



# Development of a vortex-assisted dispersive micro-solid-phase extraction using reduced graphene oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposites for the determination of chlorfenson pesticide in green tea samples by high-performance liquid chromatography-ultraviolet detection

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## Abstract

Pesticides are the group of chemicals used for the protection of plants against pests and other harmful organisms. The excessive and uncontrolled usage of pesticides may lead to the contamination of environment with pesticides posing a serious risk to human health and ecology. Based on this, the ability to detect and monitor the level of pesticides in different environmental compartments became a serious need. In this study, the reduced graphene oxide–magnetite nanocomposites (rGO-Fe<sub>3</sub>O<sub>4</sub>-NC)-based vortex-assisted dispersive micro-solid-phase extraction (VA-DMSPE) method was developed and optimized for the detection of chlorfenson pesticide by high-performance liquid chromatography-ultraviolet detection system. For this purpose, the synthesis of rGO-Fe<sub>3</sub>O<sub>4</sub>-NC was performed to be later applied as an adsorbent of the target analyte in the study. Furthermore, the extraction parameters such as the buffer pH, buffer amount, sorbent amount and eluent volume were optimized to obtain the highest detection efficiency of chlorfenson. The limit of detection (LOD) and limit of quantification (LOQ) were 0.02 and 0.07 µg L<sup>-1</sup>, respectively. The improvement in the detection power was found to be 33.5. The proposed method accuracy was tested in green tea samples where the percent recovery for two different types of green tea samples was in the range of 96–109%.

**Keywords** Chlorfenson · Dispersive micro-solid-phase extraction · Magnetite nanoparticles · Matrix matching · Green tea

## Introduction

Pesticides usage has become essential for agricultural production playing a crucial role in the protection of crops from infestations by pests and other pathogens to enhance their productivity (Bano et al. 2021). Pesticides application to the field is not always guaranteed to reach their targets noting that some of them end up in the soils to be absorbed later by plants. Zhang et al. reported that pesticides can enter

plants through different ways including seed treatment, soil application and foliar spraying (J. J. Zhang and Yang 2021). The bioaccumulation and biomagnification of these pesticides in the food chains are seriously dangerous to the food safety and human health. Besides, pesticide residues and metabolites are early reported to be associated with adverse effects on the ecology and biodiversity with neurotoxicological hazards that may lead to the death of humans and animals (Sarker et al. 2021). Chlorfenson also known as benzenesulfonic acid, 4-chloro-4-chlorophenyl ester is one of the pesticides that belong to the chemical family of sulfonates. It is a non-corrosive crystalline solid that has an insecticide and acaricide effect against mites on different fruits and vegetables. It has a long residual ovicidal activity that acts by inhibiting the phosphorylation enzymes such as NADH dehydrogenase, ATP synthase and cytochrome oxidase (Ramalingam et al. 2013).

The detection of the trace levels of insecticides in diverse sample matrices was performed using gas chromatography

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(GC) and high-performance liquid chromatography (HPLC) (Tian et al. 2020; Mohammed et al. 2019). HPLC is an analytical instrument used for the detection of different chemicals and drugs. It serves a chemical monitoring analysis based on its ability to separate and purify target analytes from a complex matrix of a defined sample. The mechanism of action refers to the mechanical passage of a liquid mobile phase through a chromatographic column filled with an immobilized stationary phase carrier that will adsorb the target analytes leading to the separation of the sample components (Weston and Brown 1997; Žuvela et al. 2019). HPLC can be used for the analysis of both volatile and non-volatile compounds using two different types of separation techniques: reversed-phase (RP) HPLC and normal-phase (NP) HPLC. RP-HPLC gained high popularity due to its versatility and adaption to various methods such as ion pair (IP), ion exchange and micellar (Joshi 2002; Boukhobza and Crans 2020). C18 columns are the mostly used reverse-phase separation columns (Guerin et al. 1999). RP-HPLC is frequently combined with ultraviolet spectrophotometric (UV) detection (Hashimoto et al. 2020) due to its high sensitivity, reliability, analysis time and repeatability (Nageswara Rao and Nagaraju 2003). UV detectors are easy to use, sensitive, compatible with LC, durable, need less maintenance and are relatively cheap (K. Zhang et al. 2019). The history of analytical chemistry proved that the accurate determination of analytes at trace levels is quite difficult without an adequate pretreatment step (Kanu 2021). Therefore, the application of preconcentration methods prior to analysis using the conventional analytical instruments results in the concentration of pesticides decreasing in turn the limit of detection. The favorable sample preparation methodology seeks nowadays to replace the classical preparation methods that use large amount of chemicals and solvent with greener and environmental friendly solvents (M. Nasiri et al. 2020). Within this scope, a wide variety of microextraction techniques have appeared for the extraction of different pesticides from environmental and water samples (Manousi et al. 2021) such as solid-phase microextraction (SPME) (Erdem et al. 2021), dispersive liquid–liquid extraction (DLLME) (Ragheb et al. 2021) and magnetic solid-phase extraction (MSPE) (J. Nasiri et al. 2017). The magnetite nanoparticles (MNPs) separate adsorbents through the application of an external magnetic field. This last was found to be environmentally friendly, easy and less expensive in removing metals from water and wastewaters (Almomani et al. 2020) and in adsorbing unwanted micropollutants such as pesticides and antibiotics in wastewaters (Wang et al. 2018). In the aim to minimize agglomeration, enhance stability and lower the likelihood of resistance, MNPs are generally used after coating with functionalized materials with one or more active chemicals (Sharma and Chauhan 2021). Graphene oxide (GO) is characterized by an extremely large surface

