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ORIGINAL ARTICLE

# Ultrasound assisted based solid phase extraction for the preconcentration and spectrophotometric determination of malachite green and methylene blue in water samples

**Siroos Shojaei** [a,*], **Mashaallah Rahmani** [a,*], **Mostafa Khajeh** [b], **Ahmad Reza Abbasian** [c]

[a] *Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan 98135-674, Iran*
[b] *Department of Chemistry, University of Zabol, PO Box 98615-538, Zabol, Iran*
[c] *Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan 98135-674, Iran*

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**KEYWORDS**

Ultrasonic-assisted magnetic solid phase extraction;
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Response surface methodology;
Spectrophotometric method

**Abstract** In this study, magnetic ferrite nanoparticles $CoFe_2O_4$ were synthesized by combustion method. Magnetic solid phase extraction was carried out by ultrasonic assisted (UAMSPE) followed by UV/Vis spectrophotometer (UAMSPE-UV/Vis) to extract malachite green (MG) and methylene blue (MB) from water samples. To investigate the effects of adsorbent dosage, solution pH, ultrasonication time and volume of eluent solvent parameters on the extraction of MG and MB by $CoFe_2O_4$, the extraction experiments through the response surface methodology (RSM) were mathematically modeled and described as parameter performance. The results of extraction tests under optimal conditions showed that $CoFe_2O_4$ had a high extraction percentage. In optimal conditions, linear range of 70–550 ng mL$^{-1}$ ($R^2$ = 0.9977) and 40–450 ng mL$^{-1}$ ($R^2$ = 0.9983) were observed for MG and MB, respectively. Limit of detection (LOD) for MG and MB were 16.5 ng mL$^{-1}$ and 11 ng mL$^{-1}$, respectively. Relative standard deviation (RSD) was obtained in good and low values of 2.9% and 2.3% was achieved for MG and MB, respectively. The results of investigating the reusability of $CoFe_2O_4$ adsorbent showed that the adsorbent can be used for up to 5 absorption and desorption cycles. Also, the developed method was finally used successfully

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* Corresponding authors.
E-mail addresses: shojaeisiroos@gmail.com (S. Shojaei), Rahmani341@hamoon.usb.ac.ir (M. Rahmani).

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in determining MG and MB in fish, fish farming water, tap water and wastewater samples with recoveries ranged in 96.46–99.82%.

## 1. Introduction

Wastewater containing dyes is one of the most important environmental problems. Textile, dying and paper industries are the main producers of wastewater containing dyes. The presence of dye in water causes problems such as lack of light penetration into the water, interference in the photosynthesis of aquatic plants and causing allergies for humans and animals (Azari et al., 2022; Babakir et al., 2022; Khajeh et al., 2020; Sarani et al., 2020; Zazouli et al., 2016).

There are several techniques to determine the dye, some of these techniques are: gas chromatography-mass spectrometry (GC–MS), high-performance liquid chromatography with ultraviolet (HPLC-UV) and ultraviolet–visible spectrophotometry (UV/Vis). Ultraviolet–Visible spectrophotometry technique compared to other methods has advantages of ease, simplicity, usability for a wide range of extractable species, and cheapness of the device for extraction. Due to the low amount of analyte and the complexity of the sample matrix, the enrichment and separation processes are of great importance before the analysis (Ghosh et al., 2021; Shojaei et al., 2021; Chandel et al., 2020; Zarei Mahmoudabadi et al., 2019).

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are some widely accepted pre-concentration techniques. LLE is time-consuming and tedious and requires huge amounts of expensive and mostly toxic organic solvents. On the other hand, SPE employs significantly smaller volumes of solvent than LLE (Oliveira et al., 2022; Sun et al., 2020; Román et al., 2011). In recent decades, improvements and developments have occurred on standard and old methods. For instance, the magnetic solid-phase extraction (MSPE) technique has received great attention. This technique is extensively used for separating and pre-concentrating various compounds, such as pharmaceutical and food samples, polycyclic aromatic hydrocarbons, insecticides, and trace amounts of toxic metal ions (Yeganeh et al., 2023; Azari et al., 2022; Ghiasi & Malekpour 2020; Mehrabi et al., 2017; Reyes-Gallardo et al., 2013). In addition, the MSPE method is a promising alternative to the LLE method because of its simplicity and safety. High recovery of the analyte, purification of extracted species, easy automation, and reduced consumption of organic solvents are the main advantages of MSPE. The simple collection of nanoparticles from the solution via an external magnetic field is another advantage of MSPE. This magnetic property is suitable for extracting species from large-volume samples, as there is no need to centrifuge or filter the sample after extraction (Baghaei et al., 2023; Ghiasi et al., 2020; Li et al., 2015).

