

Preconcentration of selected cephalosporins using waste PET-derived UIO-66 as an adsorbent before HPLC-DAD quantification

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ABSTRACT

In this work, a method for the extraction, preconcentration and determination of five different cephalosporin antibiotics in various water samples using ultrasound-assisted dispersive solid-phase extraction (UA-DSPE) and high-performance liquid chromatography coupled with diode-array detection (HPLC-DAD) was developed. The waste PET-derived UIO-66 was prepared and used as an adsorbent. The prepared adsorbent was characterised using Fourier transform infrared spectroscopy, X-ray diffraction, high-resolution scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy. The large surface area, pore volume, and microporous nature of the material were necessary to ensure there were abundant active sorption sites for the cephalosporin antibiotics (cefoperazone, ceftriaxone, cephalothin, cefaclor and ceftioxin). The factors affecting the UA-DSPE method were optimised using a central composite design. Under optimised conditions, wide linearity ranging from 0.1–700 µg/L with the determination coefficients greater than 0.99. The limits of detection and quantification were in the range of 0.026–0.096 µg/L and 0.09–0.32 µg/L, respectively. The intraday and interday spiked recoveries were 71.4–99.3 % and 72.6–99.1 %, respectively, with the relative standard deviation values less than 6 %. The UA-DSPE/HPLC-DAD method was successfully applied to real environmental samples such as wastewater and surface water. The adsorptive performance of the waste PET-derived UIO-66 material was investigated using a series of adsorption experiments. The adsorption isotherms and kinetics indicated that the Langmuir isotherm and pseudo-second-order kinetic models explained the adsorption process. The maximum adsorption capacities for the target analytes using waste PET-derived UIO-66 ranged from 68.3–106 mg/g. These results demonstrated that the waste PET-derived UIO-66 material could be used as a sustainable adsorbent for the adsorptive removal of cephalosporin antibiotics from wastewater.

1. Introduction

Cephalosporins are a class of β -lactam antibiotics that have similarities in the mechanism of action and structure with other β -lactam antibiotics, such as carbapenems, penicillins and monobactams [1,2]. Cephalosporin antibiotics have a diverse spectrum of action, and they are widely used to treat infectious diseases and livestock growth promotion [3]. The strong and wide spectrum of cephalosporin antibiotics for bactericidal action has led to increasing production and use in

aquaculture, agriculture, and human and veterinary medicine [2,4,5]. The widespread use and misuse of cephalosporin antibiotics are leading to their alarming presence in water sources like groundwater, surface water and the soil, thus posing significant threats to both the environment and public health [6–8]. Various sources of cephalosporin antibiotics in water bodies include aquaculture, irrigation with partially treated wastewater, unused drugs, landfills, and animal waste [6]. Antibiotic pollution in water bodies has sparked concern worldwide due to potential environmental problems and threats to human health [5].

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The presence of antibiotics in various water bodies is a threat to humans, and they tend to disrupt the delicate balance of the ecosystem. Antibiotics can harm microbial communities, thus affecting vital processes like nutrient cycling and decomposition [9]. Furthermore, they can directly harm aquatic animals, leading to increased mortality, gut microbiome imbalances (dysbiosis), and other health problems [7]. Moreover, antibiotic contamination causes the spread of antibiotic-resistant genes and bacteria, and subsequently threatening the entire ecosystem [10]. Therefore, there is a need to develop sensitive and reliable analytical methods for monitoring antibiotics in water bodies to safeguard the lives of humans and other organisms.

Antibiotics are present in low concentrations in various water bodies; thus, the extraction and preconcentration steps are crucial for accurate chromatographic analysis of these pollutants in complex real samples [11]. Numerous studies have used traditional solid phase extraction (SPE) utilising the commercially available adsorbent for sample clean-up and analyte enrichment. Even though the conventional SPE method is extensively used and efficient, it is laborious, time-consuming, involves multiple steps, and requires large amounts of solvents and samples, thus producing large volumes of toxic waste [12]. New insight toward achieving green analytical chemistry methods, green sample preparation advocates the development of microextraction methods that reduce environmental effects and accelerate the analytical throughput [13]. Among the newly developed miniaturised sample preparation methods, dispersive microsolid phase extraction (UA-D- μ -SPE) has gained more attraction due to its simplicity, efficiency and speed. This sample preparation approach allows direct contact between the adsorbent and the sample solution during the extraction step, as well as the solid phase material and the eluent solution during the eluting step [14].

The choice of an adsorbent plays a critical role in D- μ -SPE to allow its good dispersibility and promote high extraction efficiency of the analytes. Therefore, the design of nanomaterials has provided alternative adsorbent materials in D- μ -SPE protocols for efficient and effective isolation and enrichment of target analytes. The use of nanomaterials as adsorbents in D- μ -SPE methods offers attractive features such as large specific areas, specific functional groups and porous structures that are beneficial for adsorption, extraction and enrichment of analytes of interest [11,15]. For D- μ -SPE applications, several adsorbents have demonstrated remarkable performance in the adsorption and enrichment of antibiotics in various sample matrices. These include magnetic N-doped 3D graphene-like framework carbon [11], magnetic metal-organic frameworks [16] amide and carboxyl dual-functionalised magnetic microporous organic networks [17], magnetic molecularly imprinted polymer [18], functionalised graphene oxide [19] and Fe₃O₄/zeolitic imidazolate framework-71/polypyrrole [20].

This study reports the application of a metal-organic framework (waste PET-derived UIO-66) for efficient D- μ -SPE and determination of five traces of cephalosporin antibiotics in water samples using HPLC-DAD for separation and quantification. The waste PET-derived UIO-66 material was chosen because of its good adsorption performance, exceptional stability, high specific surface areas, controllable porosity, strong affinity towards analytes, and high extraction capabilities [21]. The efficient adsorption and extraction of cephalosporin antibiotics were governed by interactive effects such as hydrogen bonding, hydrophobic, and π - π interactions between the target analytes and waste PET-derived UIO-66 MOF material. The experimental factors affecting the D- μ -SPE were evaluated using the design of experiment approach. The developed D- μ -SPE/HPLC-DAD method was successfully applied for fast, effective and sensitive extraction and detection of cephalosporin antibiotics in real water samples.

2. Experimental

2.1. Materials and reagents

All chemicals and reagents were of high purity (analytical grade or

higher). Methanol (MeOH, HPLC grade, 99.9 %), ethanol (98 %), N-dimethylformamide, zirconium chloride (99.9 %), ethylene glycol, ethanol dimethylformamide (99 %) and were purchased from Merck (Darmstadt, Germany). For the synthesis of waste PET-derived UIO-66, waste PET bottles of water and soft drinks were collected around the University of Johannesburg premises. Deionised water was produced using a Milli-Q system from the Direct-Q® 3UV-R purifier system. Five cephalosporin antibiotics, including cefoperazone (CFRZ), cefaclor (CFCL), ceftriaxone (CFTX), cephalothin (CPLT), and cefoxitin (CFXT) were obtained from Merck. Ultrapure water, obtained from the Direct-Q® 3UV-R purifier system, was used in all experiments. Table S1 shows the chemical structure, molar masses, and pK_a values for selected cephalosporin antibiotics [23–25].