area approximately about  $736.6 \text{ m}^2 \text{ g}^{-1}$  in aqueous solutions and a wide availability of active compounds making it an excellent immobilizing material (Paz-Cedeno et al. 2021). Furthermore, additional physicochemical properties such as remarkable dispersibility, high adsorption capacity and thermal/electrical conductivity have led to the extreme interest in the usage of graphene dioxide (Dramou et al. 2021). On its own, GO application in sample preparation was reported to have some drawbacks such as the aggregation tendency of particles resulting in their difficult separation from the sample. Based on this, the combination of graphene-based materials with magnetite nanoparticles was found effective in the enrichment of the analyte in the matrix and its further facile and rapid separation. Thus, the obtained graphene-based magnetite is characterized by a high adsorption capacity resulting from  $\pi - \pi$  dispersion forces between organic compounds and graphene, the high surface area and the limited internal diffusion resistance (Yang et al. 2012; Manousi et al. 2020).

This study aimed to develop and optimize a preconcentration method for the determination of trace levels of chlorfenson using reduced GO magnetite nanocomposites (rGO-Fe<sub>3</sub>O<sub>4</sub>-NC) in the VA-DMSPE process by a HPLC–UV system. The applicability and accuracy of the developed method were proved through the recovery studies performed in green tea samples.

## Materials and methods

### Instrumentation

Chlorfenson was determined using a Shimadzu model HPLC having a chromatograph (LC-20A), a column oven (CTO-10AS) and an autosampler (SIL20A HT) coupled with an SPD-20A ultraviolet–visible detector. A Phenomenex brand C18 column (250 mm length, 4.6 mm ID and 5  $\mu\text{m}$  film thickness) was utilized for the chromatographic separation of chlorfenson in the HPLC–UV system. Chlorfenson detection studies were all performed at a wavelength of 235 nm. An isocratic mobile phase that consists of a mixture of acetonitrile solvent and water at a ratio of 80:20 (v/v) was used during the analysis at a fixed flow rate of  $1.0 \text{ mL min}^{-1}$ , an injection volume of 40  $\mu\text{L}$  and a temperature of 25 °C. The conditions of the optimal HPLC–UV system are also demonstrated in Table 1.

### Chemicals and reagents

Chlorfenson stock standard was purchased from Dr Ehrenstorfer GmbH Company. Working and calibration standards used in this study were obtained by diluting adequate aliquots from chlorfenson stock solution with a solvent

