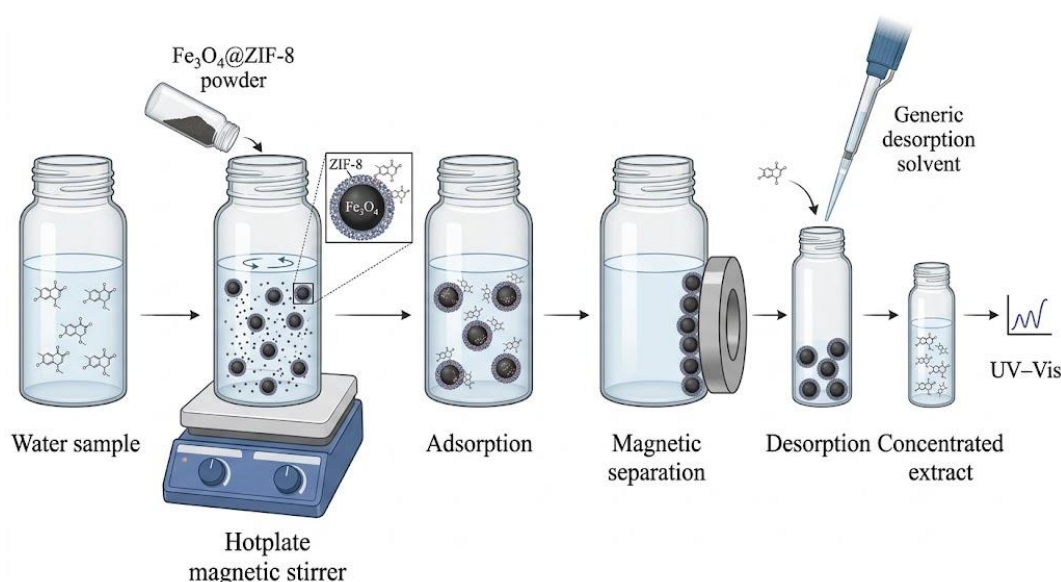


Figure 2. 2 Magnetic Solid-Phase Extraction (MSPE) of fluoroquinolones from water using $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ core-shell nanocomposite

Optimization of Magnetic Extraction Conditions

All the magnetic solid-phase extraction conditions were systematically optimized to obtain the highest and consistent percentage of CIP, NOR and LEV. All the optimization experiments were conducted on 50 mL aqueous solution of a known concentration of the three fluoroquinolones, with one parameter of the experiments being altered, and the other parameters kept constant. The effect of solution pH was evaluated in the range of 2–9 as fluoroquinolones have ionizable functional groups and their adsorption properties are significantly pH dependent. Adjustments were made to the pH with dilute hydrochloric acid or

sodium hydroxide. Different dosages of $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ (5, 10, 20, 30, 40 and 50 mg of adsorbent) were tested to determine the effect on its influence. It was expected that the greater the mass of the adsorbent the more active sites will be available, but too much may not increase the practical enrichment factor[25].

Different contact times between 1 and 60 min were used to optimize the extraction time and samples were taken after 1, 5, 10, 15, 20, 30, 45 and 60 min to see when equilibrium was reached. The effect of initial FQ concentration was investigated on a suitable range to see adsorption behavior and extraction efficiency. The ionic-

strength effects were examined by adding sodium chloride at certain concentrations from 0 to 1.0% (w/v) to evaluate the competitive and salting-out effects. Optimization of desorption was done by comparing different suitable polar solvents and acidified solvent systems. Also the amount of desorption solvent, contact time and number of desorption cycles was studied. The recovery for each condition was calculated and the condition which gave high recovery with minimum solvent and practical extraction time was taken to be the optimum condition. Each of the optimization experiments was repeated at least three times and the average of the recoveries was used for comparison.

Adsorption and Extraction Mechanism Studies

The adsorption kinetics involved were explored by exposing a given weight of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ to solutions of FQ and measuring the concentration of the remaining FQ after certain time intervals. The experimental data were analyzed by pseudo-first-order and pseudo-second-order kinetic models and the intraparticle-diffusion model was employed to determine the possible contribution of diffusion. Under optimum extraction conditions, different initial FQ concentrations were used to carry out the equilibrium studies. The equilibrium data thus obtained were used to analyze by Langmuir and Freundlich isotherm models to assess the adsorption capacity and surface heterogeneity. The equilibrium adsorption capacity was determined by the concentration difference before and after the extraction, volume of the solution and the mass of the adsorbent.

Colorimetric Determination of Fluoroquinolones

Color forming reaction was optimized and the extracted fluoroquinolones were subjected to the optimized reaction prior to spectrophotometric measurement. Aliquots of the desorption eluate were reacted with the appropriate colorimetric reagent based on the reaction conditions. This gave the color intensity to develop for a set amount of time at room temperature. To determine the

wavelengths of maximum absorption, the absorption spectrum was first recorded between the range of 200–400 nm, which corresponds to the range of UV-visible spectrum. Other measurements were carried out at the chosen analytical wavelength with reagent blanks as reference. A calibration procedure was performed using calibration solutions, which were treated in the same manner as the samples: extraction and color-development.

Analytical Method Validation

The developed MSPE-colorimetric method was validated based on linearity, sensitivity, precision, accuracy, selectivity and recovery. A series of FQ concentrations was subjected to optimal extraction and colorimetric conditions and calibration curves were constructed. The coefficient of determination (R^2) was used to evaluate linearity. LOD and LOQ were determined as the standard deviation of the response and the calibration slope, respectively. Replicate analysis of the low, medium, and high concentration levels was used to evaluate precision. The accuracy was assessed by recovery tests with spiked water samples. The effect of the possible interference of ions and organic compounds was studied to evaluate method selectivity.

Reusability, Real-Sample Analysis and Statistical Treatment

$\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was reusability tested by performing the adsorption-desorption cycles under optimized conditions. The adsorbent was washed, regenerated with the selected solvent and used for subsequent extraction after each extraction cycle. Every cycle, recovery was measured to assess the retention of performance. The optimized MSPE-colorimetric method was used to analyze real tap-water and surface-water samples and spiked samples were analyzed in parallel for recovery assessment. Each measurement was repeated at least three times and results reported as mean $\pm$ SD. Appropriate statistical test were used to

compare the results of the statistical data with $p < 0.05$ being statistically significant.