Nanomaterials have become one of the most remarkable items among the various adsorbents used in solid phase microextraction. The unique properties of nanomaterials give an excellent perspective to devise new methods and instruments for chemical analysis. Homogeneous distribution of dispersed nanoparticles in solution transfers the ideal mass to surfaces and can capture magnetic discharged materials. In addition, dispersed adsorbents prevent problems such as interruptions in filtration and deposition in packed columns and membranes (Abdel-Lateef et al., 2022; Reghioua et al., 2021; Khan et al., 2020; Kraus et al., 2009). Magnetic nanoparticles are widely used because of their wide range of applications in wastewater treatment, biological cell labeling, high density data storage, biochemical sorting and separation, magnetic resonance imaging (MRI), and drug delivery. The most important advantage of using magnetic nanoparticles as solid phase extraction is to collect particles through a magnetic field in a batch system. This feature makes magnetic nanoparticles excellent candidates to combine adsorption properties and phase separation (Shahryari et al., 2022; Nouri et al., 2020; Rabiee et al., 2020; Noormohamadi et al., 2018; Galaburda et al., 2017).

The design of experiments (DOE) is a technique applied to reduce process time and costs. DOE is a very practical method for attaining correct information about the studied factors and variables. Identifying a suitable model's experimental data requires statistical design principles, modeling techniques, and optimization methods (Esfe et al., 2022; Azari et al., 2021). These requirements are collectively met in the response surface methodology (RSM), which is among the most common methods in optimization and simulation. The RSM is method to design experiments that are useful to reduce the number of experiments and the interaction between factors, and it has been reported by many researchers (Arabkhani & Asfaram.2022; Srimoke et al., 2022; Rahmani et al., 2017). RSM is a laboratory optimization tool that involves complex mathematical calculations. The first goal for RSM is to find the optimum response. It helps the researcher determine the best laboratory design by the relationship between the variables. With the help of this tool, the optimization process with all variables examined in a short time in the laboratory stage becomes more valid (Jafari et al., 2022; Srimoke et al., 2022; Hashemi et al., 2021). Thus, the RSM method can be used to improve and optimize the process.

In this study, magnetic nanoparticles CoFe2O4 were synthesized and used as adsorbent to determine a small amount of MG and MB followed by UV/Vis analysis. RSM method was also used to investigate the effect of important operational parameters such as pH, adsorbent amount, solvent volume and ultrasonication time on adsorption capacity. Finally, the application of the method for MG and MB analysis in fish and environmental water samples was investigated.

## 2. Materials and methods

### 2.1. Reagents and instrumentation

All chemicals such as malachite green (MG), methylene blue (MB), sodium hydroxide, hydrochloric acid, ethanol, acetonitrile, methanol, glycine, iron nitrate, potassium chloride, cobalt nitrate, and acetone were used without further refining and were purchased from Merck KGaA (Darmstadt Germany). The standard stock solutions of MG and MB (100 mg $L^{-1}$) was prepared and then, the working solutions were prepared daily by diluting the standard stock solutions with double distilled water. Nanoparticles were characterized by X-ray diffraction (XRD) model Advance D8, Bruker, and scanning electron microscopy (SEM) model KYKY-EM3900M. UV/Vis spectrophotometer was used to determine the concentration of dyes equipped with a microcell. An ultrasonic device (Lk-D31-KDC 200B, Zhengzhou) equipped with digital timer was used for the ultrasound-assisted procedure. The pH was adjusted by sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) and measured using a pH meter. In this study, Design-Expert 10 software was applied for experimental design and data analysis. In all experiments, double distilled water was used.

### 2.2. Synthesis of $CoFe_2O_4$

In the present study, cobalt ferrite nanostructures were synthesized by the combustion method. The synthesis of cobalt ferrite powders was carried out considering the ratio of fuel (glycine) to total oxidants (iron and cobalt nitrates) equal to one and also the molar ratio of iron nitrate to cobalt nitrate equal to 2. Salt (potassium chloride) was used in the amount of two-thirds of the total amount of metal nitrates used. A solution with a certain pH (value 4) was prepared for the synthesis. To prepare an acidic solution, nitric acid was added to double distilled water to reach the desired pH. In each experiment, 10 mmol of cobalt nitrate, 20 mmol of iron nitrate, 44.4 mmol of glycine and 20 mmol of potassium chloride were dissolved in 60 mL of a solution with a certain pH. The dissolution process was carried out on a heater with a temperature of 80 °C. After the complete dissolution of all raw materials in the solvent, the temperature of the heater was set to the maximum possible. In this way, while the solution was being stirred, the gradual evaporation of the solvent started and with its continuation, it reached a stage where the solution changed color. At this stage, the stirring of the solution was stopped, and with the continued heating, a combustion reaction occurred, leading to the production of a powder product. The resulting powder was a mixture of cobalt ferrite particles and residual combustion products. Due to the insolubility of cobalt ferrite particles in water, the soluble impurity of the synthetic powder was separated by washing the resulting powder in hot water. The resulting powders were dried in an oven and studied by SEM and XRD.