2.2. Synthesis and preparation of the waste PET-derived UIO-66

The method for producing measurements from waste PET bottles was adopted from existing literature [26]. The material was synthesised by first collecting waste PET bottles (water and soft drinks) from the University of Johannesburg, Doornfontein campus. The first thing was to remove the plastic around the bottles. Then, the waste PET bottles were cut into small pieces, cleaned with deionised water, and dried at 50 °C. In a Teflon-lined reactor, 5 g of PET plastic was added into 100 mL of deionised water, followed by the addition of 5 mL ethylene glycol, and the mixture was heated at 210 °C for 12 h. The resulting material was washed with water and ethanol and then subjected to a drying process at 70 °C for 24 h. To synthesise the final material, 2.12 g of zirconium chloride and 1.36 g of treated plastic flakes were mixed with 100 mL of purified water. Subsequently, 10 mL of formic acid was added, and everything was blended with sound waves for 30 min. This mixture was then sealed in a special container and heated to 160 °C for 12 h. Finally, the resulting white product was filtered, washed with ethanol, centrifuged, and dried overnight in a vacuum oven at 50 °C.

2.3. Ultrasound-assisted dispersive micro-solid phase extraction (UA-D- μ -SPE) procedure

The analytes were extracted using a waste PET-derived UIO-66 composite in a UA-D-SPE process. The procedure involved placing 10–50 mg of the composite in 50 mL amber sample bottles and adding a 20 mL synthetic sample with a pH range of 2–9 containing CPLT, CFZ, CFRZ, CFXT, and CFTX at 100 μ g/L. After sonication (5–30 min) and centrifugation (5 min), the supernatant was removed, and 300–1000 μ L of an eluent solution was added and sonicated for 5–15 min to desorb the analyte from the material. This step was followed by centrifugation for 5 min to separate the eluent from the adsorbent. Eventually, the eluent was filtered through a 0.22 μ m PVDF membrane filter, and the analyte concentration was determined using HPLC-DAD.

2.4. Optimisation strategy

The selected experimental variables, their experimental domain, and their level are illustrated in Table S2. It should be noted that the experimental sequence was randomised to reduce the uncontrollable parameters during the FrFD experimental design. Each experiment was carried out in triplicate. Response surface methodology based on central composite design (CCD) was used to examine the effect of the most influential independent variables in the extraction and preconcentration of cephalosporin antibiotics identified using the FrFD approach. These independent variables were the mass of the adsorbent, the sample pH, and the extraction time. These parameters were tested at five levels, as shown in Table S3.

2.5. Instrumentation and chromatographic conditions

The analysis was performed using an Agilent 1200 Infinity HPLC

system with a photodiode array detector from Agilent Technologies. The chromatographic separation of antibiotics was achieved using an Agilent Zorbax Eclipse Plus C18 column (4.6 × 150 mm, 3.5 μm) maintained at 30 °C. The mobile phases A and B corresponded to 100 % methanol and 0.1 % formic acid in water. This study employed the following gradient program: 0.0 min 10 % A, 2.0 min 60 % A, 3.0 min 70 % A, 4.0 min 80 % A, 5.0 min 90 % A, 6.5 min 98 % A, 7.5 min 98 % A, 8.0 min 10 % A, and 10 min 10 % A; the gradient was controlled by mobile phase A. The flow rate of the mobile phase was 0.75 mL/min with an injection volume of 10 μL. The optimal analytical wavelength for cephalosporin antibiotics was found to be 254 nm. A calibration curve was created for the selected cephalosporins within a concentration range of 10–1000 μg/mL by diluting the working solution with methanol.

The powder X-ray diffraction (P-XRD, PANalytical, Almelo, Netherlands) investigated the waste PET-derived UiO-66 crystal structure. Transmission electron microscopy (TEM) using a (TEM, JEM-2100, JEOL, Japan) and scanning electron microscope/energy dispersive spectroscopy (SEM/EDS, Tescan, Brno, Czech Republic) confirmed the dimensions, morphology and elemental composition of the material. Fourier transform infrared spectroscopy (FTIR) was conducted using a Perkin-Elmer Spectrum 100 spectrometer (PerkinElmer, USA), which was utilised to characterise the functional groups. The N₂ adsorption-desorption analysis was conducted to determine the surface area, pore structure, and pore volume of waste PET-derived UiO-66 (BET) ((ASAP2020 V3. 00H, Micromeritics Instrument Corporation, Norcross, USA).

2.6. Analytical performance of the method

The analytical performance of the developed method was conducted following the criteria for the development of analytical methods in complex matrices. The analytical method characteristics that were validated included limits of detection (LOD), limits of quantification (LOQ), linearity, matrix effect, specificity, accuracy, and precision. The linearity of the UA-D-μ-SPE/HPLC-DAD method was evaluated using matrix-matched standards (0–1000 μg/L) by analysing ultrapure water, tap water, surface water and wastewater samples. The accuracy and precision of the method were examined using spiked recovery and repeatability (interday and intraday) experiments. These experiments were performed for each sample matrix spiked at three concentration levels (0.5, 1.0 and 2.0 μg/L). The intraday precision and accuracy were evaluated by analysing seven replicates of each spiked sample, whereas interday precision and accuracy were assessed by analysing three replicates for five consecutive days. The LODs and LOQs were investigated by processing the spiked samples at a lower concentration of the calibration using the developed methods. They were estimated by multiplying the standard deviation of the measured concentrations by 3 and 10 (signal-to-noise ratio). The specificity of the UA-D-μ-SPE/HPLC-DAD method, defined as the method's ability to accurately distinguish between samples containing target analytes versus those that do not include them, was assessed by comparing the chromatograms of the blank (unspiked) and spiked surface water samples.

The matrix effect (ME) was examined by assessing the area from the solvent and matrix-matched standard solutions at the same concentration levels (1.0 μg/L, 2.0 μg/L and 5.0 μg/L). The ME was calculated using the Eq. (1):

$$\%ME = \frac{A_2 - A_1}{A_1} \times 100 \quad (1)$$

where A_1 and A_2 are the average peak areas ($n = 4$) of the analytes in the solvent matrix-matched sample at a specific concentration.

2.7. Adsorption experiments

The batch adsorption experiments were performed by placing 43 mg waste PET-derived UiO-66 into 50 mL model sample solutions containing a series of concentrations (1–10 mg/L) of the analytes. The sample bottles were sonicated for 25.5 min to reach sorption equilibrium at 25 °C. The separation of the adsorbent from the aqueous solutions was achieved via centrifugation for 5 min. The residual concentrations at equilibrium were quantified using HPLC-DAD. The adsorption capacities at equilibrium were calculated using Eq. (2).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e (mg/L), V (L), m (g) C_0 and C_e (mg/L) refer to the adsorption capacity, volume of the samples, mass of adsorbent, initial and equilibrium concentrations, respectively.

The kinetics studies were carried out by performing similar adsorption experiments at a fixed concentration of 10 mg/L at different times (3–60 min). The adsorption capacity at time t , q_t (mg/g) was calculated by using Eq. (3).

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

2.8. Application to real samples

Twelve different water (WWTP influent, WWTP effluent and surface water) samples obtained from local wastewater treatment plants and receiving surface water were analysed using the developed UA-D-μ-SPE/HPLC-DAD method.

3. Results and discussion

3.1. Characterisation of waste PET-derived UiO-66

3.1.1. Functional groups and crystallinity of the material

Waste PET-derived UiO-66 was characterised by FTIR, and the results are shown in Fig. 1(a). The broad peaks around 3419 cm⁻¹ show the presence of an OH group on the surface of the adsorbent, which emanates from the carboxylic acid group of the terephthalic acid ligand. The broad peak at 1655 cm⁻¹ was attributed to the stretching vibration of the carbonyl (C=O) bond. The peak at 1582 cm⁻¹ was ascribed to the stretching vibrations of C=C bonds within the benzene ring of the terephthalic acid ligand of UiO-66 adsorbent. Additionally, the bands at 1500 cm⁻¹ and 1396 cm⁻¹ were assigned to the C—C stretching of the aromatic ring and C—O in-plane bending vibrations of the carboxylic acid (—COOH) groups, respectively. Lastly, the waste PET-derived UiO-66 sample exhibits peaks at 478–746 cm⁻¹, which can be attributed to the vibrations of the Zr—O bonds within the framework of the material, thus confirming the successful formation of the adsorbent.