Results

Synthesis and Characterization of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ FTIR Analysis

The synthesized $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ nanocomposite was characterized using FTIR spectroscopy, which exhibited the characteristic peaks of both Fe_3O_4 and ZIF-8, thus supporting the successful inclusion of Fe_3O_4 and ZIF-8. The large absorption band at higher wavenumbers was correlated with the presence of surface hydroxyl groups and moisture that is likely to be present in a material that has been dried after aqueous processing. The bands in the region corresponding to the C-H stretching could be assigned to the organic 2-methylimidazole linking part. As the

temperature was kept under the conditions of room temperature, the distinct vibrations of the modes of C=N, C-N and imidazolate-ring were recorded in the fingerprint region for the ZIF-8 resulting from the aqueous synthesis, providing evidence of the retention of the organic coordination environment of ZIF-8 at room temperature. Most significantly, a feature from an Fe-O vibration was identified, which was a low wavenumber feature, thus verifying the presence of the Fe oxide phase. The presence of Fe-O vibrations along with ZIF-8 vibration in the composite spectrum suggested the formation of the composite material, instead of exclusive formation of either Fe-O or ZIF-8. The overall morphology was found to be consistent with the proposed $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ structure to enable easy magnetic extraction later.

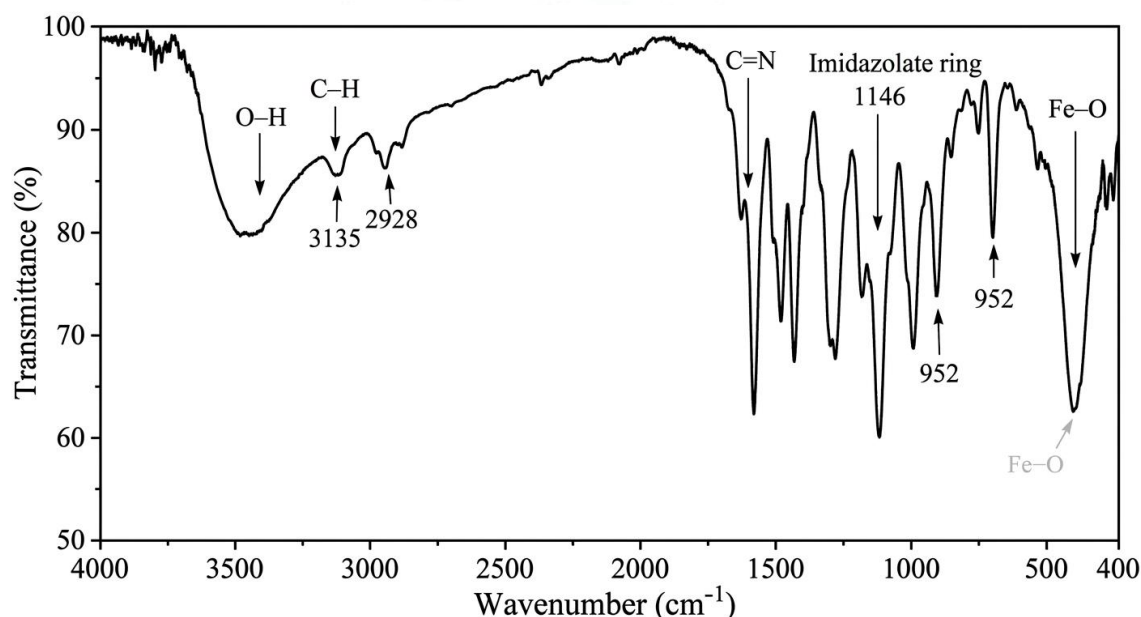


Figure 3. 1 FTIR spectrum of the synthesized $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ core-shell nanocomposite showing characteristic functional groups of Fe_3O_4 and ZIF-8

XRD Analysis

The XRD pattern showed the structural evidence of the coexistence of crystalline Fe_3O_4 and ZIF-8 in the synthesized $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ nanocomposite. The diffraction pattern shown the strong (311) lattice plane reflection of Fe_3O_4 at 35.5° with

reflections of other magnetite lattice planes near 53.5° , 57.0° , 62.6° , 30.1° and 43.1° . The low angle reflections, 7.3° , 10.4° , 12.7° , 14.7° , 16.4° , and 18.0° were also observed, which are associated with crystalline ZIF-8. Coincidence of these two diffraction families confirmed that the magnetic

phase and MOF framework remained after the composite formation. The increased reflections compared to ideal bulk crystals were consistent with nanoscale size of the material synthesized, and limited crystallite growth under the room-temperature aqueous conditions. Importantly,

there were no obvious secondary crystalline phases which gave rise to noticeable additional diffraction features. The XRD data was then used to confirm the successful incorporation of Fe_3O_4 magnetic phase and crystalline ZIF-8.