### 2.3. Extraction experiments

In this study, experiments were done individually for each analyte. Ultrasonic preconcentration experiments were undertaken to increase the diffusion coefficient of dyes and mass transfer in batch mode. In this system, the experiments were done in test tube containing 15 mL of dyes at the optimum level of each parameter. In each experiment, a particular concentration of dye was transferred into the test tube. The initial pH of the samples was adjusted using HCl and NaOH 0.1 M. Then, after weighing, the required amount of $CoFe_2O_4$ was added to the samples. After that, the mixture was dispersed in an ultrasonic bath at room temperature. Finally, sampling was performed at a specific time and nanoparticles containing dyes were collected using an external magnetic field and the liquid phase was discarded. The analytes (dyes) were eluted from the adsorbent by adding of methanol to the adsorbent. Then, the test tube was placed in an ultrasonic bath for 5 min so that the solvent detaches the analyte-adsorbent bond and elutes the analyte from the surface of the adsorbent. The system was then exposed to a strong magnet and the solution was separated from the adsorbent. Finally, spectrophotometric measurements were done on a UV/Visible spectrophotometer at a maximum wavelength of MG (620 nm) and MB (665 nm). Extraction recovery was used to evaluate the extraction efficiency under different conditions. Enrichment factor (EF) was calculated through the following equation (1).

$$\mathrm{EF} = \frac{C_{sed}}{C_0} \tag{1}$$

where, $C_{sed}$ and $C_0$ were dye concentrations (ng $mL^{-1}$) in organic solvents and initial dye concentrations in aqueous samples, respectively. Extraction recovery (%ER) was defined as the percentage of total decomposition ($n_0$) extracted into organic solvent ($n_{sed}$) (Equation (2)).

$$\begin{aligned}\%ER &= \frac{n_{sed}}{n_0} \times 100\% = \left(\frac{C_{sed}}{C_0} \times \frac{V_{sed}}{V_{aq}}\right) \times 100\% \\ &= EF \times \left(\frac{V_{sed}}{V_{aq}}\right) \times 100\% \end{aligned} \tag{2}$$

where, $V_{sed}$ and $V_{aq}$ were organic phase volume and aqueous solution, respectively (Biparva et al., 2012).

### 2.4. Determination MG and MB in real samples

In order to study the efficacy of the UAMSPE method in the analysis of real samples, different samples (fish, fish farming water, tap water and wastewater) were used. Since the samples examined in this research were taken from natural and environmental water samples, only a preliminary preparation was done on the samples, which included filtering the samples and passing them through a 0.45 μm cellulose filter to separate the suspended solid particles that cause errors and light scattering in the measurement from the sample. The desired dyes were extracted from water samples without adding dye and by adding dye according to the proposed method.

In order to check the fish sample, some carp fish were prepared from Zabol city (Iran). The amount of 20 g of fish tissue was separated and weighed and mixed in 200 mL of 10% ethanol. Then it was mixed in an ultrasonic bath for 30 min. Then 100 mL of the obtained product was separated and 5 mL of sodium hydroxide (1 M) was added to the solution to precipitate the fatty acids in the fish tissue. After 20 min, the mixture was centrifuged at 3500 rpm for 10 min. Then the supernatant solution was poured into 15 mL test tubes and kept until the next step. After that, the experiments were carried out according to the proposed method. According to the results, the desired dyes were not found in the sample. In order to check the effect of the sample texture, the test was repeated in the presence of the added amount of the desired dyes to the test tubes, and by calculating the amount of dye obtained, the ER% was obtained.

### 2.5. Response surface methodology

As an important topic in the statistical design of experiments, the Response Surface Methodology (RSM) method is a set of useful mathematical and statistical techniques for process modeling and analysis in which the reciprocal response is influenced by several variables that aim to optimize the response. RSM has played an important role in the design, development and analysis of new scientific studies and products. Experimental statistical process design can reduce process changes, test time, and overall cost by improving the process. In general, the process analysis has 4 stages: I) Determining the factors and conditions of the test II) Building experimental methods III) Analyzing, and IV) Validating the experiments. RSM design requires a minimum number of tests to be done. The total number of experiments conducted in this type of design is generally obtained from the equation $2^n + 2n + n_c$. In this equation, $2^n$ is the factorial experiment, 2n is the axial experiment, and $n_c$ is the central experiment. n is the number of independent process variables. Optimization involves evaluating the coefficients in a mathematical model and predicting the response and evaluating the adequacy of the model. The response model may be expressed as (3):

$$Y = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{4} b_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} b_{ij} x_i x_j \quad (3)$$