**Table 1** Parameters used in the HPLC–UV system

Parameters	Values
Column	Phenomenex C18, 250 mm length $\times$ 4.6 $\mu$ m ID $\times$ 5 $\mu$ m film thickness
Mobile phase	ACN (%80, v/v), H <sub>2</sub> O (%20, v/v)
Wavelength	235 nm
Flow rate	1.0 mL min <sup>-1</sup>
Injection volume	40 $\mu$ L
Column temperature	25 °C

containing ultrapure water and ACN at a ratio of 95:5 (v/v). Ultrapure water was obtained from an Elga Flex 3 Water Treatment System having a resistivity of 18.2 M $\Omega$  cm. Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, acetone (> 99.8%), ethanol (> 99.0%), ammonium hydroxide (25.0%), hydrogen peroxide, hydrazine (98.0%), sulfuric acid, potassium permanganate and hydrochloric acid (37.0%) used in the synthesis of the adsorbent material were purchased from Merck (Germany). Potassium hydrogen phthalate, tris-hydroxymethyl aminomethane, potassium dihydrogen phosphate, disodium tetraborate decahydrate, sodium hydroxide, HPLC grade acetonitrile and methanol used in the preparation of buffer and mobile phase solutions and the development of the DMSPE method were also obtained from Merck.

### Synthesis of reduced graphene oxide–magnetite nanocomposite

The first synthesis procedure of graphene oxide was published early in the literature by Hummers et al. (1958). The method consists of adding a volume of 46.0 mL concentrated sulfuric acid into an Erlenmeyer flask containing an amount of 2.0 g graphite powder. The mixture was stirred on a magnetic stirrer for about an hour. Subsequently, 6.0 g of potassium permanganate was slowly added into the flask having a fixed temperature at 20 °C which was controlled via an ice bath. The mixture was stirred at 35 °C for 2.0 h. After then, 92 mL of distilled water was added to the mixture which was stirred for an additional 1 h. At the end of the stirring period, 280 mL of distilled water was poured into the flask followed by the addition of 10.0 mL of H<sub>2</sub>O<sub>2</sub> (35%) leading to the transformation of color from dark brown to yellow. Finally, the mixture was left overnight in order to enhance better decantation. The obtained mixture was washed several times with acetone, hydrochloric acid (5.0%, v/v) and ultrapure water before being dried in the oven for 24 h at 60 °C.

In this study, reduced graphene oxide–magnetite iron nanocomposite (rGO-Fe<sub>3</sub>O<sub>4</sub>-NC) was synthesized using the co-precipitation method previously developed by Er and coworkers. (Er et al. 2019). The method consists of

dissolving of 0.25 g of graphene oxide in 250 mL of distilled water. The mixture was sonicated in an ultrasonic bath for 1.0 h. In another container, 8.109 g of FeCl<sub>3</sub>.6H<sub>2</sub>O and 5.883 g of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O were dissolved in 50 mL of distilled water and then added to the graphene oxide–water suspension. In the subsequent step, the solution temperature was adjusted to 80 °C and a volume of 30.0 mL ammonia solution was added to the mixture. Mixture temperature was brought to 90 °C and 250  $\mu$ L of hydrazine was subsequently added to the mixture and the reaction temperature was fixed at 90 °C. Under the inert atmosphere, the mixture was stirred for 4.0 h at 90 °C. Finally, obtained nanoparticles were separated using a magnet, washed several times with distilled water and ethanol and dried for one day at 55 °C. Characterization studies of nanocomposite material have been reported in the study which was used in the preparation of (Er et al. 2019).

### Extraction procedure

The extraction procedure relies on weighing 25 mg of sorbent in a 50 mL centrifuge tube. Then, 30 mL of standard/sample solution (in 5.0% ACN) and 1.50 mL of pH 7.0 buffer solution were added to the tube. The mixture was mixed using a vortex for 30 s to distribute the magnetic adsorbent homogeneously in the aqueous solution and to ensure maximum interaction within the solution. After that, the mixture was centrifuged at 3000 rpm for 2.0 min to facilitate the separation of the adsorbents and target analytes from the aqueous phase. The target analyte adsorbed on the surface of the synthesized rGO-Fe<sub>3</sub>O<sub>4</sub>-NC were collected and held at the bottom of the tube using a strong magnet. The aqueous phase was then decanted and the analyte was eluted through the addition of 150  $\mu$ L of acetonitrile. Finally, the eluent phase was separated from the MNPs adsorbent with the help of a magnet and the fraction of eluent was taken into the inner vial for further analysis by HPLC system. The extraction procedure is presented in Fig. 1. This schematic presentation was drawn using the BioRender software.

### Sample preparation

The proposed method was tested in green tea samples. For this aim, two different types of tea were purchased from a local Turkish market in Istanbul. 4.0 g of each tea sample was brewed in 400 mL of water. The liquid part was then separated from tea leaves through the application of a simple filtration process. Using the matrix matching method, different concentrations of chlorfenson were spiked into the filtrated tea samples. Adequate dilutions were performed using 5% ACN.