The powder X-ray diffraction patterns of waste PET-derived MOF material are shown in Fig. 1(b). Sharp peaks throughout the pattern indicate a well-crystallised material. The powder X-ray diffraction (XRD) patterns of UiO-66(Zr) MOFs reveal distinctive peaks that may be indexed to the (111), (200), (220), (311), and (400) planes of the cubic UiO-66(Zr) crystal structure. The diffraction peaks at around $2\theta = 4.2^\circ, 8.9^\circ, 12.4^\circ, 17.2^\circ, 25.2^\circ$ and 27.8° correspond to the reflections of the UiO-66 crystal structure [27]. These peaks validate the effective synthesis of UiO-66(Zr) MOFs and demonstrate the remarkable crystallinity of the material [28,29]. The relative intensities and positions of these peaks match those reported in the literature and cif file no. 733458 for UiO-66. Furthermore, the peak positions of the waste PET-derived MOF material were consistent with the reference pattern for UiO-66 in the Crystallography Open Database (COD), confirming the successful synthesis of the MOF [30].

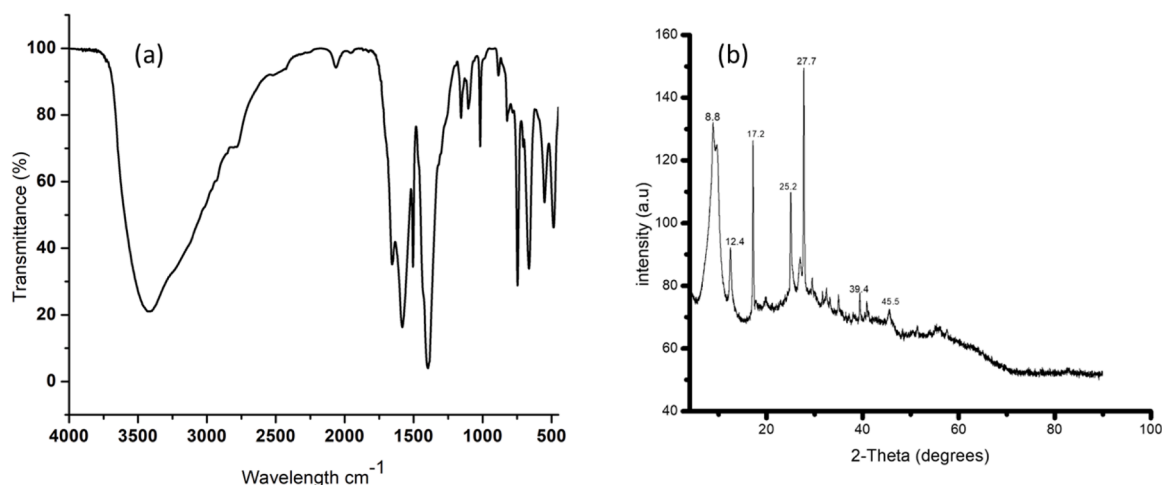


Fig. 1. (a) FTIR spectrum and (b) Powder X-ray diffractogram of waste PET-derived UIO-66 (Zr).

3.1.2. Dimensions, morphology, and elemental analysis for waste PET-derived UIO-66

High-resolution scanning electron microscopy (HR-SEM) analysis in Fig. S1(a) revealed that the waste PET-derived UIO-66 particles consisted of a mixture of cubic and hexagonal morphology. Fig. S1(b) shows the TEM image of waste PET-derived UIO-66, which has a diameter of 182 ± 34 nm. The EDS spectrum Fig. S1(c) revealed the presence of zirconium (Zr) from the metal nodes, carbon (C) and oxygen (O) from the terephthalic acid (TPA) ligand. These results confirm the successful synthesis of waste PET-derived UIO-66 instead of commercial terephthalic acid. The spectrum analysis indicated that, apart from Zr, C, and O, no peaks associated with other elements were detected, confirming the high purity of the synthesised UIO-66 using waste PET bottles without any impurities [27]. The results are in accordance with the literature when using commercial terephthalic acid as an organic linker [21].

3.1.3. Point of zero charge and textural properties for waste PET-derived UIO-66

Fig. 2(a) shows the zeta potential of the waste PET-derived UIO-66 solution at different pH levels. The graph shows that the zeta potential becomes more negative as the pH increases, which suggests that the particles in the suspension are becoming more negatively charged. Also, this is because the Zr—OH groups deprotonate, resulting in a negatively charged surface. Based on the data, the isoelectric point (where the net surface charge is zero) for the waste PET-derived UIO-66 falls at a pH of 4.9.

The N₂ adsorption-desorption analysis was conducted to determine the surface area, pore structure, and pore volume of waste PET-derived

UIO-66. As presented in Fig. 2(b), waste PET-derived UIO-66 exhibits a type II isotherm, which is typical for microporous materials [27,30,31]. There is a distinct micropore filling at a relative pressure of less than 0.1, which confirms the presence of micropores. The Barrett, Joyner, and Halenda (BJH) pore diameter distribution (desorption branch) shows a discontinued peak around 1.8 nm, substantiating the presence of micropores, Fig. 2(c). The BET surface area (S_{BET}) was calculated using the Rouquerol criteria [29], and it was found to be $732 \text{ m}^2/\text{g}$. The micropore surface area (S_{mic}) contributed $641 \text{ m}^2/\text{g}$ to the S_{BET} , which confirms that waste PET-derived UIO-66 is a microporous material. The total pore volume (V_{tot}) of $0.342 \text{ cm}^3/\text{g}$, and 80 % of the pore volume was attributed to micropore volume (V_{mic}), which was $0.273 \text{ cm}^3/\text{g}$. The S_{mic} and V_{mic} were calculated using a t-plot method [30,31]. The large surface area, pore volume, and microporous nature of the material were necessary to ensure there were abundant active sorption sites for the targeted analytes.

3.2. Optimisation strategy

3.2.1. Selection of eluent type

In this work, different solvents or combinations (MeOH, ACN, MeOH-ACN, MeOH-%FA, ACN-%FA, and MeOH-ACN-%FA) were used to determine the best solvent for eluting cephalosporin antibiotics from the surface of the waste PET-derived UIO-66 adsorbent. The pre-concentration tests were done in duplicate. Fig. S2 demonstrates that the combination of MeOH, ACN, and 0.1 % FA is the best eluent compared to other combinations or protic solvents because it was able to reach into the tiny openings (pores) of waste PET-derived UIO-66. The 0.1 % FA is acidified because the pKa of the amine group in the cephalosporin

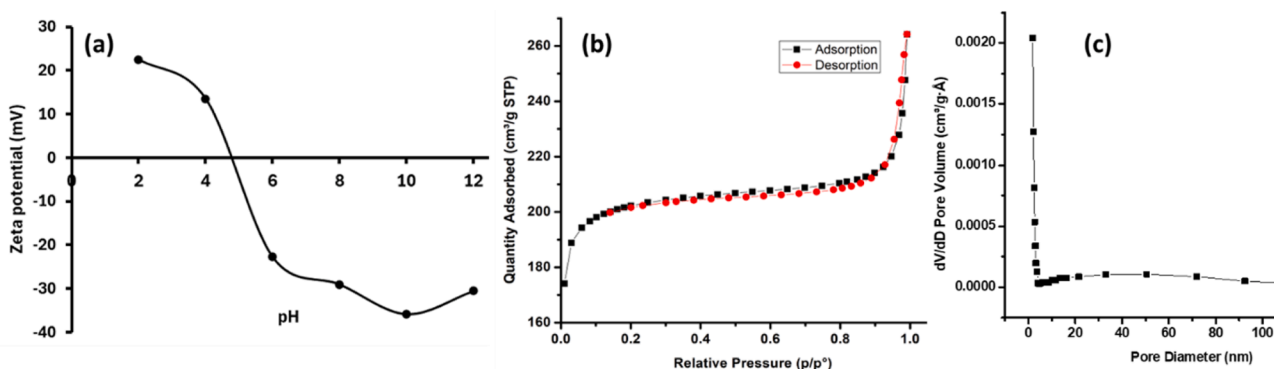


Fig. 2. (a) Point of zero charge, (b) Nitrogen adsorption-desorption isotherm, and (c) BJH pore diameter distribution (desorption) for waste PET-derived UIO-66.

