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Magnetic Nanocomposite (CDs@Fe₃O₄) for Preconcentration and Ultra-Sensitive Determination of Sulfathiazole in Wastewater Spectrophotometrically

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ABSTRACT

There has been serious environmental and health damage caused by the excessive discharge of organic wastewater. In this article, a magnetic nanocomposite adsorbent, cyclodextrin@Ferrous-ferric oxide (CDs@Fe₃O₄), was used for the efficient adsorption of sulfathiazole (STZ) from wastewater due to its special amphiphilicity. The amount of separated STZ was determined using a diazotization-coupling reaction with 1,5-dihydro naphthalene. It was determined whether initial drug concentration, pH, dosage of adsorbent, contacting time, and temperature influenced the adsorption process. The proposed method showed a linear range from 0.5 to 4.0 µg/mL STZ. With an STZ concentration of 20 µg/mL and 80 mg of adsorbent, CDs@Fe₃O₄ has the best adsorption and removal effect on STZ at a pH of 7.0 and room temperature that reaches 99.1%. An external magnetic field can quickly separate CDs@Fe₃O₄ adsorbed with STZ drug, and then HCl treatment can easily regenerate the composite. Despite recycling five times, the magnetic composite is able to remove more than 99% of STZ. The proposed method was applied successfully using synthetic water samples. The obtained results showed recovery values from 96.27 to 100.02% with RSDs ranging from 0.32 to 2.48%. Thus, an environmentally friendly and economical method will be developed to treat drug wastewater.

1. Introduction

Different types of medications have been found in both fresh and marine waterways; some of these compounds are capable of causing harm to the aquatic middle. Their impact on the environment, their transit to natural aquatic systems, and their effect have all been the subject of scientific investigation. The human body can eliminate sulfonamides in their unaltered form through urine. The areas closest to hospital and animal wastewater outflows have the highest amounts of sulfonamide contamination. Routine analysis of these contaminants needs to be done quickly, easily, and accurately (Wagenlehner et al., 2006). Prior quantitation step, a sensitive and trustworthy pre-concentration process must be used to monitor drugs at trace and sub-trace levels in wastewater and other samples. This will remove matrix interference and increase the trace levels of sulfonamide residues. A number of extraction and pre-concentration techniques for sulfonamide drugs have been published (Karami-Osboo et al., 2014, Maham et al., 2013). Conventional pre-treatment techniques have several drawbacks, including the need for huge volumes of hazardous organic solvents. That being said, they are laborious, time-consuming, and very costly.

Sulfonamides are most used synthetic antimicrobial medications. They are pharmacologically utilized as a broad spectrum for the treatment of bacterial infections in humans and animals (Ovung and Bhattacharyya, 2021). Sulfonamides are among the most often used antibacterial medicines in both human and veterinary medicine due to their low cost, minimal toxicity, and relevant efficiency against many common bacterial diseases (Becheker et al., 2014). Sulfathiazole (STZ) was determined using a wide range of analytical techniques, including spectrophotometric techniques (Omar et al., 2021, Akkab and Hamidi, 2024), high-performance liquid chromatographic techniques (Nowacka-Kozak et al., 2024), flow-injection method (Gui-Hua et al., 2012), FT-Raman technique (López-Sánchez et al., 2008), paper-based analytical device (Sanaan Jabbar, 2024),

an electrochemical method (Que et al., 2025) and chemiluminescence method (Liu et al., 2009).

Because of their unique characteristics, nanoscale adsorbents have garnered a lot of attention (Bao et al., 2014, Jabbar, 2024). Various organic and inorganic chemicals have been successfully extracted and removed using magnetic nanoparticles (MNPs) as the adsorbents (Zhai et al., 2012, Jabbar et al., 2024). Due to their extreme paramagnetic nature, MNPs are easily isolated, tracked, and manipulated in the presence of external magnetic fields. Centrifuging or filtering is not necessary while performing magnetic solid phase extraction (MSPE), resulting in a simpler and quicker separation process. Pure magnetic particles have several intrinsic limits, such as the propensity to form aggregates and the ability to alter the magnetic properties in complex biological and environmental materials, despite the many advantages of using MNPs. A protective coating on magnetic particles has been the subject of numerous investigations in an effort to overcome the drawbacks of these adsorbents (Wang et al., 2023). The coating of metal oxide NPs with carbon dots (CDs) is a significant advancement in nanotechnology, particularly for enhancing adsorption properties. This combination leverages the unique properties of both materials to create a synergistic effect that improves their performance in various applications, especially in environmental remediation. This improvement is achieved through several mechanisms by increase the surface area, functional groups, and improved stability (Stachowska et al., 2022).