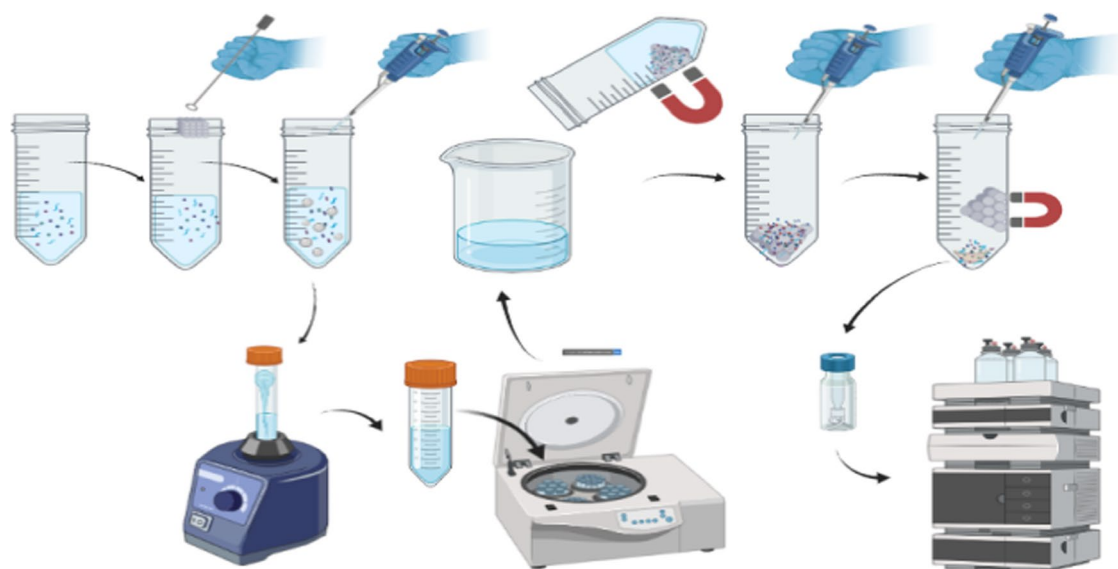


Fig. 1 Developed rGO-Fe<sub>3</sub>O<sub>4</sub>-NC-VA-DMSPE method procedure

## Results and discussion

In the aim to develop a VA-DMSPE method for the determination of chlorfensone by HPLC–UV system, different parameters such as the HPLC–UV system parameters, buffer pH and amount, nanoparticle type and amount, mixing time and eluent volume were optimized. Optimization studies were carried out by keeping all parameters constant and changing a single parameter. All optimization studies were performed in triplicate. The recovery of chlorfensone from tea samples was tested using the developed method.

### Optimization of HPLC–UV system parameters

In this study, HPLC–UV system was used for the determination of the chlorfensone analyte. Based on this, the HPLC–UV system variables have been optimized to ensure a symmetrical chromatographic signal and good chromatographic separation of the analyte. Firstly, Zorbax C8 column (dimension of 250 × 4.6 mm, 5 μm) and Phenomenex brand C18 (4.6 × 250 mm, 5 μm) as reverse-phase columns were compared for their chromatographic separation and peak resolution of chlorfensone by keeping the ACN: H<sub>2</sub>O mobile phase constant at the ratio of 80:20 (*v/v*). The best chromatographic separation for chlorfensone was obtained with the Phenomenex brand C18 (4.6 × 250 mm, 5 μm) column. Therefore, this column was chosen as the optimum one for the separation of analyte in the study. In the next step, the mobile phase was optimized by testing several ratios of acetonitrile/water with the aim to obtain the most symmetrical and smooth peak shape. Tested mobile phase composition was as follows: 70:30, 80:20 and 85:15 (ACN: H<sub>2</sub>O,

*v/v*). The results show that the best peak shape of the target analyte was obtained at the ratio of 80:20 (*v/v*) which was selected as the optimum mobile phase ratio. Within the same context, another mobile phase composition that consists of a mixture of methanol and water was tested but obtained peaks were not symmetrical enough in comparison with the acetonitrile and water mixture mobile phase.