structure is typically around 5–6. Therefore, in this study, we decided to use a mixture of methanol (MeOH), acetonitrile (ACN), and 0.1 % formic acid (FA) in a specific ratio (25 parts MeOH, 25 parts ACN, and 50 parts FA) for further analysis/experiment.

3.2.2. Screening of significant variables using fractional factorial design

A two-level FrFD involving 16 (2^{5-2}) experiments was performed to examine the significance of five experimental factors. The FrFD matrix and respective response (percentage recoveries, %R) are presented in Table S4. The importance of the experimental variables investigated in the screening step was presented in the form of Pareto charts in Fig. S3. As shown in these charts, the standardised effects of the analytes of interest were produced from the analysis of variance (ANOVA) tests. The importance or effect of each parameter is proportional to the length of the respective bar in the Pareto chart. As shown in Fig. S3(a), the Pareto charts of the main effects revealed that sample pH, mass of adsorbent, and extraction time were significant variables for the adsorption of CFPZ at a 95 % confidence level. In Fig. S3(b), sample pH, ET, MA, and ELT were statistically significant for the preconcentration of CFTX. Sample pH, Ma, ET, and EV played a substantial role in the extraction and preconcentration of CFCR Fig. S3(c). Meanwhile, in Fig. S3(d), samples ET and EV were found to have a significant influence on the analytical response of CPLT. Fig. S1E shows that the sample pH and EV are substantial at 95 % confidence level. It was observed that for the adsorption of CFXT, only the sample pH was important at a 95 % confidence level. As can be seen, sample pH, MA, and ET had a considerable impact on the extraction and preconcentration of most analytes. As a compromise, these three parameters were optimised using CCD. Eluent volume and

elution time were fixed at 1000 μ L and 10 min.

3.2.3. Response surface methodology

The CCD was used to optimise the most significant factors for the extraction and concentration of cephalosporin antibiotics from the aqueous samples. The experimental results in Table S5 were analysed using the Statistica 14 software. The 3D response surface plots of analytical response (%R) against two independent variables at constant levels of other factors in Fig. 3 were used to study the effect of the main and interactive effects on the simultaneous extraction and preconcentration of five cephalosporin antibiotics from aqueous solutions. As shown in Fig. 3(a-c), the 3D response surface plots reveal that there is curvature, indicating that the interaction effects between the independent variables are significant to the analytical response. Fig. 3(a) presents the combined interaction effect of sample pH and mass of adsorbent. It was observed that decreasing sample pH (from 10 to 0.99) and increasing MA promoted the adsorption of the analytes on the surface of the adsorbent. The pH of the solution was the most significant parameter for the adsorption of the target analytes.

Fig. 3(a&b) shows that quantitative recovery values were observed between pH 0.99 and 6, and the adsorption efficiency decreased with increasing pH values. The pH_{pzc} of PET-derived UIO-66 adsorbent was determined to be 4.9. This suggests that the adsorbent was positively charged below the pH_{pzc} value and negatively charged above the 4.9. The pK_a values of the analytes are presented in Table S1, and this data suggests that from pH 2.0 to 4.0 ($>pK_a$), the carboxylic acid groups of molecules of the target analytes become deprotonated, thus leading to anionic species. This phenomenon enhanced the electrostatic attraction

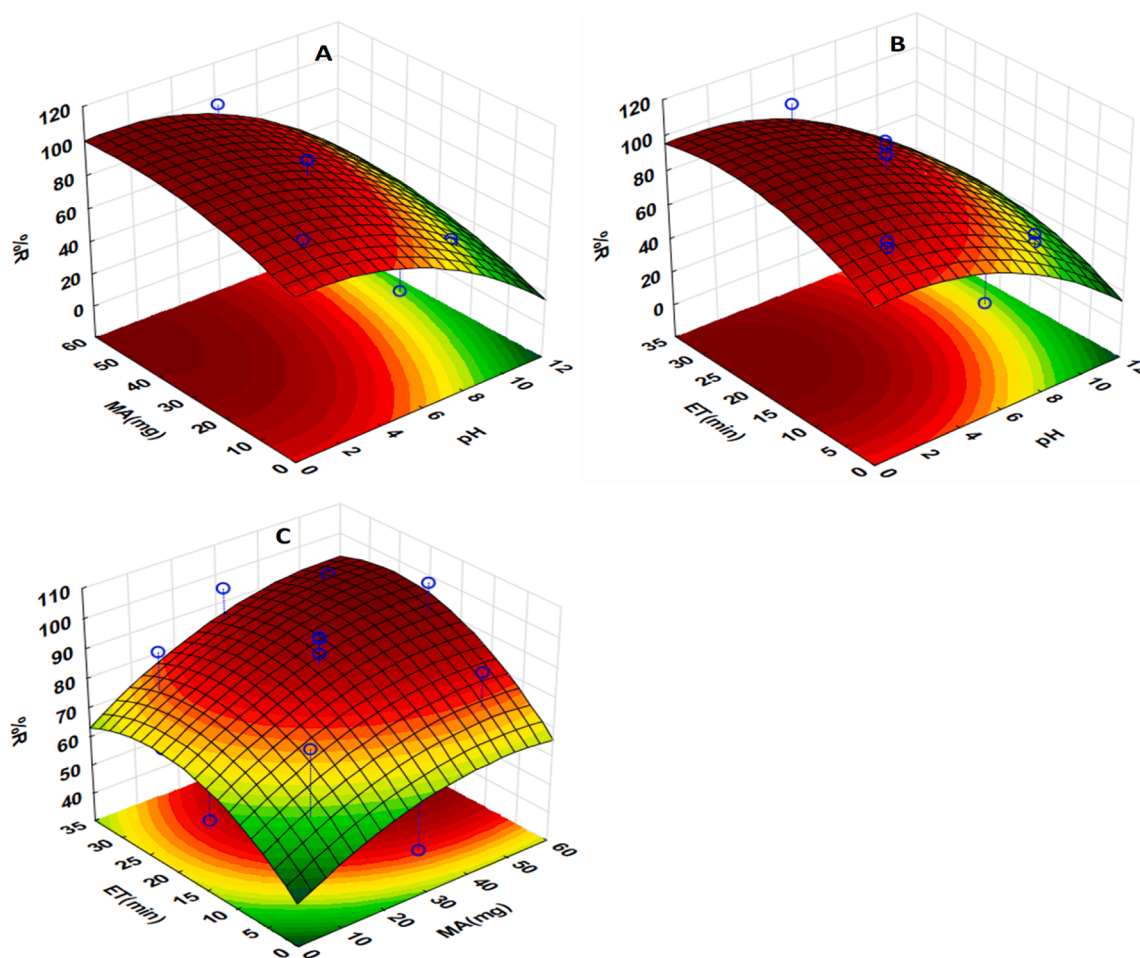


Fig. 3. 3D plots illustrating how multiple factors interact, including MA (mg) and pH, ET (min) and pH, ET (min), and MA (mg).

between the positively charged adsorbent and anionic analytes [32]. Furthermore, the target analytes have electron-rich aromatic rings, thus further improving the extraction of the cephalosporin antibiotics on the positively charged waste PET-derived UIO-66 adsorbent via electrostatic attractions [33].