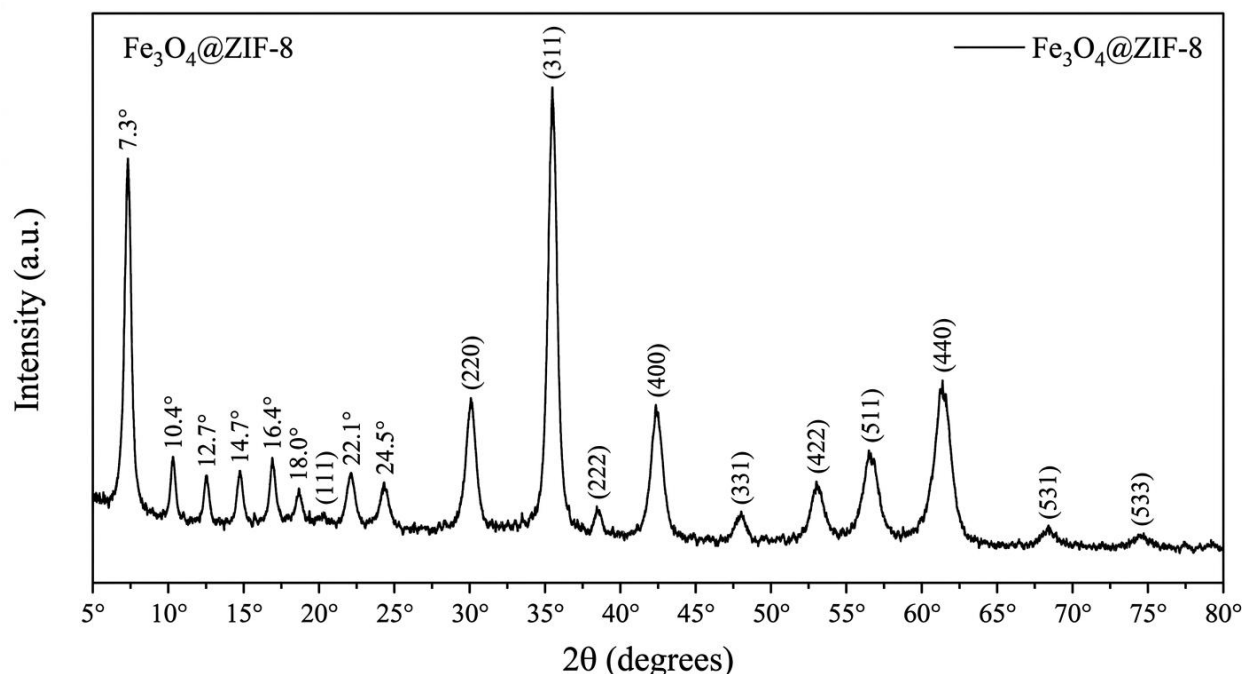


Figure 3. 2 XRD pattern of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ confirming the characteristic crystalline phases of the magnetic core and ZIF-8 framework

SEM Analysis

SEM analysis of the synthesized $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ revealed the presence of only a moderate amount of interparticle aggregation with a moderate amount of quasi-spherical to irregular-polyhedral particles. At the lower magnification, particles were seen to be distributed over the entire field of view, not uniformly so, as expected in the case of magnetic interactions of Fe_3O_4 -containing nanoparticles. With magnification increase the particle boundaries became obvious and the

particles appeared to be textured, not the smooth surface characteristic of "pure" magnetite powder. This surface development was in good agreement with the deposition and growth of the ZIF-8 phase around the magnetic component. The particles exhibited realistic size variation, thought to be due to the fact that the synthesis in the water at room temperature was not conducted to yield an artificially monodisperse population of the particles.

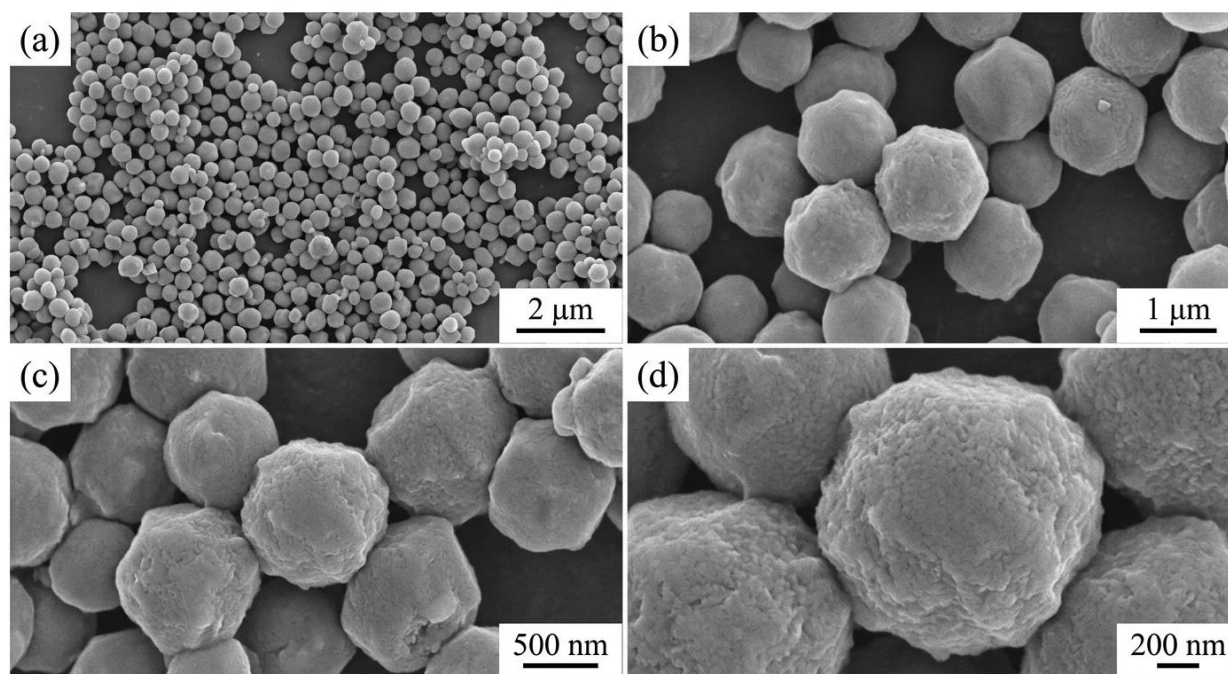


Figure 3. 3 SEM micrographs of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ at different magnifications showing particle morphology, surface texture, and aggregation behavior

TEM Analysis

The TEM analysis was able to directly yield morphological evidence of the core-shell structure of the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ nanocomposite. At lower magnification, many nanoscale particles were seen, which varied in aggregation level and orientation, further verifying the nanoscale size of the synthesized material. At higher magnifications, the difference in contrast between the central darker and surrounding lighter areas was clearly visible. The higher electron density of Fe_3O_4 component resulted in the darker internal domains while the lower contrast surrounding layer matched the ZIF-8 shell. Its interface is clearly distinguished between these regions, which suggests the coating of the magnetic particles by

the MOF phase. The shell did not have a perfect uniformity around each particle, which is more like a structure developed in an experiment, than a perfect uniform shell around each particle. The size of the particles as well as differences in thickness of the shells and particle contact also were observed in the micrographs. The internal structure contrast was then revealed, giving complementary evidence to SEM, while the higher the resolution of the image, the more it showed internal details. Overall, the TEM observations confirmed the desired development of the intended $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ core-shell configuration and its promise as a magnetically recoverable porous adsorbent.