The absorption wavelength of chlorfensone was varied between 220, 235, 254 and 270 nm to get high signal/noise ratio. The optimal wavelength was selected to be 235 nm as it gives the best absorption signals of chlorfensone. Finally, the flow rate and injection volume of the mobile phase were tested in the range of 0.9 and 1.1 mL/min and between 10, 20, 30, 40 and 50 μL, respectively. The results showed that the best symmetrical signal was obtained at a flow rate of 1.0 mL/min and an injection volume of 40 μL. Thus, further analysis was performed using the all these optimized parameters. The total analysis time of chlorfensone was found to be 7.0 min.

### Optimization of buffer solution pH and amount

pH greatly affects the surface properties of adsorbent. Therefore, pH adjustment is a crucial step that must be performed prior to the adsorption process affecting thus the whole process (Mollahosseini et al. 2019). The ionic strength of the buffer solution has a significant effect on the adsorption capacity of the target analyte onto the adsorbent within the DMSPE process (Buyuktiryaki et al. 2020). This can be explained by the protonation and deprotonation of the analyte affecting in turn the adsorption and extraction rate from the aqueous solution. Besides, pH was found to affect

the physicochemical characteristics of the adsorbent such as the charge and the ionization rate of the adsorbents (Moradi et al. 2013; Rezaei et al. 2022). Therefore, the effect of pH on the target analyte extraction was investigated by varying the pH value between 2.0 and 12. The obtained results showed that the best signals refer to a pH value of 7.0 which was used in further analysis. In the next step, the buffer solution amount was changed between 0.50, 1.0, 2.0 and 3.0 mL and the highest peak area values were obtained for a buffer volume of 1.5 and 2.0 mL. However, 1.5 mL of buffer solution was chosen as the optimum buffer volume emphasizing the importance of less chemical solvent usage. Marzi et al. (2021) studied the effect of the ample solution pH on the analyte. In the study, it was reported that the structure of the analyte can be hydrolyzed or decomposed in various pH values during the extraction of the target analytes. The pKa values of the desired analytes were investigated in the study and the pH effect of the sample solution was evaluated in different pH ranges from 2 to 10. (Marzi Khosrowshahi et al. 2021).

### Nanoparticle type and amount optimization

The selection of sorbent is a key factor in the DMSPE method as it ensures effective interaction between target analytes and sorbent material. The amount of sorbent parameter overcomes the importance of the sample amount. Insufficient amounts of a sorbent may cause the breakthrough of the analytes while higher amounts will increase the time and cost of the applied analytical method. Furthermore, higher amounts of material as sorbent may adversely affect the recoveries if the back extraction or "elution" of the analytes from the sorbent is not quantitative (Pardasani et al. 2011). Different kinds of sorbent materials were tried for the extraction/pre-concentration of chlorfenson such as uncoated nanoparticles (nickel nanoparticles, iron oxide nanoparticles, zirconium nanoparticles, silica nanoparticles and cobalt nanoparticles) and coated (oleic acid, salicylic acid and amido sulfonic acid) iron oxide–magnetite nanoparticles and reduced graphene oxide–magnetite nanocomposite. The extraction efficiencies of the tested nanoparticles were investigated and compared. It was found that the highest peak area was attributed to rGO-Fe<sub>3</sub>O<sub>4</sub>-NC. The hydrophobicity of the tested nanomaterials affects no doubt the recovery results. The usage of hydrophobic sorbent makes the elution step of the large hydrophobic analytes more critical exhibiting in turn strong interactions (Pardasani et al. 2011). Therefore, this nanomaterial was chosen as the optimum adsorbent for the DMSPE procedure. After then, nanoparticle amount optimization was performed to select the adequate weighing of rGO-Fe<sub>3</sub>O<sub>4</sub>-NC. Several amounts of sorbent were tested in the range of 10–50 mg. Figure 2 reflects the effect of sorbent amount as the peak area of chlorfenson increases with the