According to previous studies, cephalosporin antibiotics are not stable in alkaline solutions [34]. Therefore, increasing pH values led to lower adsorption efficiency of the adsorbent. In alkaline solution, the adsorption mechanism was dominated by electrostatic repulsion between anionic analytes and negatively charged adsorbent. Fig. 3(c) displays the simultaneous effect of MA and EC and %R of the target analytes. The results show that increasing the MA resulted in enhanced extraction efficiency due to increased adsorption sites available for the adsorption of the analyte. Similarly, the analytical response increased with increasing extraction time. This might be because the mass transfer of the analytes from the liquid samples to the adsorbent required a specific time to reach equilibrium.

3.2.4. Determination of optimum conditions using the desirability function

Fig. S4 presents the profile for predicted values and desirability for the dependent variable (%R). The desirability scores, depicted on the right-hand side of Fig. S4, 0.0 (undesirable), 0.5 (middle), and 1.0 (desirable), were used to select optimum experimental conditions that could lead to the maximum desirable analytical response. The individual desirability scores for each parameter are presented on the bottom left-hand side of Fig. S4. As shown, the desirability score of 1.0 led to the attainment of maximum analytical response (top left-hand side). Therefore, the desirability score of 1.0 was selected as the target value, and the overall desirable response obtained from these plots is summarised in Table S6. Hence, the optimum experimental conditions were found to be 3.2, 43 mg, and 25.5 min for sample pH, mass of adsorbent, and extraction time.

The optimum conditions (pH 3.2, MA 43 mg, ET 25.5, EV 1000 μ L, and ELT 10 min) were confirmed and validated experimentally by performing six replicates of extraction and preconcentration of the target analytes. The experimental and predicted percentage recoveries are presented in Table S6. The student's *t*-test (paired two samples for means) was used to compare the predicted and experimental analytical responses. The *t*-calculated value, t_{cal} , was equated to the two-tailed critical value ($t_{crit} = 2.78$, degrees of freedom = 4) for the appropriate four degrees of freedom at a 95 % confidence level. The t_{cal} (1.56) was less than the t_{crit} , suggesting that there was no significant difference between the predicted and experimental results. Therefore, these findings confirmed the accuracy and validity of the RSM model and that it was a helpful procedure for obtaining the optimum conditions.

3.3. Adsorption kinetics and isotherms

Fig. S5A shows the effect of contact time on the adsorption of the target analytes onto the surface of the adsorbent. As seen, the adsorption of the antibiotics occurred fast at the start of the adsorption process, followed by the plateau over time equilibrium above 25 min. The adsorption capacities of 64.4 mg/g, 83.1 mg/g, 102 mg/g, 77.3 mg/g and 95.4 mg/g for CFPZ, CFTX, CFCR, CPLT and CFXT, respectively. The data was fitted to two kinetics models, pseudo-first-order and pseudo-second-order models. As illustrated in Table 1, the correlation coefficient and calculated adsorption capacities (closest to the experimental q_e) show that the pseudo-second-order model better describes data. These results suggest that the rate of adsorption was dependent on the concentrations of the target analytes adsorbed on the waste PET-derived UIO-66 and the amount at equilibrium. This conclusion is based on the hypothesis that the adsorption of the analytes on the surface of waste PET-derived UIO-66 material was dominated by chemisorption.

The effect of initial concentration on the adsorption of antibiotics is presented in Fig. S5B. As shown, the adsorption capacities increased with the initial concentration of the analytes, and Fig. S5B indicates that

Table 1

Parameters obtained from the kinetic and isotherm models to the experimental data.

	CFPZ	CFTX	CFCR	CPLT	CFXT
q_{expt} (mg/g)	65.5	84.2	103	77.6	95.5
Pseudo-first-order model					
k_1 (1/min)	0.0841	0.0826	0.0845	0.109	0.132
q_e (mg/g)	56.7	73.5	88.6	67.5	81.3
R^2	0.8932	0.9457	0.9461	0.9731	0.9707
Pseudo-second-order model					
k_2 (g/(min mg))	0.0518	0.0622	0.0641	0.0566	0.0573
q_e (mg/g)	66.8	89.7	99.6	78.9	94.6
R^2	0.9490	0.9754	0.9776	0.9729	0.9780
Langmuir					
q_{max} (mg/g)	68.3	89.5	106	80.8	98.6
K_L	0.96	0.94	0.85	0.93	0.86
R^2	0.9640	0.9854	0.9895	0.9727	0.9842
Freundlich					
K_F	30.4	38.2	49.1	36.4	41.7
N	2.3	2.2	1.57	2.4	2.0
R^2	0.9204	0.9738	0.9707	0.9558	0.9808

the equilibrium was reached at higher concentrations. This phenomenon could suggest that at the first stages, the concentration of the antibiotics was low, and the adsorbent had more sorption sites. On the other hand, increasing initial concentrations of the analytes leads to a sharp decrease due to limited or saturated active sites. In addition, Fig. S5B shows that the waste PET-derived UIO-66 material has the possibility of adsorbing high concentrations of the antibiotics, which are higher than the normal environmental measured concentrations (ng/L- μ g/L). These results suggest that the waste PET-derived UIO-66 material can be used for adsorptive removal of multiple classes of pollutants in environmental matrices.

The experimental data was analysed using adsorption isotherm models (Langmuir and Freundlich isotherm). The linear plots of Langmuir and Freundlich isotherms were used to calculate the parameter values for the models, and the results are summarised in Table 1. The results obtained showed that adequately high correlation coefficients were observed for the Langmuir model. This demonstrated that this isotherm model reasonably described the adsorption of cephalosporin antibiotics onto the surface of waste PET-derived UIO-66 material. Furthermore, maximum adsorption capacity values estimated using the Langmuir model agree with the experimental q_e values (Table 1).

3.4. Method validation

The UA-DSPE, in tandem with the HPLC-DAD technique, was validated for parameters such as accuracy, precision, LOD, LOQ, matrix effects and specificity.

3.4.1. Linearity, limits of detection and quantification of the developed UA-DSPE/HPLC-DAD method

The linearity of the UA-DSPE/HPLC-DAD method was assessed using matrix-matched standard solutions, and the results are presented in Table 2. As seen, the method had acceptable linear ranges and correlation of determination ($R^2 \geq 0.99$) in various water matrices for all analytes. The values of LODs and LOQs for the target antibiotics in five environmental water matrices are presented in Table 2. Generally, the LOD and LOQ values in less complicated matrices such as ultrapure and tap water were relatively lower than those of surface water and wastewater samples. The relatively low LODs and LOQs indicated that the UA-DSPE/HPLC-DAD method had sufficient sensitivity for the simultaneous determination of five cephalosporin antibiotics in real water samples.

3.4.2. Evaluation of the matrix effects and specificity

The application of the sample preparation step before the quantification of target analytes aims to reduce or eliminate the sample matrix [35]. It is, therefore, important to evaluate the matrix effect (ME) on the

Table 2

Analytical characteristics of the UA-DSPE/HPLC-DAD method for the preconcentration and quantification of five cephalosporins in various water samples.