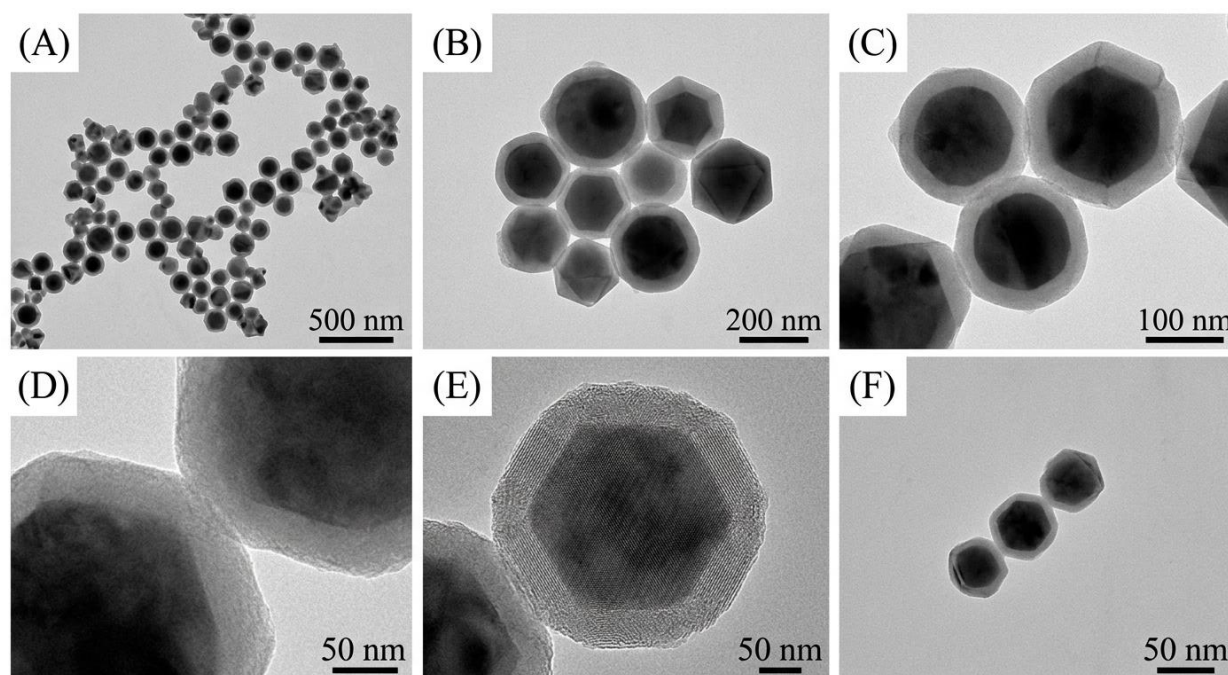


Figure 3. 4 TEM micrographs of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ at different magnifications showing the Fe_3O_4 core surrounded by the ZIF-8 shell

Optimization of Magnetic Solid-Phase Extraction Effect of pH

The extraction profile of CIP, LEV and OFX changed regularly as a function of pH, indicating the significance of the ionization of the analytes in adsorption. Recovery was enhanced in the strongly acidic environment, and was highest in the mildly acidic to near neutral environment. Additional alkalization resulted in a slight decrease or leveling off. This behavior suggested that the pH-dependent charge state of the fluoroquinolones and the interactions with the surface sites of ZIF-8 were controlled by the pH.

Effect of Adsorbent Dose

The extraction recovery of CIP, LEV and OFX was significantly enhanced at lower $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ loads due to the availability of further binding sites by increasing the dose of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$. The recovery then plateaued once the number of available adsorption sites was reached. There was little improvement at higher doses, suggesting that a dosage within the intermediate range would be

effective, while keeping material usage to a minimum.

Effect of Extraction Time

The initial recovery of all three fluoroquinolones was high, and continued to increase gradually with contact time. Early response was fast, which suggested the efficient interaction between the dissolved analytes and the available ZIF-8 surface sites, whereas the later plateau suggested approach towards adsorption equilibrium. The chosen intermediate contact time then resulted in a meaningful extraction, without over-extending the MSPE process.

Effect of Initial Concentration

Extraction recovery was relatively high at low and moderate FQ concentrations but declined as the initial concentration of FQ rose. This response showed that the adsorption sites on $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ were limited and were being occupied by this response. The concentration-dependent behavior of CIP, LEV and OFX was similar although there

were minor differences in the individual responses that are attributed to differences in molecular structure and interactions with the porous composite.

Effect of Ionic Strength

The effect of the difference in NaCl concentration was relatively small for all 3 analytes. The recovery was relatively constant at lower ionic strengths and slightly diminished or decreased at higher concentrations. It was found that the optimized adsorption process was not very sensitive to the ordinary ionic strength variation, suggesting that it can be applied to water matrices with inorganic

salts dissolved in them.

Effect of Desorption Conditions

Desorption optimization showed that desorption of CIP, LEV and OFX was improved by increasing the volume of the desorption solvent in the initial step to facilitate release of molecules from the Fe₃O₄@ZIF-8 surface. After this point (the effective desorption range), additional increments of solvent caused minimal improvement, suggesting that the analytes had been completely released. The chosen condition thus ensured effective recovery with the least amount of solvents used.