Thus, the aim of this article is to develop an improved spectrophotometric method for the determination of trace sulfathiazole that is present as residues in wastewater using CDs@Fe₃O₄ as a cheap and effective adsorbent for the pre-concentration of STZ to increase the sensitivity prior determination.

2. Materials and Methods

2.1. Instruments

A UV-Visible spectrophotometer (UV-Vis./Visible Spectrophotometer AE/S60 model, 200-800 nm) was used in this investigation to evaluate

absorption. The UV-visible scanning spectrum was acquired using a quartz cell with a path length of 1.0 cm. Additionally, A Benchtop Tabletop pH Meter with a Multiparameter from China (PHS550) was used.

2.2. Materials

The chemicals employed in this study included sodium nitrite (99.99%) (Sigma Aldrich, Merck, Darmstadt, Germany), ethanol (99.80%) (Honeywell Fluka, Vantaa – Finland), 1,5-dihydro naphthalene (99%), sulfathiazole ($\geq 99\%$), and hydrochloric acid (36%) were obtained from (Fluka Chemie AG, Buchs, Switzerland). Without any additional purification. Throughout the experiment, distilled water was used as a solvent. CDs@Fe₃O₄ was obtained from the Research Lab/Department of Chemistry/College of Science/Salahaddin University and was synthesized and used in previous research (Esmail et al., 2024).

Every solution was made with distilled water. To make standard solutions of sulfathiazole (250 µg/mL), 250 mg of sulfathiazole was dissolved in 5 mL of ethanol, and the final volume of 1000 mL was achieved by diluting with distilled water in volumetric flasks. The sulfathiazole solution was further diluted to provide a working standard solution. 1% aqueous sulfamic acid solution, 1 mol/L hydrochloric acid solution, 0.1 mol/L aqueous nitrite (NaNO₂) solution, and 0.25 % w/v solution of 1,5 dihydroxy naphthalene in ethanol were utilized in the studies.

2.3. Calibration curve

Each of the series of 10 mL flasks added aliquots of sulfathiazole solutions ranging from 0.05-0.4 mL (100 µg/mL), 1.0 mL of NaNO₂ (0.1 mol/L), and 1.0 mL of 1 mol/L HCl were added with swirling at room temperature. After 5.0 min, 1.0 mL of sulfamic acid (1 % w/v) and 1.0 mL of 1,5-dihydroxy naphthalene (0.25 % w/v) were added with swirling. After using distilled water to adjust the volumes as needed, the solutions were thoroughly mixed. The absorbances of the orange-colored solutions were measured after 2 min at 484 nm against the reagent blank.

2.4. Adsorption of sulfathiazole in wastewater

Batch adsorption studies were performed by mixing 50 mg CDs@Fe₃O₄ adsorbent with 20 ml of synthesized wastewater containing 20 µg/mL

STZ in a flask. pH adjustments were carried out using standard solutions of 0.1 mol/L NaOH and 0.1 mol/L HCl. An external magnetic field was used to separate the adsorbent after equilibrium was reached. The adsorbed analyte on the CDs@Fe₃O₄ composite was desorbed after 10 min using 5 mL of 1.0 mol/L HCl. The concentration of STZ was measured by the proposed procedure in previous section. To obtain reproducible experimental results, adsorption experiments were carried out three times. Optimizing criteria are based on extraction recovery (ER%) and enrichment factor (EF) as defined in Equation (1) and Equation (2) (Esmail and Jabbar, 2023).

$$EF = C_{ads} / C_o \dots\dots\dots 1$$

$$ER\% = [(C_{ads} \times V_{ads}) / (C_o \times V_{aq})] \times 100 = EF \times [(V_{ads}) / (V_{aq})] \dots\dots\dots 2$$

C_o and C_{ads} represent the concentrations of analytes in aqueous and adsorbent samples (µg/mL), respectively. To calculate C_{ads}, we used the STZ standard solution calibration graph. The real sample and adsorbent volumes are V_{aq} and V_{ads}, respectively (mL).