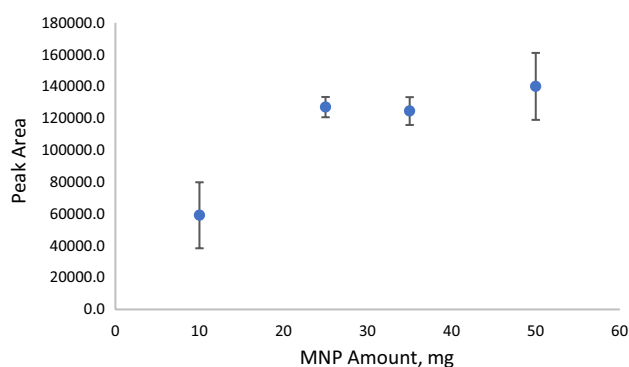
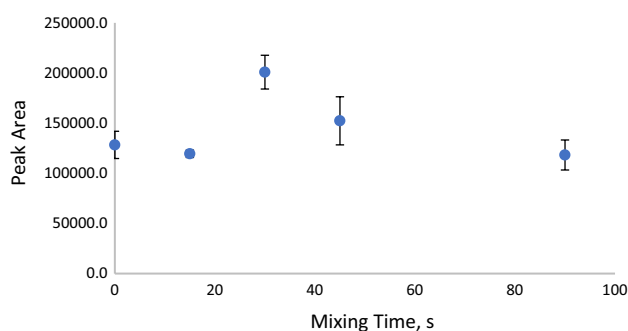


Fig. 2 Effect of adsorbent amount on the extraction of chlorfenson

increase in the sorbent amount from 10 to 25 mg. Higher amounts of sorbent lead to a slight increase in the peak area. In the context of developing environmentally friendly methods that aim to limit the overuse of chemicals, the optimum amount of sorbent was chosen to be 25 mg. This can be explained with the increase in the specific adsorption sites at higher amounts of the adsorbent material. On the other hand, Salisaeng et al (2016) performed a study on the determination of carbamate insecticides by the vortex-assisted dispersive micro-solid-phase extraction using cetyltrimethylammonium bromide (CTAB)-modified zeolite. In this study, it was found that the optimal amount of solid sorbent was 40 mg and further increase of this concentration did not affect the adsorption rate. This is compatible with the results obtained in this study as the rate of adsorption increases with the concentration of the sorbent until an optimum concentration where a higher concentration will not affect greatly the adsorption rate (Salisaeng et al. 2016).

### Mixing time optimization

Mixing time is an important parameter that affects the extraction efficiency. It is related to the specific time required for the target analytes in an aqueous solution to completely adsorb onto the sorbent material (H.-F. Zhang and Shi 2012). In another term, it improves the efficiency of the method by increasing the contact area between the sample and the sorbent and thus results in the reduction in the extraction time period of the analytes. Therefore, optimizing the adsorption time is also important in terms of shortening the time required for the analyte adsorption process. Therefore, the effect of vortex mixing time was tested in the range of 0–90 s. According to the results obtained in Fig. 3, 30 s was found as the best mixing time which was selected to be used for further studies. This result indicates that the transfer of target analytes from the solution to the sorbent is fast, which is one of the primary characteristics of the DMSPE procedures (Galán-Cano et al. 2011).



**Fig. 3** Effect of mixing time on the on the extraction of chlorfenson

### Eluent volume optimization

Desorption of the target analyte from the sorbent surface should be ensured through the use of eluent. The volume of eluent was optimized by varying the added volume between 100 and 250  $\mu\text{L}$ . The highest peak area referred to the 150  $\mu\text{L}$  volume of the eluent. Higher volume of eluent leads to a decrease in the peak area of chlorfenson. This can be explained by the dilution effect of the target analyte caused by an excessive usage of eluent (Nazari et al. 2017). Within the same context, Li et al. (2021) evaluated the effect of desorption volume on the recoveries of fluoroquinolones that includes ciprofloxacin (CIP), norfloxacin (NOR) and enrofloxacin (ENR) using novel polyethyleneimine-functionalized  $\text{Fe}_3\text{O}_4/\text{attapulgite}$  magnetic particles. In this study, the eluent volume was tested for its effect on the sorbent recovery. It was found that a desorption volume of about 0.5–1.0 mL was sufficient to reach a maximum recovery values of the sorbent (Li et al. 2021) (Table 3).