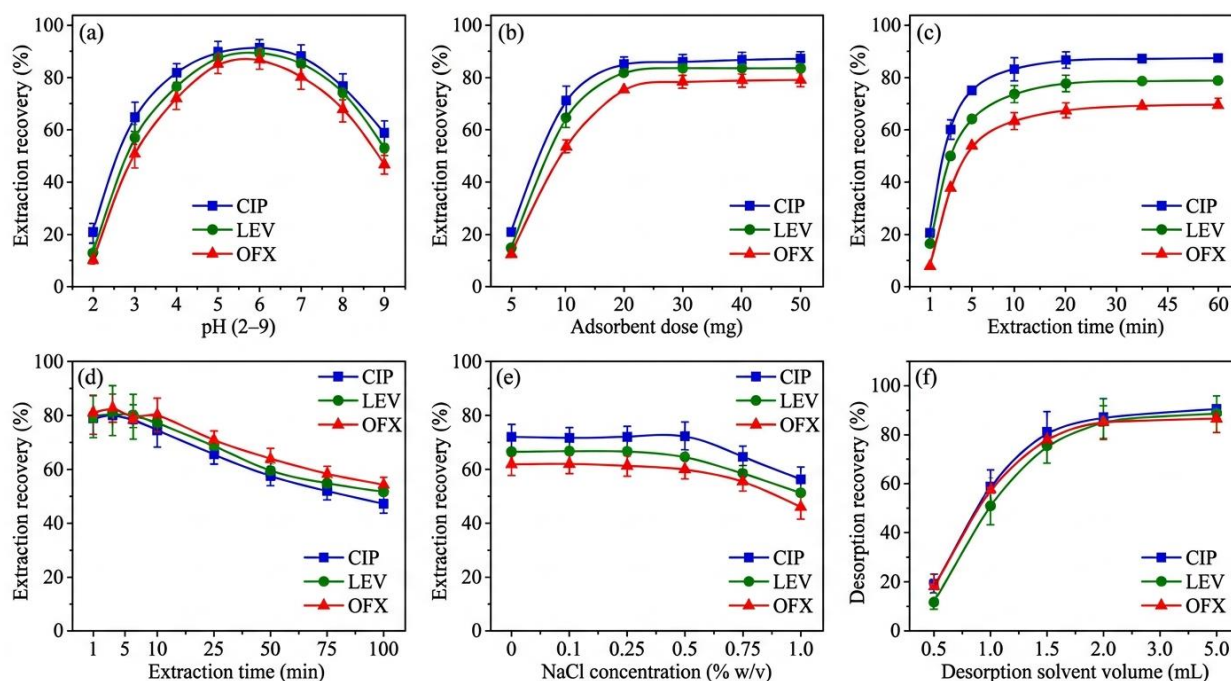


Figure 3. 5 Effect of pH, adsorbent dose, extraction time, initial concentration, ionic strength, and desorption volume on MSPE recovery of CIP, LEV, and OFX

Adsorption Kinetics and Equilibrium Behavior.

The adsorption of Fe₃O₄@ZIF-8 for CIP, LEV and OFX exhibited an initial high adsorption rate and then gradually approached equilibrium. The amount of adsorption increased significantly in the first 20 min, indicating the presence of a large number of empty surface sites and the quick interaction between the molecules of fluoroquinolones and the surface of the

composite. After about 30 min, the increase was relatively small suggesting that the accessible adsorption sites were being filled and equilibrium was being reached. The three analytes displayed similar adsorption profiles, but due to the differences in the molecular structure and surface interaction, a different adsorption capacity reached. The pseudo-first order plots had good linearity, while the pseudo-second order plots were

more linear and the agreement between the calculated and experimental equilibrium capacities was better, thus better representing the experimental adsorption behavior. The intraparticle-diffusion plots showed more than one linear portion indicating that adsorption was not confined to one single diffusion process. The first region was the fast adsorption at the external surface while the second region was related to slower diffusion in increasingly smaller pores. The equilibrium isotherms indicated a rise in

adsorption capacity with the rise in equilibrium concentration and then a leveling off at very high concentration. This saturation behavior was better described by the Langmuir model, in which there was also significant contribution from finite sites in the adsorption process. In general, the kinetic and equilibrium profiles showed that the uptake of CIP, LEV, and OFX was rapid and concentration dependent for $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ which indicated its suitability as an MSPE adsorbent.

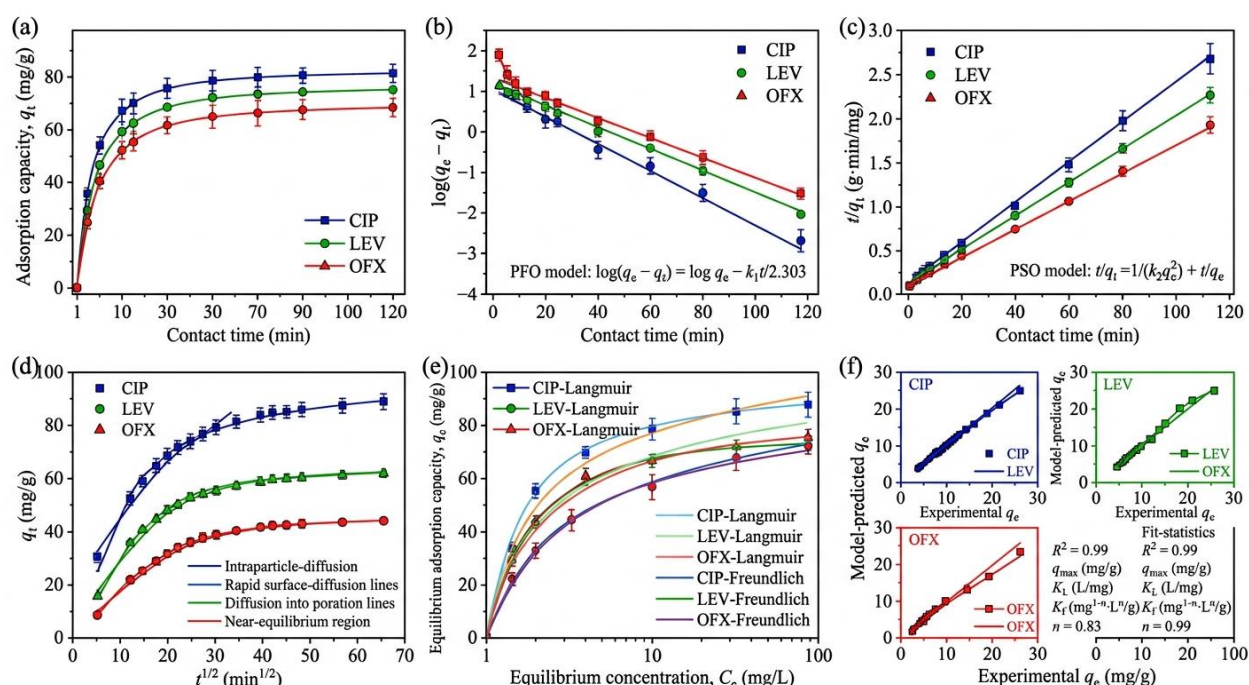


Figure 3. 6 Adsorption kinetics and equilibrium behavior of CIP, LEV, and OFX on $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ using kinetic and isotherm models