3. Results and discussion

3.1. Reaction mechanism

The diazotization of the aromatic amines in the presence of a nitrite solution in an acidic medium to generate a diazonium salt is the basis for the color reaction. The excess nitrous acid is then removed from the process by adding sulfamic acid. The procedure entails combining the sulfathiazole drug with 1,5-dihydroxy naphthalene after it has diazotized in an aqueous medium to produce an orange-colored azo product (Ellaithy et al., 1986). The suggested reaction mechanism is shown in Figure 1a. The formed azo compound has a λ_{max} of 484 nm, in contrast to the reagent blank, which gives almost no absorption in the region of 400 – 700 nm as shown in Figure 1b. While in previously published articles for determination of STZ various λ_{max} values were obtained including 595 nm (Boiko et al., 2011), 517 nm (Al-hilfi and Jadou, 2022), and 372 nm (Sanaan Jabbar, 2024).

3.2. Optimization of the experimental reaction conditions

Experiments were conducted to establish a

simple, sensitive, and rapid spectrophotometric measurement of STZ. 1,5-Dihydro naphthalene is rarely employed as a coupling agent for spectrophotometric determination of pharmaceutically active compounds. Various variables including the HCl, NaNO₂, 1,5-dihydro naphthalene concentrations, and reaction time were studied. The effect of these variables on the determination of the drug was investigated.

The effect of NaNO₂ concentration was investigated by varying the volume from 0.3 to 2.0 mL using 0.1 mol/L sodium nitrite. The results are shown in Figure 2a which indicates that maximum absorbances were obtained using 1.5 mL NaNO₂. Further increase produces unstable and noisy readouts due to the possibility of generating nitrogen gas. The excess nitrous acid must be removed using a sulfamic acid solution.

The effect of hydrochloric acid concentration on the diazotization reaction was studied in the range of 0.1 to 1.5 mL using 1.0 mol/l HCl. As Figure 2b shows, maximum diazotization was obtained using 0.6 mL HCl. Higher acid concentration weakens the medium (increase the pH) required for obtaining the color of azo dye. While, at lower HCl concentration the production of nitrous acid is not enough to form the intense color of the azo dye. Therefore, 0.6 mL was considered for further studies.

A sulfamic acid solution was used to remove the excess sodium nitrite because excess NaNO₂ generates nitrogen gas that leads to instability of obtained absorbances. Thus, the effect of sulfamic acid solution in the range of 0.7 to 2.5 mL using 1.0% solution was studied. As shown in Figure 2c, a stable response was obtained using 1.0 mL of 1.0% sulfamic acid solution. Volumes higher than 1.0 mL lead to a decrease the absorbance due to an increase in the acidity of the solution because of the acidic properties of sulfamic acid.

The effect of a coupling reagent (1,5- dihydro naphthalene) concentration upon the analytical response was examined in the range of 0.2 to 1.5 mL of 0.25%. Maximum response was obtained using 1.0 mL reagent as shown in Figure 2d. Volumes higher than 1.0 mL of coupling reagent have not affected the results due to the complete consumption of formed

diazonium salt. Therefore, this concentration was employed in subsequent experiments.

Using the optimized reactant concentrations, the effect of reaction time for the diazotization reaction and coupling reactions was studied. As illustrated in Figure 2e, after 5 min the diazotization reaction (Time 1) was completed, and after 2 min the coupling reaction (Time 2) was completed. Reaction times higher than the obtained results have no effect on the absorption value because all reactants react completely.

The results that were obtained are as follows: 1.5 mL NaNO₂, 0.6 mL HCl, 1.0 mL sulfamic acid, 1.0 mL of 1,5- dihydro naphthalene, 5 min for diazotization reaction, and 2 min for coupling reaction. The formed color is stable for more than 75 min as shown in Figure 2f.

3.3. Optimization of CDs@Fe₃O₄-based adsorption parameters

The important adsorption conditions including pH, adsorbent dosage, contacting time, and temperature were optimized. Distilled water containing 20 µg/mL STZ drug was mixed with CDs@Fe₃O₄ nanocomposite.

In the first step, the adsorption process was carried out using CDs, Fe₃O₄, and CDs@Fe₃O₄ as adsorbent, and the obtained ER% results were 34%, 52%, and 84.6%. This enhancement with the using of nanocomposite is driven by the increased surface area, functionalization potential, and stability provided by the carbon dots (Stachowska et al., 2022).