Analytes	Parameters	Ceftriaxone	Cephalothin	Cefoperazone	Cefoxitin	Cefaclor
Ultrapure water	Linearity ($\mu\text{g/L}$)	0.1–400	0.1–450	0.1–550	0.1–500	0.1–600
	Regression equation	$y = 13.7x + 1.18$	$y = 17.2x + 1.70$	$y = 12.6x + 1.93$	$y = 15.7x + 1.83$	$y = 21.7x + 1.05$
	R^2	0.9992	0.9996	0.9991	0.9993	0.9991
	LOD ($\mu\text{g/L}$)	0.031	0.026	0.022	0.037	0.029
	LOQ ($\mu\text{g/L}$)	0.10	0.09	0.07	0.12	0.10
Tap water	Linearity ($\mu\text{g/L}$)	0.2–400	0.1–500	0.1–500	0.2–550	0.2–400
	Regression equation	$y = 14.6x + 1.67$	$y = 19.3x + 1.38$	$y = 14.1 + 1.55$	$y = 14.5x + 1.77$	$y = 22.5x + 2.89$
	R^2	0.9987	0.9990	0.9987	0.9977	0.9985
	LOD ($\mu\text{g/L}$)	0.053	0.035	0.034	0.055	0.048
	LOQ ($\mu\text{g/L}$)	0.18	0.12	0.11	0.18	0.16
Surface water	Linearity ($\mu\text{g/L}$)	0.2–350	0.2–500	0.1–400	0.2–500	0.2–400
	Regression equation	$y = 16.4x + 1.66$	$y = 21.4x + 2.13$	$y = 14.6x + 1.22$	$y = 15.4x + 1.28$	$y = 21.9 + 1.86$
	R^2	0.9955	0.9978	0.9981	0.9966	0.9987
	LOD ($\mu\text{g/L}$)	0.064	0.047	0.042	0.067	0.055
	LOQ ($\mu\text{g/L}$)	0.21	0.16	0.14	0.22	0.18
Effluent	Linearity ($\mu\text{g/L}$)	0.2–500	0.2–400	0.2–500	0.3–500	0.2–550
	Regression equation	$y = 15.4 + 1.57$	$y = 18.4x + 1.54$	$y = 12.3x + 1.45$	$y = 15.6x + 1.67$	$y = 21.5x + 1.54$
	R^2	0.9943	0.9956	0.9968	0.9951	0.9967
	LOD ($\mu\text{g/L}$)	0.073	0.056	0.055	0.076	0.068
	LOQ ($\mu\text{g/L}$)	0.24	0.19	0.18	0.25	0.23
Influent	Linearity ($\mu\text{g/L}$)	0.3–600	0.3–550	0.3–500	0.3–650	0.3–700
	Regression equation	$y = 11.6x + 1.01$	$y = 16.7x + 2.11$	$y = 15.9x + 1.33$	$y = 16.8x + 1.67$	$y = 19.5x + 1.44$
	R^2	0.9923	0.9916	0.9928	0.9931	0.9917
	LOD ($\mu\text{g/L}$)	0.096	0.075	0.074	0.081	0.078
	LOQ ($\mu\text{g/L}$)	0.32	0.25	0.25	0.27	0.26

analytical performance of a developed method. In this study, wastewater samples were selected to assess the impact of ME on the extraction of the target analytes using the developed sample preparation method. As illustrated in Fig. S6, the %ME ranged between -18% and 18% . The relatively low ME% demonstrated that the UA-DSPE method established in this study could effectively reduce the sample matrix, thus improving the sensitivity, reliability, and accuracy of the HPLC-DAD technique. Furthermore, these results suggested that the UA-DSPE/HPLC-DAD method had great potential for application in real environmental samples.

The specificity of the UA-DSPE/HPLC-DAD method was investigated by determining the target analytes in blank and spiked surface water samples. The results were compared with the standard solution. Fig. S7 shows the typical chromatograms of the analytes in spiked surface samples. As can be seen, the complexity of the sample did not affect the determination of the analytes, and the peak position was not affected by the existence of other analytes in water. Despite this, it was concluded that the UA-DSPE/HPLC-DAD method could separate and detect the analytes in spiked samples at the environmental samples without any significant shift in the retention times. These findings suggest that the developed UA-DSPE/HPLC-DAD method had satisfactory specificity.

3.5. Application to real samples

The applicability, validity and practicability of the proposed UA-DSPE/HPLC-DAD method was investigated for the extraction, enrichment separation and determination of five cephalosporin antibiotics in real water samples. Firstly, the accuracy and precision of the developed UA-DSPE/HPLC-DAD method were examined using spiked recovery experiments conducted on the same day and five consecutive days. Various water samples were spiked at three different concentrations of the mixed standard containing five cephalosporin antibiotics and processed using the developed method. The intraday and interday average recoveries and %RSD of the five analytes are presented in Table 3. As shown, the intraday and interday recoveries were in the range of $71.4\text{--}99.3\%$ and $72.6\text{--}99.1\%$. At the same time, the intraday and interday relative standard deviation were less than 6% . These findings revealed that the proposed UA-DSPE/HPLC-DAD procedure was suitable for accurate, precise, reliable, and applicable simultaneous separation and quantification of the target analytes in real water samples. The UA-DSPE/HPLC-DAD method was applied to determine the target analyte of twelve water samples (influent, effluent, and surface water). In wastewater and surface wastewater, the cephalosporin antibiotic residues were below their respective LOQs.

Table 3Recoveries (mean \pm %RSD) of five cephalosporin antibiotics in various spiked water samples.