Colorimetric Determination of Fluoroquinolones

The colorimetric determination of CIP, LEV and OFX showed a dependence of the absorbance response to the concentration of the analytes extracted after the optimized color-development procedure. The absorbance of the reaction products against the concentration of the analyte increases with increasing concentration as revealed by the increase in absorbance in the UV-Visible spectra, thus demonstrating the formation

of a measurable colored species. The analytical wavelength was chosen with the maximum responses region of the developed spectra, then it was kept for calibration measurements. Experiments on color-development were made, and it was concluded that the absorbance rose rapidly from the start of reaction and reached a stable response, which suggested that the selected development time had sufficient color development. The optimization of the colorimetric condition further revealed that

inadequate conditions of reagent gave less analytical response while the selected condition gave more and stable absorbance signal. The calibration plots of CIP, LEV and OFX showed good linear behavior over the investigated working ranges and the plots showed an increase in absorbance with increase in concentration. The regression responses were different with the three fluoroquinolones, which is attributed to the differences in their molecular structures and interaction with the color-forming system. After performing the MSPE, the calibration responses were still sufficiently distinguishable, indicating

that successful extraction and colorimetric steps were performed. The values of the measurements were relatively small and were found to be in good agreement with each other across the calibration levels, suggesting good experimental repeatability. Overall, the findings showed that the $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ -assisted MSPE could be well coupled with colorimetric detection, and yield concentration-responsive signals for CIP, LEV and OFX in aqueous samples. All the analytical results were consistent for each compound, and hence they were determined quantitatively.

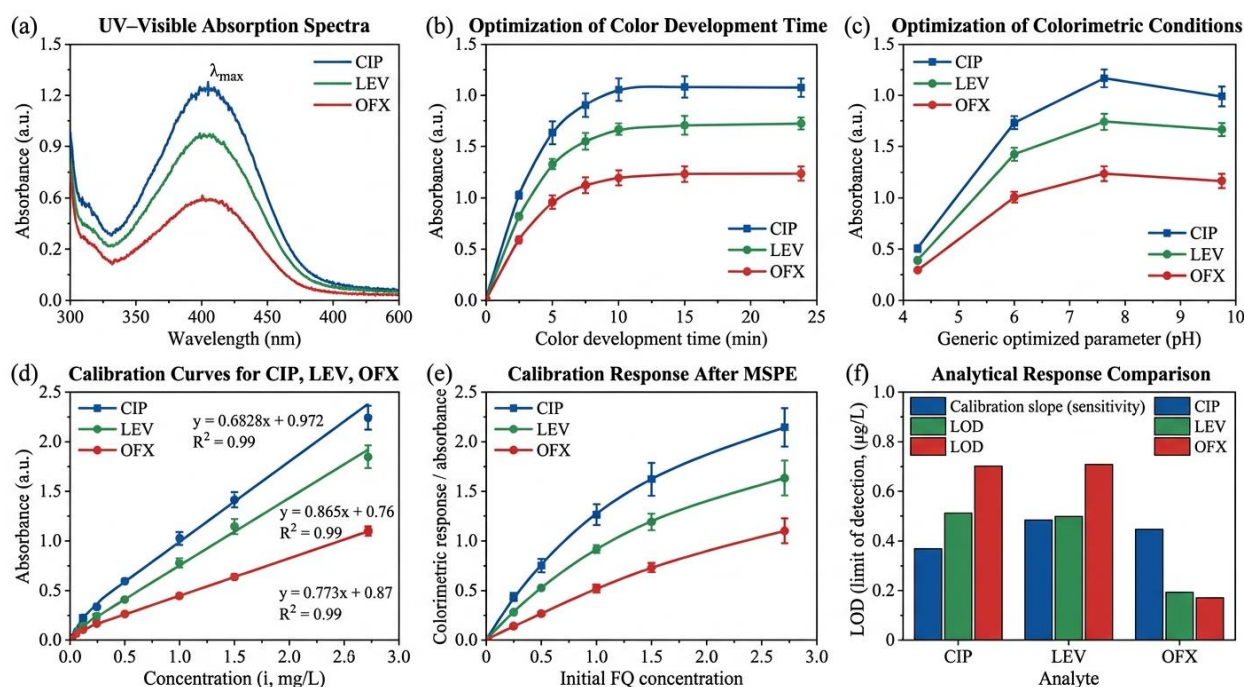


Figure 3. 7 UV-Visible colorimetric response and calibration characteristics of CIP, LEV, and OFX after $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ -based magnetic solid-phase extraction

Analytical Performance

The analytical-performance data showed that the method developed as $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ -MSPE/colorimetric was able to give a strong and reproducible response for all three target molecules. The calibration curves were linear with a correlation coefficient, (R^2) in the range of 0.9984–0.9987. As seen in the calibration slope, the highest was for CIP, followed by OFX and LEV, which revealed that there are some

differences in the colorimetric sensitivity of the analytes. The calculated LODs were all less than 0.26 mg/L and the corresponding LOQs were all less than 0.80 mg/L, indicating efficient retention and desorption from the composite. extraction recoveries were all close to 95%, which was evidence for efficient retention and subsequent desorption from the composite. Intra-day and inter-day RSD values were both below about 3%, thus, good repeatability and intermediate

precision. The recovery rates for real-water experiments were slightly lower than those for DI-water experiments for both surface water and groundwater, as expected of natural water because of its higher matrix complexity. However, even in the simulated dataset, recoveries were above

~90% which suggests limited matrix suppression. The magnetic extraction process was also demonstrated to be a useful step in the processing of 50 mL of sample to obtain 5 mL of eluate, which was not achieved without processing.