3.3.1. Elution solvent optimization

To ensure that all analytes will be eluted from the adsorbent, the elution solvent should be strong enough. Figure 3a shows that various inorganic and organic solvents were tested to determine which was the best one for eluting STZ from the composite. Among these were HNO₃, H₂SO₄, HCl, ethanol, DMF, and acetone. We were able to achieve the best elution of STZ with 1.0 mol/L HCl, which was chosen as the elution solvent because of its strong dissolving abilities and ability to bind STZ. In comparison with nonpolar solvents, polar solvents exhibit better elution capabilities because they interact more with the polar groups on the STZ (Maham and Karami-Osboo, 2017, Ning et al., 2021). Additionally, eluent volumes ranging from 250-1250 µL were

examined. To achieve quantitative desorption, 500 μL of eluent is required. Thus, this eluent volume was chosen as the optimum for the subsequent experiments.

3.3.2. STZ initial concentration optimization

Using 50 mg of $\text{CDs@Fe}_3\text{O}_4$ under pH 7 and a concentration of STZ drug ranging from 5 $\mu\text{g/mL}$ to 50 $\mu\text{g/mL}$, the influence of the initial concentration of STZ drug on the adsorption effect was studied. Figure 3b shows the results. With increasing STZ initial concentrations, $\text{CDs@Fe}_3\text{O}_4$'s adsorption capacity toward STZ drug increases. The increase in adsorption capacity may be attributed to the fact that with increasing STZ concentration, drug molecules, and $\text{CDs@Fe}_3\text{O}_4$ adsorbent have more frequent collisions, making adsorption easier (Ning et al., 2021). With a higher STZ concentration (more than 20 $\mu\text{g/mL}$), the $\text{CDs@Fe}_3\text{O}_4$ adsorbent's active sites become insufficient, which results in fewer drug molecules being attracted, which decreases the rate of drug removal. When STZ initial concentration is increased to 20 $\mu\text{g/mL}$, the ER value increases to 85.2%. Accordingly, the optimal initial STZ concentration for subsequent tests is 20 $\mu\text{g/mL}$ based on a large adsorption capacity and extraction recovery.

3.3.3. pH effect on the STZ removal

During the adsorption process, pH is crucial since it influences the surface charge of the adsorbent and drug ionization. Hence, the effects of pH in the range of 2 – 10 were investigated at 25°C using STZ at an initial concentration of 20 $\mu\text{g/mL}$ and $\text{CDs@Fe}_3\text{O}_4$ at a concentration of 50 $\mu\text{g/mL}$. It is clear from Figure 3c that at a pH value of 7 or more, STZ adsorbs more on $\text{CDs@Fe}_3\text{O}_4$ and is extracted at an overall recovery greater than 85%. The changes in their peaks are slow with increasing pH (7-10), suggesting that although pH is certain to influence the adsorption of STZ on $\text{CDs@Fe}_3\text{O}_4$, its influence is not evident at neutral and basic mediums based on electrostatic attraction between adsorbent and the analyte (Shen et al., 2009). Moreover, the results suggest that many kinds of drug wastewater can be treated with the proposed adsorption technique at a variety of pH levels. As can be seen, the extraction recovery and rate of drug removal both reach their

maximum when pH is 7, indicating that pH 7 is ideal.

3.3.4. Optimization of adsorbent dosage

In order to assess the effect of the amount of adsorbent on drug adsorption, experiments must be conducted on both active sites and effective surface area. An adsorbent dosage of 10 mg to 120 mg was used with a 20 $\mu\text{g/mL}$ STZ under pH 7 at 25 °C in order to study the effects of $\text{CDs@Fe}_3\text{O}_4$ on adsorption. Figure 3d illustrates the results. It seems that when the dosage of $\text{CDs@Fe}_3\text{O}_4$ is increased from 10 mg to 80 mg, the extraction recovery increases from 23.5% to 97.1%. If the $\text{CDs@Fe}_3\text{O}_4$ dosage is increased from 80 mg to 120 mg, the extraction recovery tends to remain nearly constant. The STZ removal rate may have improved due to more active sites being available to attract drug molecules when the $\text{CDs@Fe}_3\text{O}_4$ dosage is increased. It is however true that, if the dosage of the adsorbent is increased to a certain extent, the active sites will be sufficient for drug molecules to bind to them. Therefore, the higher the amount of adsorbent used, the more vacant the active sites are, and the rate of removal increases (Shen et al., 2009). A dosage of 80 mg of $\text{CDs@Fe}_3\text{O}_4$ is therefore selected as the most effective adsorbent for the adsorption of STZ drugs.