### Evaluation of system analytical performances

The system analytical performance under the optimum conditions was evaluated. In this context, parameters such as limit of detection (LOD), limit of quantification (LOQ), coefficient of determination ( $R^2$ ), relative standard deviation values (RSD), linear operation range and the enhancement in the detection power (EDP) were determined. The analytical performances of the systems are summarized in Table 2. Thanks to the developed method, the detection power of the HPLC–UV system increased about 33.5 times based on LOD comparison. A good linearity was obtained between 0.10 and 10  $\mu\text{g L}^{-1}$  registering a coefficient of regression of 0.9999. The LOD and LOQ were calculated as 0.02 and 0.07  $\mu\text{g L}^{-1}$ , respectively. Considering all these parameters, this method developed for the determination of chlorfenson has been presented as more sensitive, cheaper, more environmentally friendly method compared to the studies existing in the literature (Table 2, 3).

### Accuracy check

Recovery tests in the tea samples were carried out to assess the applicability and accuracy of the developed method. To confirm the absence of chlorfenson in the studied samples, in the first part, tea samples were analyzed under the optimum conditions. According to the results, chlorfenson was not detected in the tested tea samples reflecting its absence or its possible presence at a concentration lower than the system detection limit. Tea samples were spiked at final concentrations of 1.0, 2.0, 5.0, 10 and 20  $\mu\text{g L}^{-1}$ . Furthermore, a matrix matching calibration technique was utilized to improve recovery findings and to overcome the possible matrix interference on the target analyte. The concentration of spiked samples was then calculated using the calibration plot of matrix-matched standards. This method eliminated

**Table 2** The analytical features of the developed methods

System	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )	%RSD	Linear range	$R^2$	EDP
HPLC–UV	0.67	2.23	7.7	3.0 $\mu\text{g L}^{-1}$ –5.0 $\text{mg L}^{-1}$	1.000	–
rGO- $\text{Fe}_3\text{O}_4$ -NC-VA-DMSPE-HPLC–UV	0.02	0.07	6.2	0.10–10 $\mu\text{g L}^{-1}$	0.9999	33.5

**Table 3** Comparison with chlorfenson determination methods published in the literature

Method	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )	References
QuEChERS-GC/ECD	0.10	0.50	Miao et al. (2013)
SPE-GC/ED	1.0 $\mu\text{g/kg}$	3.50 $\mu\text{g/kg}$	Zhao et al. (2016)
PLE-GC/QqQ-MS/MS	0.3 $\mu\text{g/kg}$	1.7 $\mu\text{g/kg}$	Vidal et al. (2010)
SPE-GC/MS	10 $\mu\text{g/kg}$	30 $\mu\text{g/kg}$	Yang et al. (2011)
GC/MS-TIC	8.47	25.41	EL-Saeid et al. (2021)

**Table 4** The percent recoveries of the chlorfensol spiked in green tea samples

Matrix	Spiked concentration	Recovery (%)
Green tea sample 1	1.0 $\mu\text{g L}^{-1}$	97.7 $\pm$ 13.9
	2.0 $\mu\text{g L}^{-1}$	113.6 $\pm$ 3.2
	5.0 $\mu\text{g L}^{-1}$	100.3 $\pm$ 8.2
	10 $\mu\text{g L}^{-1}$	109.4 $\pm$ 2.4
	20 $\mu\text{g L}^{-1}$	101.9 $\pm$ 7.1
	2.0 $\mu\text{g L}^{-1}$	108.1 $\pm$ 14.8
Green tea sample 2	5.0 $\mu\text{g L}^{-1}$	85.4 $\pm$ 5.3
	10 $\mu\text{g L}^{-1}$	96.1 $\pm$ 6.5
	20 $\mu\text{g L}^{-1}$	101.6 $\pm$ 6.0

the effect of complex tea matrix and improved the accuracy and applicability to real sample. The percent recoveries of the target analyte spiked in green tea samples are summarized in Table 4.

## Conclusion

A preconcentration method using reduced graphene oxide  $\text{Fe}_3\text{O}_4$  nanocomposite-based VA-DMSPE for the determination of chlorfensol by HPLC–UV system was developed. The method shows superiority in the limited of detection and limit of quantification registering values of 0.02 and 0.07  $\mu\text{g L}^{-1}$ , respectively. The method under optimum conditions shows an improvement of 33.5 in the detection power in comparison with the classical HPLC–UV system with a relative standard deviation of 6.2%. Recovery studies performed in tea samples using the matrix matching methodology shows the superiority of this method by giving recovery percentage between 96 and 109%. This work will accordingly serve as the reference method for an accurate and sensitive determination of chlorfensol in similar matrices.

## Declarations

**Conflict of interest** None.

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