Analytes	Added	Ceftriaxone		Cephalothin		Cefoperazone		Cefoxitin		Cefaclor	
		Intraday	Interday	Intraday	Interday	Intraday	Interday	Intraday	Interday	Intraday	Interday
Ultrapure water	0.5	94.6 \pm 4.6	95.3 \pm 4.1	95.1 \pm 4.8	96.2 \pm 5.4	94.7 \pm 3.9	95.3 \pm 4.8	94.1 \pm 4.7	93.8 \pm 5.2	95.3 \pm 4.7	94.3 \pm 4.7
	1.0	96.7 \pm 3.2	97.5 \pm 4.5	98.3 \pm 3.7	98.8 \pm 4.3	96.8 \pm 4.1	97.2 \pm 3.8	96.5 \pm 4.7	97.3 \pm 4.4	98.2 \pm 3.8	97.6 \pm 3.9
	2.0	98.9 \pm 2.5	99.1 \pm 3.8	98.7 \pm 3.5	97.9 \pm 3.6	97.5 \pm 2.6	97.8 \pm 3.7	98.7 \pm 3.1	98.4 \pm 4.3	99.3 \pm 3.4	98.7 \pm 4.1
Tap water	0.5	95.1 \pm 3.7	94.3 \pm 5.3	93.7 \pm 4.7	94.6 \pm 4.1	95.4 \pm 4.4	96.2 \pm 4.3	94.8 \pm 4.4	95.5 \pm 4.3	94.1 \pm 5.3	93.2 \pm 4.7
	1.0	97.5 \pm 3.1	96.8 \pm 4.1	96.4 \pm 3.5	97.1 \pm 3.8	96.4 \pm 3.3	97.1 \pm 4.4	95.2 \pm 3.3	97.1 \pm 4.9	98.2 \pm 4.4	97.8 \pm 4.5
	2.0	98.3 \pm 2.7	98.7 \pm 4.5	97.7 \pm 3.2	97.5 \pm 3.4	98.7 \pm 3.4	98.3 \pm 3.8	99.1 \pm 3.5	98.4 \pm 3.6	98.7 \pm 4.5	99.1 \pm 2.9
Surface water	0.5	93.4 \pm 4.4	92.6 \pm 5.6	89.4 \pm 5.1	91.2 \pm 4.5	93.3 \pm 4.8	92.0 \pm 5.3	93.1 \pm 4.6	93.5 \pm 4.8	90.6 \pm 5.8	87.9 \pm 4.9
	1.0	96.5 \pm 3.3	97.7 \pm 4.6	93.6 \pm 3.2	94.3 \pm 3.9	94.3 \pm 3.5	93.8 \pm 4.8	94.3 \pm 3.6	95.4 \pm 3.9	93.4 \pm 4.1	91.9 \pm 3.8
	2.0	98.3 \pm 3.4	99.2 \pm 3.7	96.2 \pm 4.7	95.9 \pm 3.6	95.6 \pm 4.6	96.2 \pm 4.3	95.9 \pm 3.4	96.6 \pm 3.7	95.8 \pm 3.8	96.2 \pm 3.3
Effluent	0.5	85.7 \pm 5.1	84.4 \pm 4.8	85.6 \pm 5.4	83.9 \pm 4.7	84.7 \pm 5.1	85.4 \pm 4.9	85.7 \pm 3.1	87.3 \pm 4.8	83.2 \pm 4.7	79.5 \pm 5.1
	1.0	91.3 \pm 3.6	87.6 \pm 4.5	89.6 \pm 4.5	87.9 \pm 4.5	86.7 \pm 4.1	85.8 \pm 5.1	88.7 \pm 2.8	89.2 \pm 4.1	85.9 \pm 4.7	83.7 \pm 4.8
	2.0	93.7 \pm 3.4	91.4 \pm 4.2	90.8 \pm 3.7	88.7 \pm 4.8	89.2 \pm 3.9	91.4 \pm 4.5	93.1 \pm 3.7	92.6 \pm 4.4	89.6 \pm 2.7	88.3 \pm 3.7
Influent	0.5	73.5 \pm 5.4	76.8 \pm 5.1	77.8 \pm 4.8	75.1 \pm 5.5	73.7 \pm 5.6	72.6 \pm 4.6	75.6 \pm 5.7	77.3 \pm 5.2	71.4 \pm 5.5	73.7 \pm 5.6
	1.0	84.1 \pm 3.6	83.9 \pm 4.5	83.2 \pm 4.1	79.7 \pm 4.7	77.6 \pm 4.6	78.4 \pm 3.9	80.2 \pm 4.1	81.2 \pm 3.7	78.9 \pm 3.8	77.3 \pm 3.8
	2.0	88.5 \pm 3.7	86.3 \pm 4.1	86.7 \pm 3.5	87.8 \pm 3.9	81.4 \pm 3.8	83.6 \pm 4.1	84.5 \pm 3.4	86.9 \pm 4.1	81.7 \pm 4.7	83.0 \pm 4.5

3.6. Comparison of the developed method with previous studies

Table 4 in this study compares the suggested method to previously described methods for extracting and preconcentration of selected cephalosporin antibiotics in different matrices. The table shows that the linearity of the current method was wider than those reported in the literature [22,36–38]. However, the LOD and LOQ values of the UA-DSPE/HPLC-DAD method were higher than those reported by Refs. [36,38], which was attributed to the use of more sensitive techniques (LC-MS/MS). The %RSD and recoveries were comparable to those reported in Table 4. These results proved that the developed UA-DSPE/HPLC-DAD could be used for extraction, preconcentration and quantification of trace cephalosporin antibiotics in water bodies.

3.7. Greenness and whiteness assessment of the UA-DSPE/HPLC-DAD method

This study also evaluated the greenness of the UA-DSPE/HPLC-DAD method to analyse cephalosporin antibiotics; metrics, analytical Eco-Scale, AGREE, and AGREEprep, were employed for this analysis. Analytical Eco-Scale is an extensively used green analytical chemistry (GAC) assessment tool, probably due to its simplicity [39]. This concept is based on assigning a base score of 100 for an ideal green analytical method with limited hazardous chemicals, generated waste, occupational risk, and high energy consumption [40,41]. For any deviation from this "ideal" analytical method, penalty points (PP) are subtracted from 100. Here, the analytical Eco-Scale was 80, which means the study has an excellent green analysis [40], and a total of 13 PP deductions were attributed to hazardous eluting reagents (acetonitrile, formic acid, and methanol), as shown in Table 5.

On the other hand, AGREE, the most recommended metric, is based on the 12 principles of GAC, and this assessing tool uses both colour and numerical results [42]. Table 5 shows the principles and input based on the UA-DSPE/HPLC-DAD method and a pictogram displaying the results. The centre shows the overall score and colour, indicating the greenness of the technique, and the segments around the centre represent the 12 principles that are transformed into a 0–1 scale and coloured from dark green to red based on greenness. The AGREE calculator shows that the method is green, with a score of 0.63; principles 4, 6, 9, and 12 were dark green, suggesting that the technique is high green when measured against these principles. AGREEprep is centred around the ten principles of green sample preparation (GSP), which evaluated the

greenness of the sample preparation technique that was overlooked in the AGREE metric [39]. Table 5 shows the ten GSP principles, input based on the UA-DSPE/HPLC-DAD method, and a pictogram with the score and colour in the centre. The AGREEprep is assessed similarly to the AGREE metric in terms of colour and score. The AGREEprep score was 0.52, indicating that the sample preparation method was below green; only criteria 3, 4, 6, and 8 were green. The poor score on criteria 2 and 10 was ascribed to the three hazardous reagents, acetonitrile, methanol, and formic acid, and using at least one of the reagents with water would increase the total score above 0.60, which is green. Therefore, the sample preparation method will be improved by reducing/eliminating the number of hazardous reagents.

This study also evaluated the performance and sustainability of the UA-DSPE/HPLC-DAD method utilising the RGBfast model, a new version of RFG, a known and widely accepted assessment technique for the whiteness of analytical methods [43,44]. This model evaluates six criteria of analytical methods: the first three criteria, R1, R2, and R3, focus on the analytical performance using the crucial validation parameters; the other three green-blue criteria, B1, G1, and G2/B2, cover various features including chemical hazards, quantity of reagents and waste, energy and instrument cost. Fig. 4 presents the outcome of the UA-DSPE/HPLC-DAD developed here and compared SPE/HPLC-UV [22] and SPE/LC-MS/MS methods [38], which used solid-phase extraction to preconcentrate cephalosporins and other antibiotics from water and determined by HPLC. The UA-DSPE/HPLC-DAD method achieved the highest score (57.0) in red, suggesting a better overall performance than others. It also was only scored lowest on R3 because of the lowest LOD, while SPE/LC-MS/MS scored the highest (82.2) due to high sensitivity owing to the MS/MS detector. Our method achieved the highest score (70.9) on greenness due to the limited use of hazardous materials during the sample preparation step compared to the traditional cartridge-based SPE used by other methods that consume large volumes of hazardous solvents. Lastly, the UA-DSPE/HPLC-DAD achieved the highest whiteness score (64), confirming that it has high analytical performance, poses a low environmental risk, and has low cost-effectiveness. Therefore, it is considered a sustainable method for determining cephalosporins from water.

4. Conclusion

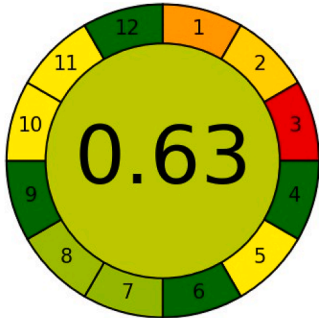
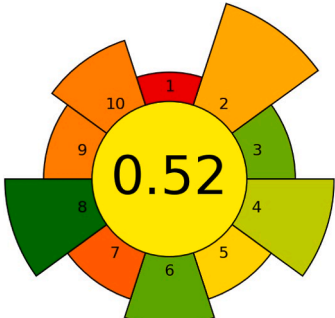
The waste PET-derived UIO-66 material was prepared and used as an adsorbent and was applied in UA-DSPE of cephalosporin antibiotics in

Table 4
Comparison with previous studies.