3.3.5. Optimization of contacting time on the adsorption

To study the effect of contacting time on STZ adsorption, further experiments were carried out using 80 mg $\text{CDs@Fe}_3\text{O}_4$ nanocomposite at 25 °C and pH 7, with the contacting time varying from 1 to 90 minutes. The effect of contacting time on STZ extraction recovery is shown in Figure 4a. According to this study, STZ adsorption rates are highly time-dependent, that is, the longer the contact time, the higher the ER. As the contact time increases, adsorbate molecules have enough time to collide with the catalyst surface and set on the vacant site of the adsorbent. However, when equilibrium is established after 12 minutes the adsorbent surface is fully saturated with adsorbate and adsorption becomes constant. Thus, longer contact times (more than 12 minutes) had only a slight effect on the adsorption percentage, which

was not favorable due to the longer energy expenditure (Farooq et al., 2022).

3.3.6. Optimization of temperature

According to previous studies, the adsorption process was strongly influenced by temperature. Thus, the effect of temperature on the adsorption of sulfathiazole was investigated in the range of 20 °C to 60 °C (293.15K to 333.15K) at pH 7.0, with an initial STZ concentration of 20 µg/mL and a CDs@Fe₃O₄ concentration of 80 mg. According to Figure 4b, the extraction recovery and removal rate increases with increasing temperature. The ER value is as high as 99.1% even at 25°C (room temperature). Based on these results, CDs@Fe₃O₄ have excellent adsorption properties for STZ at temperatures ranging from 20 to 45 °C. It follows that the adsorption of STZ by CDs@Fe₃O₄ is endothermic. In response to rising temperatures, STZ drug molecules move faster, causing more STZ drug molecules to collide with CDs@Fe₃O₄ and be attracted to its surface (Ning et al., 2021). Using CDs@Fe₃O₄ as adsorption removal catalyst, 25 °C is selected as the most suitable temperature to save costs and energy.

Thus, the experimental conditions for STZ adsorption by CDs@Fe₃O₄ can be optimized as follows: 20 µg/mL STZ initial concentration, at pH 7, CDs@Fe₃O₄ adsorbent dosage of 80 mg, contact time of 12 minutes, and at room temperature. The calculated desorption efficiency (Carneiro et al., 2024) before and after optimization were calculated using 20 µg/mL. the results showed that optimization leads to increase desorption efficiency from 84.4% to 99.2%.

3.4. Analytical and optical parameters

For the sulfathiazole drug under investigation, optical properties such as limits of Beer's law, molar absorptivity, correlation coefficient, regression equation, quantification limit (QL), detection limits (DL), slope standard deviation, and intercepts standard deviation were determined. All obtained optical and analytical parameters are displayed in Table 1. Measurements of the absorbance at λ_{max} for the modified Bratton-Marshall method were conducted under optimal conditions, with sulfathiazole concentrations between 0.5 and 4

µg/mL. For the determination of sulfathiazole, the linear regression equation is $Y=0.0913 X + 0.0102$ with a coefficient of determination (R^2) of 0.9990 as shown in Figure 4c. In practical terms, sensitivity is the slope of the calibration curve that follows from graphing the analyte concentration against the response; the sensitivity value that was achieved was 0.0913. For the sulfathiazole drug, the LOD and LOQ were determined using $3 \times Sa/S$ and $10 \times Sa/S$ respectively, where S is the linear calibration curve's slope and Sa is the intercept's standard deviation. The obtained findings revealed that the improved method was sensitive to identifying and quantifying sulfathiazole at a low concentration level, as shown in Table 1.

3.5. Application

The proposed pre-concentration spectrophotometric determination of STZ was applied to four synthetic wastewater samples using tap water from two different positions (New Zanko Village, and Farmanbaran-Erbil), distilled water (Analytical Research Lab, Department of Chemistry), and deionized water samples (General Research Lab, Department of Chemistry). A comparison takes place between the results by calculating recovery values as shown in Table 2. In all cases, the data were in good agreement within added amounts and the value recovery ranged from 96.27 to 100.02% and relative standard deviations less than 2.5%. Table 3 illustrates the proposed methods' results were compared with previously reported methods using different catalysts.