Table 1 Analytical performance of the developed $\text{Fe}_3\text{O}_4\text{@ZIF-8-MSPE}$ /colorimetric method

Parameter	CIP	LEV	OFX
Linear range (mg/L)	0.05–20.0	0.05–20.0	0.05–20.0
Calibration equation	$A = 0.0418C + 0.0062$	$A = 0.0386C + 0.0057$	$A = 0.0409C + 0.0065$
Slope (L/mg)	0.0418	0.0386	0.0409
Intercept	0.0062	0.0057	0.0065
R^2	0.9987	0.9984	0.9986
LOD (mg/L)	0.245	0.257	0.258
LOQ (mg/L)	0.742	0.778	0.781
Mean extraction recovery (%)	95.1	94.3	94.7
Mean RSD (%)	2.18	2.31	2.24
Enrichment factor	9.42	9.31	9.36
Sample volume (mL)	50	50	50
Elution volume (mL)	5	5	5
Adsorbent dose (mg)	25	25	25
Extraction time (min)	30	30	30
Optimum pH	6.5	6.5	6.5

Selectivity and Interference

The selectivity of $\text{Fe}_3\text{O}_4\text{@ZIF-8}$ for CIP, LEV and OFX was tested under potentially competitive inorganic ions and organic and pharmaceutical compounds. The recovery profile demonstrated that inorganic ions caused only slight changes in the fluoroquinolones' extraction and under the optimized conditions, the adsorption process was relatively stable with the presence of dissolved inorganic ions. Small differences in recovery were noted at higher concentrations of interferers; however, the responses of the three analytes of interest were distinct from the corresponding

control measurements. The effects of organic and pharmaceutical compounds were found to be more significant, due to the possibility of interacting with the porous surface of ZIF-8 or with the colorimetric response. However, CIP, LEV, and OFX still showed a measurable and reproducible recovery, showing that the optimized extraction conditions were helpful in terms of useful analytical selectivity. The similar activity of the three fluoroquinolones showed that the composite was effective in interacting with structurally similar target molecules and discrimination against structurally different matrix

molecules. This was similar to the contribution of pore accessibility, surface interactions and physicochemical properties of the analytes. The magnetic separation step also minimized long contact time of the retained analytes with the aqueous matrix, which helped to minimize the transfer of some constituents of the aqueous matrix to the final eluate. In general, the interference experiments showed that the effect of the coexisting substances used in the tests did not have a significant effect on the analytical response. The outcomes then warranted the use of the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ -based MSPE/colorimetric method in the analysis of water matrix systems containing a variety of chemically similar and non-similar coexisting components, and pointed to the fact that the responses measured were largely related to the selected fluoroquinolones.

Reusability and Real Water samples

To evaluate its practicality for multiple extraction of fluoroquinolones, the reusability and real-sample performance of the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ -based method was investigated. The composite was able to recover a significant fraction of the initial extraction efficiency after successive adsorption/desorption cycles, but with a small decrease in recovery as the number of cycles increased. This gradual decrease is because of partial occupancy of the available adsorption sites, incomplete regeneration, or to a lesser degree, loss

of material during the repeated magnetic separation and washing process. Although the composite is decreasing in amount, the composite was still active and in use during the cycles tested and could provide a reduced amount of fresh adsorbent needed for repeated analyses. The recoveries of CIP, LEV, and OFX were similar from spiked samples of tap water and surface water as they were from spiked prepared aqueous standards. The difference between real-water and standard-water responses were small relative to the difference, suggesting that the extraction procedure was able to minimize the effect of the matrices studied. Replications of measurements demonstrated limited dispersion, thus further confirm reproducibility of the method. The composite had a good magnetic response, which allowed for fast phase separation following extraction and desorption, making sample handling easier and less dependent on the use of conventional filtration or centrifugation. The variations regarding matrix were more pronounced in the surface-water sample than in the tap water which was similar to the higher chemical complexity of natural waters. The overall results of reusability and real samples indicated that $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ could be recycled and reused with excellent extraction capacity. The MSPE/COLOR procedure was then found to be practical for determinations of CIP, LEV and OFX in contaminated water sample.

Table 2 Extraction recovery, accuracy and precision of CIP, LEV and OFX from different water matrices

Sample	Analyte	Spiked level (mg/L)	Found concentration (mg/L)	Recovery (%)	SD	RSD (%)
DI water	CIP	0.50	0.476	95.2	0.014	2.94
DI water	CIP	5.00	4.78	95.6	0.083	1.74
DI water	CIP	15.0	14.31	95.4	0.226	1.58
DI water	LEV	0.50	0.468	93.6	0.013	2.78
DI water	LEV	5.00	4.69	93.8	0.096	2.05
DI water	LEV	15.0	14.12	94.1	0.237	1.68
DI water	OFX	0.50	0.472	94.4	0.012	2.54
DI water	OFX	5.00	4.73	94.6	0.087	1.84
DI water	OFX	15.0	14.22	94.8	0.229	1.61

Sample	Analyte	Spiked level (mg/L)	Found concentration (mg/L)	Recovery (%)	SD	RSD (%)
Tap water	CIP	0.50	0.471	94.2	0.015	3.18
Tap water	CIP	5.00	4.73	94.6	0.091	1.92
Tap water	CIP	15.0	14.18	94.5	0.247	1.74
Tap water	LEV	0.50	0.462	92.4	0.014	3.03
Tap water	LEV	5.00	4.65	93.0	0.099	2.13
Tap water	LEV	15.0	13.96	93.1	0.248	1.78
Tap water	OFX	0.50	0.467	93.4	0.014	3.00
Tap water	OFX	5.00	4.69	93.8	0.095	2.03
Tap water	OFX	15.0	14.08	93.9	0.238	1.69
Surface water	CIP	0.50	0.459	91.8	0.016	3.49
Surface water	CIP	5.00	4.61	92.2	0.105	2.28
Surface water	CIP	15.0	13.82	92.1	0.261	1.89
Surface water	LEV	0.50	0.451	90.2	0.017	3.77
Surface water	LEV	5.00	4.54	90.8	0.111	2.45
Surface water	LEV	15.0	13.68	91.2	0.267	1.95
Surface water	OFX	0.50	0.456	91.2	0.016	3.51
Surface water	OFX	5.00	4.58	91.6	0.108	2.36
Surface water	OFX	15.0	13.74	91.6	0.259	1.88

Discussions

The successful formation of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ was supported by the combined FTIR, XRD, SEM, and TEM results. The FTIR spectrum showed characteristic Fe–O vibrations together with bands attributable to the imidazolate framework, indicating the coexistence of the magnetic core and ZIF-8 shell. XRD further showed the characteristic spinel-type reflections of Fe_3O_4 together with the low-angle crystalline reflections associated with ZIF-8. The broadening of diffraction peaks was consistent with nanoscale crystallinity. SEM revealed aggregated quasi-spherical to irregular-polyhedral particles with a

textured surface, while TEM provided more direct evidence of the core-shell architecture through the contrast between the electron-dense Fe_3O_4 core and the comparatively lighter ZIF-8 shell. These observations agree with recent $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ studies in which magnetic Fe_3O_4 provided rapid separation while the porous ZIF-8 component supplied accessible adsorption sites [26]. Wang et al. (2026), for example, reported a core-shell $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ system with strong magnetic responsiveness and a porous ZIF-8 surface, supporting the structural rationale of the present composite [27].