Sample	Analyte	Sample preparation method	Detection method	Linearity ($\mu\text{g/L}$)	LODs($\mu\text{g/L}$)	% Recoveries	%RSD	Refs
Wastewater	CFCR	SPE	LC-MS/MS	0.012–200	0.0038	76.7–108	5.8–6.5	[36]
Lake water	CFCR	SBSE	HPLC-DAD	12–320	3.5	87.1–98.6	<7	[37]
Treated water	CFTX	SPE	LC-MS/MS	0.025–0.5	0.01	96	2.0	[38]
Groundwater	CFCR and CFPZ	SPE	HPLC	0.05–10.00 & 0.04–20.00	0.029 & 0.041	85.1, 84.2	–	[22]
Surface water	CFCR and CFPZ	SPE	HPLC	0.04–20.0	0.034 & 0.045	76.7, 71.2	–	[22]
Influent WWTP	CFCR & CFPZ	SPE	HPLC	0.05–10.00 & 0.04–20.00	0.042 & 0.059	61.3, 68.5	–	[22]
Effluent WWTP	CFCR & CFPZ	SPE	HPLC	0.05–10.00 & 0.04–20.00	0.035 & 0.037	70.2, 72.1	–	[22]
Ultrapure water	CFTX, CPLT, CFPZ, CFXT & CFCR	UA-DSPE	HPLC-DAD	0.1–600	0.026–0.037	94.1–991	2.5–5.4	This work
Tap water	CFTX, CPLT, CFPZ, CFXT & CFCR	UA-DSPE	HPLC-DAD	0.1–550	0.034–0.055	94.3–99.1	2.7–5.3	This work
Surface water	CFTX, CPLT, CFPZ, CFXT & CFCR	UA-DSPE	HPLC-DAD	0.1–500	0.042–0.067	89.4–99.2	3.2–5.6	This work
Effluent water	CFTX, CPLT, CFPZ, CFXT & CFCR	UA-DSPE	HPLC-DAD	0.2–550	0.055–0.076	83.2–92.6	2.7–5.1	This work
Influent water	CFTX, CPLT, CFPZ, CFXT & CFCR	UA-DSPE	HPLC-DAD	0.3–700	0.074–0.096	71.4–87.8	3.4–5.6	This work

Table 5

Greenness evaluation of the UA-DSPE/HPLC-DAD method using analytical Eco-Scale, AGREE, and AGREEprep metrics.

Analytical eco-scale	AGREE	AGREEprep			
Reagent	Penalty points				
					
H ₂ O	0	12 principles of GAC	Input	Criterion	Input
Formic acid	3			1 Sample preparation placement	Ex-situ
Methanol	6			2 Hazardous materials	1.00 Ml
Acetonitrile	4	1 Sample treatment	Offline	3 Sustainability, renewability, & reusability of materials	75 % of reagents and materials are sustainable and renewable
Instruments	Penalty points	2 Sample amount	5 mL	4 Waste	1.043
HPLC-DAD	0	3 Device positioning	Offline	5 Size economy of the sample	5.00 Ml
Ultrasonic bath	1	4 Sample preparation stages	3 and fewer	6 Sample throughput	27
Centrifuge	0	5 Automation, miniaturisation	Manual, miniaturised	7 Integration and automation	No. of sample prep. steps: 3 steps; degree if automation: Manual systems
Occupation hazard	Penalty points	6 Derivatisation	N/A	8 Energy consumption	3.22
Vapour emission to the atmosphere	0	7 Waste	1.043	9 Post sample preparation configuration for analysis	Liquid chromatography, gas chromatography with quadrupole detection, etc.
Waste	PP	8 Analysis throughput	5 analytes, 4 samples	10 Operator's safety	3 hazards
1.043 mL/g	3	9 Energy consumption	HPLC-DAD, 0.017 KWh		
No treatment	3	10 Source of reagents	Some are biobased		
Analytical Eco-Scale total	80	11 Toxicity	Yes, 2.5 mL (acetonitrile, methanol, and formic acid)		
Comment	Excellent green analysis	12 Operator's safety	No threats		

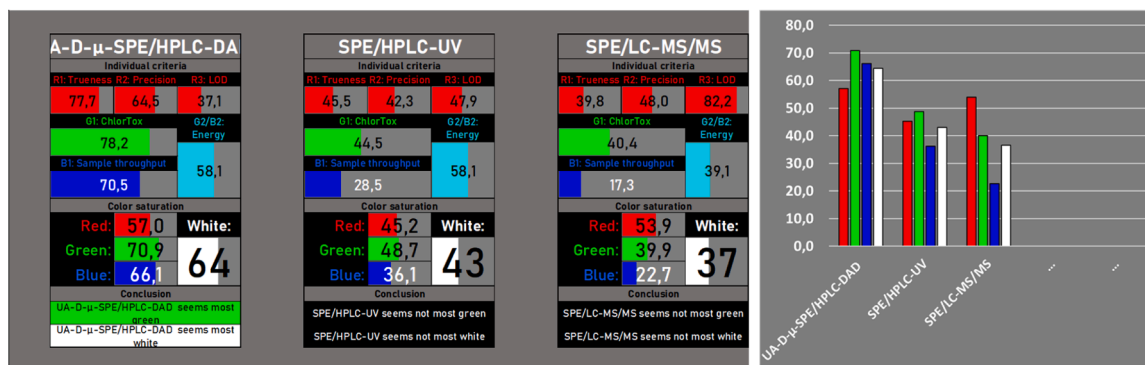


Fig. 4. Automatically generated tables/pictograms and graphs based on the two compared methods for determining five cephalosporins from water using the RGBfast model.

environmental samples prior to HPC-DAD detection. The prepared adsorbent exhibited the highest extraction efficiency and adsorption affinity towards the target analytes. Furthermore, the developed UA-DSPE-HPLC-DAD approach provided satisfactory analytical performance such as wide linear range, acceptable %RSD, high recoveries with acceptable %RSD and high sensitivity (low LODs and LOQs). Moreover, the developed method had a low matrix effect and high specificity, allowing the effective application of the UA-DSPE-HPLC-DAD approach for the analysis of cephalosporin antibiotics in various water samples.

The data for cephalosporin antibiotics adsorption on the waste PET-derived UIO-66 material were better fitted to the Langmuir model. These results suggested that the adsorption of target analytes was homogeneous and formed a monolayer on the adsorbent surface. Furthermore, the experimental data was explained by a pseudo-second-order kinetic model suggesting that the adsorption process was dominated by chemical adsorption through electrostatic transfer between waste PET-derived UIO-66 material and cephalosporin antibiotics. The waste PET-derived UIO-66 proved to be a promising adsorbent for the

adsorption and enrichment of five cephalosporin antibiotics.

Ethical approval

We declare that we have no human participants, human data, or human tissues.

Consent to participate

Not applicable.

Consent to publish

Not applicable.

CRediT authorship contribution statement

Andisiwe Bangani: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Mthokozisi Mnguni:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Conceptualization. **Thollwana Andretta Makhetha:** Writing – review & editing, Visualization, Supervision, Methodology, Conceptualization. **Elisabete Oliveira:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Conceptualization. **José Luis Capelo-Martínez:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Conceptualization. **Carlos Lodeiro:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Conceptualization. **Philiswa Nosizo Nomngongo:** Writing – review & editing, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.greeac.2025.100272](https://doi.org/10.1016/j.greeac.2025.100272).

Data availability

Data will be made available on request.

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