The method's reliability in measuring STZ under all investigated situations was demonstrated by the recovery values, which varied from 96.27% to 100.02%. Excellent precision was demonstrated by the relative standard deviation (RSD) values, which consistently stayed below 2.5%. Remarkably, the first tap water sample's 20 µg/mL STZ concentration yielded the maximum recovery value (100.02%), whereas the second tap water sample's 5 µg/mL STZ concentration yielded the lowest recovery (96.27%). These findings demonstrate that, even at lower analyte concentrations, the procedure operates reliably. With low RSDs and good recovery values, both tap water samples indicated little interference

from dissolved ions and other substances commonly present in tap water. For example, in "Drink water 2," the recovery ranged from 96.27% to 99.73%, with the RSD peaking at 2.48% for the lowest STZ concentration (5 µg/mL). This illustrates how the approach is resilient when dealing with actual water matrices. Compared to tap water, recovery values for distilled and deionized water samples were marginally higher and more reliable, most likely because there were no interfering chemicals present. In distilled water, for example, the recovery was 98.40% at 5 µg/mL and marginally increased at higher concentrations. Similarly, recovery rates for deionized water ranged from 96.67% to 98.55%, with RSDs as low as 0.32%. These findings show that matrix simplicity has no effect on the approach. Table 3 compares the method's results with those of other ways that have been published utilizing other catalysts, further highlighting the method's effectiveness. The suggested approach is notable for its low RSDs, high recovery rates, and easy pre-concentration procedure. Because it doesn't require complicated or costly materials like other catalytic systems do, this method provides a dependable and affordable substitute for routine STZ analysis in wastewater.

Conclusions

CDs@Fe₃O₄ magnetic nanocomposite has been successfully used, with high adsorption performances for STZ drug removal. The method based on separation of STZ using nanocomposite. Then, coupling of diazotized drug with 1,5-dihydroxy naphthalene and measuring the absorbance at 484 nm. The results indicate that the synthesized nanocomposite has the best adsorption and removal action for STZ when the initial concentration of drug is 20 µg/mL and the adsorbent dosage is 80 mg at pH of 7.0 and room temperature. Further studies on the recovery results, CDs@Fe₃O₄ adsorbent is found to show high adsorption performance and good reproducibility after being recycled five times. The maximum removal of STZ was 99.1%. The proposed method is comparable in sensitivity to many of the existing spectrophotometric methods for the determination of STZ in pharmaceutical

formulations and drug quality control. Thus, CDs@Fe₃O₄ adsorbents will provide a new eco-friendly, simple, fast, minimal reagent consumption, ultra-sensitive, and low detection limit method for treating STZ in wastewater.

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Statements and Declarations

The author declares no conflict of interest, financial or otherwise.

Conflict of interest

The author declares no competing interests.

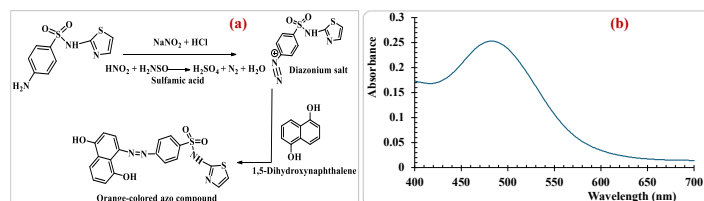


Figure 1. (a) Reaction mechanism for the formation of azo compound and coupling reaction; and (b) Absorption spectra for the orange-colored azo compound.

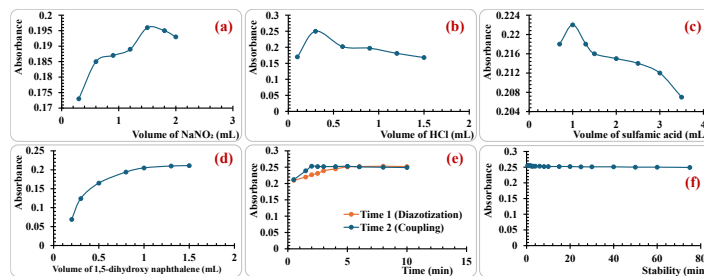


Figure 2. Effect of (a) NaNO₂ concentration; (b) HCl concentration; (c) sulfamic acid volume; (d) 1,5-dihydroxy naphthalene concentration; (e) mixing time on the reaction: Time 1 represents the required time for the diazotization reaction, and Time 2 represents the required time for the complete coupling reaction; and (f) Stability of the formed color.