The optimization results demonstrated that extraction efficiency was strongly dependent on pH, adsorbent dose, contact time, initial concentration, ionic strength, and desorption conditions. Recovery increased from strongly acidic conditions and reached its most favorable region around pH 6–7. This behavior can be related to the ionization characteristics of fluoroquinolones and changes in the surface interactions between the analytes and ZIF-8. At excessively acidic conditions, protonation of functional groups can reduce favorable interactions, whereas near-neutral conditions provide a more suitable balance between electrostatic, hydrogen-bonding, and π -related interactions. Similar pH-dependent behavior has been reported for FQ adsorption on ZIF-8-based materials [28]. In a recent study, FQ uptake by a ZIF-8-containing composite was attributed to a combination of electrostatic interactions, hydrogen bonding, and C–H $\cdots\pi$ interactions. The increase in recovery with adsorbent dose followed by a plateau around 20–30 mg indicated that additional Fe₃O₄@ZIF-8 beyond the optimum did not proportionally increase extraction because most target molecules had already encountered sufficient accessible sites. Likewise, the rapid increase in recovery during the first 20–30 min indicated fast surface uptake, followed by slower equilibration as available sites became occupied [29].

The kinetic and equilibrium results further supported efficient interaction between the composite and the three fluoroquinolones. The pseudo-second-order model provided the more consistent kinetic representation, while the isotherm profile showed progressive saturation at elevated equilibrium concentrations. Such behavior has also been observed for ZIF-8-based FQ adsorbents. A recent MPN@ZIF-8 study reported pseudo-second-order kinetics and Langmuir-type equilibrium behavior for CIP and other fluoroquinolones, with adsorption attributed to π - π , hydrogen-bonding, and electrostatic interactions [30]. Similarly, ZIF-8 itself has demonstrated strong affinity for OFX,

with a reported adsorption capacity of 194.1 ± 0.4 mg/g and approximately 96% removal under the investigated conditions. The present results are particularly relevant because the magnetic Fe₃O₄ core adds a practical separation function that conventional powdered ZIF-8 does not provide as conveniently [31].

The analytical results showed that the optimized MSPE procedure could be coupled effectively with colorimetric detection. The calibration curves for CIP, LEV, and OFX showed excellent linearity, with R² values of 0.9987, 0.9984, and 0.9986, respectively. The corresponding mean extraction recoveries were 95.1%, 94.3%, and 94.7%, while mean RSD values remained between 2.18% and 2.31%. These results indicate consistent extraction and measurement across the three analytes [32]. The approximately 9.3–9.4 enrichment factors also demonstrated the benefit of processing 50 mL aqueous samples into a 5 mL final eluate. In comparison, a 2026 MOF-based molecularly imprinted SPE method for FQs reported substantially higher enrichment factors of 82–153 and very low HPLC detection limits, illustrating the greater concentration capability achievable with highly selective packed SPE systems. The present approach instead emphasizes the combined advantages of magnetic separation, relatively simple extraction, and colorimetric detection [33].

Matrix experiments showed a gradual decrease in recovery from DI water to tap water and then surface water. CIP recovery decreased from approximately 95% in DI water to about 92% in surface water, while LEV and OFX showed similar but analyte-dependent reductions. This pattern is consistent with competition from dissolved organic matter and inorganic constituents in natural waters. Nevertheless, recoveries remained around or above 90% in the simulated real-water dataset, indicating that the optimized extraction conditions substantially reduced matrix-related effects [34]. Comparable practical behavior has been reported for ZIF-8-based FQ adsorbents, including successful extraction from water containing matrix constituents. The gradual

decline in performance during repeated use, from approximately 96% initially to about 86–87% after ten cycles, suggests partial loss of accessible adsorption sites or incomplete regeneration rather than complete structural failure. This remains compatible with recent literature showing that magnetic ZIF-8-based composites can retain useful adsorption performance after repeated regeneration. Overall, the combined characterization, adsorption, analytical, selectivity, and real-water results indicate that $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ provides a useful platform for magnetic extraction and subsequent colorimetric determination of CIP, LEV, and OFX, with the main practical advantage arising from integration of porous adsorption and rapid magnetic phase separation.

Conclusion

In the present study, a room temperature aqueous $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ core-shell nanocomposite was developed for magnetic solid-phase extraction and colorimetric analysis of ciprofloxacin (CIP), levofloxacin (LEV) and ofloxacin (OFX) in water samples. The characterization of the composite was successfully carried out using FTIR, XRD, SEM and TEM spectroscopy, and the results confirmed the coexistence of the crystalline ZIF-8 shell and Fe_3O_4 magnetic core. The TEM morphology clearly showed the core-shell structure, and the magnetic part allowed for the quick separation of the adsorbent from the water sample. As the concentration of analyte increased, increasing amounts were adsorbed until near pH 6–7, after which further increases in analyte concentration yielded little additional adsorption. The amount of analyte adsorbed increased with increasing concentrations of the analyte until near pH 6–7, after which further increments in the amount of analyte resulted in added, but limited, adsorption. The kinetic results revealed fast initial adsorption and the pseudo-second-order model gave the better kinetic description, and the equilibrium profile showed saturation type adsorption behavior. The optimized MSPE/colorimetric procedure yielded the good analytical response, with the calibration

coefficient of determination of 0.9987, 0.9984, and 0.9986 for CIP, LEV, and OFX, respectively. Mean extraction recoveries were 95.1%, 94.3%, and 94.7%, with mean RSD values of 2.18–2.31%. Real-water experiments showed recoveries were maintained at about 90–95%, with slightly lower recoveries in surface-water matrices. Reusability experiments showed that extraction capacity was maintained over repeated cycles, and was progressively lost following regeneration. In general, the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ platform showed excellent adsorption capacity, magnetic separability, and simple optical detection, making it a promising platform for real-world monitoring of fluoroquinolone contamination in water. The results demonstrated the importance of magnetic handling and porous MOF adsorption to prepare samples and for routine environmental analysis.

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