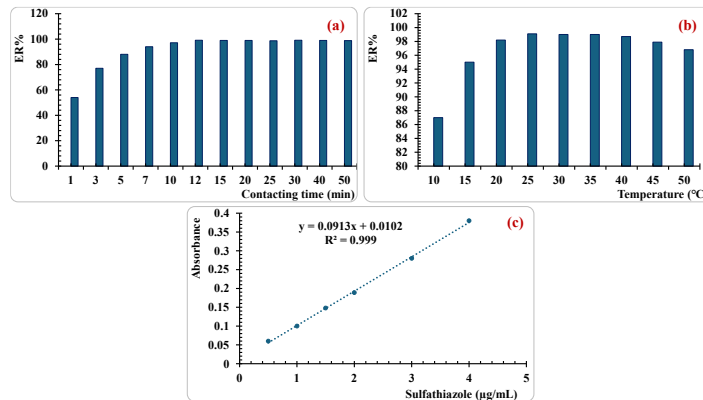
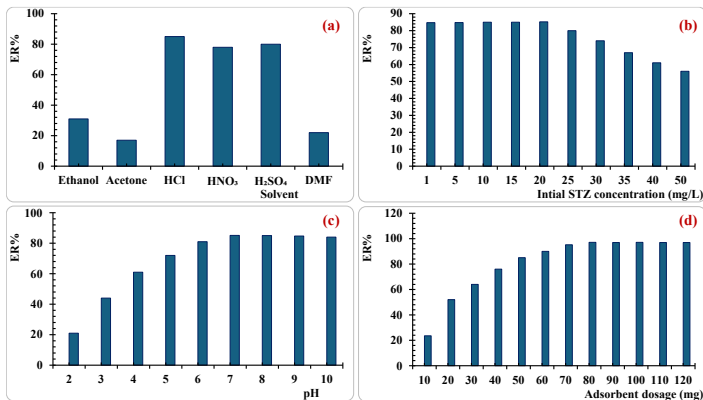


Figure 3. Effect of (a) elution solvent; (b) initial STZ concentration; (c) pH; and (d) CDs@Fe₃O₄ dosage.

Figure 4. (a) Effect of contacting time on the adsorption process; (b) Effect of temperature on the adsorption; and (c) Calibration curve of sulfathiazole at 484 nm.

Table 1. Some optical and analytical parameters for the determination of sulfathiazole spectrophotometrically.

Parameter	Observation
Color	Orange
λ _{max} (nm)	484
Detection limit (µg/mL)	0.3236
Quantification limit (µg/mL)	0.9806
Molar absorptivity (L/mol.cm)	38,956
Beer's law range (µg/mL)	0.5–4.0
Slope	0.0913
Intercept	0.0102
Coefficient of correlation (r)	0.9989
Standard deviation of slope (S _b)	0.0036
Standard deviation of intercept (S _a)	0.0089

Table 2. Application of the proposed pre-concentration method on synthetic water samples.

Sample	STZ (µg/mL)*		SD	RSD	Recovery%
	Added	Found			
Drink water 1	5.0	4.84	0.030	0.60	96.87
	10	9.70	0.079	0.82	97.00
	20	20.0	0.025	0.126	100.02
Drink water 2	5.0	4.81	0.119	2.48	96.27
	10	9.97	0.17	1.69	99.73
	20	19.86	0.21	1.05	99.30
Distilled water	5.0	4.92	0.10	1.90	98.40
	10	9.77	0.18	1.87	97.70
	20	19.79	0.28	1.42	98.97
Deionized water	5.0	4.83	0.015	0.32	96.67
	10	9.82	0.079	0.81	98.20
	20	19.71	0.216	1.10	98.55

* Average of five replications.

Table 3. Comparison of the proposed methods' removal efficiency with previously reported methods.

Detection method	Catalyst	Sample	Removal %	Reference
UV – HPLC	Oxygen-based membrane biofilm	Synthetic samples	87.0	(Kim et al., 2010)
UV – HPLC	Fe – H ₂ O ₂	Hospital wastewater	99.0	(Perini et al., 2018)
UV spectrophotometry	N-Fe co-doped TiO ₂	Pharmaceutical wastewater	88.0	(Hayati et al., 2020)
UV – HPLC	Covalent organic frameworks (COFs)	Industrial wastewater	88.3	(Niu et al., 2021)
UV – HPLC	CCNDs-embedded pullulan nanofibers	Wastewater	99.4	(Aijaz et al., 2022)
Visible spectrophotometry	CDs@Fe ₃ O ₄	Synthetic samples	99.1	This work

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