In this equation, Y is the predicted response, $b_0$ is the constant coefficient, $b$i is the linear coefficient, $b_{ii}$ is the quadratic coefficient, $b_{\mathrm{ij}}$ is the interaction coefficient, $X_i$ and $X_j$ are the encoded values of the process variables (Azari et al., 2022; Oyekanmi et al., 2019). After defining the range of each process variable, they were set to ± 1 for factorial points, 0 for central points, and ± α for axial points. Numerical values of variables are considered valid values as (4);

$$Zi = \frac{\mathrm{Xi} - \mathrm{X0}}{\Delta \mathrm{Xi}} \; i = 1, 2, 3, \cdots, \mathrm{k} \quad (4)$$

The design matrix consists of four variables at five levels (-α, −1, 0, +1, α + ). The experimental amplitude and levels of the variables studied in this study are presented in Table 1. The coded variables are obtained according to the following equation (5):

$$\mathrm{X} = \frac{x - [xmax + xmin]/2}{[xmax - xmin]/2} \quad (5)$$

Where × is the variable under consideration, X is the coded variable, and $x_{max}$ and $x_{min}$ are the maximum and minimum values (Manousi et al., 2020).

Different parameters of UAMSPE such as adsorbent amount, pH, eluent volume and ultrasonication time potentially affect the extraction. Each factor was coded at five levels according to Equation (3), the values of which are shown in Table 1.

## 3. Results and discussion

### 3.1. Characterization of sorbents

Phase analysis of $CoFe_2O_4$ nanoparticles was done by XRD in the room using Cu K radiation. XRD of the calcined $CoFe_2O_4$ powder (Fig. 1a), shows all the $CoFe_2O_4$ peaks identified by their indices with standard JCPDS card no. 0426–077 (Wu and Ishihara 2019). No other peaks or impurities were detected. This observation and broadening of the diffraction peaks showed that $CoFe_2O_4$ nanoparticles were formed in the size of nanoparticles. Therefore, XRD investigated the formation of pure phase $CoFe_2O_4$. The morphology and particle size of the adsorbents were examined by SEM and shown in Fig. 1b. The normal surface morphology and topography of the nanostructured powders showed a cluster of small particles and the least amount of clumping and agglomeration was observed. Porosity in these nanomaterials can be the cause of gas products such as water vapor, carbon dioxide and nitrogen. The things that can be seen are that the prepared nanoparticles have a high surface area and a high capacity for the fast analyte.

### 3.2. Desorption conditions

A suitable solvent should remove the analyte from the adsorbent in small volumes. The leaching rate of the adsorbed analytes using a suitable solvent can be effectively measured on the rate at which the analytes leave the adsorbent and enter the solution. Therefore, the effects of different eluents such as methanol, ethanol, acetone and acetonitrile in extraction recovery from MG and MB was examined (Fig. 2). The results showed that methanol is the most suitable solvent for this purpose due to better reproduction and highest determinant yield.

Sample volume is one of the important parameters affecting the pre-absorption factor and the amount of extraction in the analysis of real samples. Extraction was evaluated by adding a certain volume of 5 to 20 mL dyes solutions to $CoFe_2O_4$, while the total amount of adsorbent was kept constant during the experiments. The extraction efficiency reduction in volumes higher than 15 mL can be due to the dilution of the solution and the reduction of the contact area of the adsorbent particles with the analyte species. Therefore, the volume of 15 mL was selected for the following experiments so that the experiment could be performed easily and quickly.

### 3.3. Analysis of CCD

CCD was carried out to investigate the main and reciprocal role of variables in recovery from MG and MB. The effect of four independent variables (adsorbent amount, pH of solution, Eluent volume and ultrasonication time) was investigated. Table S1 and S2 shows the recovery rate for the studied dyes. The adequacy of the developed models and the statistical significance of regression coefficients were tested using analysis of variance (ANOVA) and the results related to ANOVA were shown in Tables S3 and S4. The results showed that these models were very significant for the extraction of MG and MB on $CoFe_2O_4$. The fit between the experimental model and the experimental data was analyzed through coefficient of determination, F-value and p-value. The quality of the selected model is expressed by a coefficient of determination ($R^2$) of 0.95, which is confirmed by a high and reasonable value of the coefficient of determination ($R^2_{\mathrm{adj}} > 0.99$ for both

**Table 1** Design matrix for the central composite designs.

| Variables | Unit | Levels | | | | |
|---|---|---|---|---|---|---|
| | | Low (-1) | Central (0) | High (+1) | α- | +α |
| Adsorbent amount | g | 0.02 | 0.03 | 0.04 | 0.01 | 0.05 |
| pH of the solution | — | 6 | 7 | 8 | 5 | 9 |
| Eluent volume | µL | 150 | 200 | 250 | 100 | 300 |
| Ultrasonication time | min | 4 | 6 | 8 | 2 | 10 |

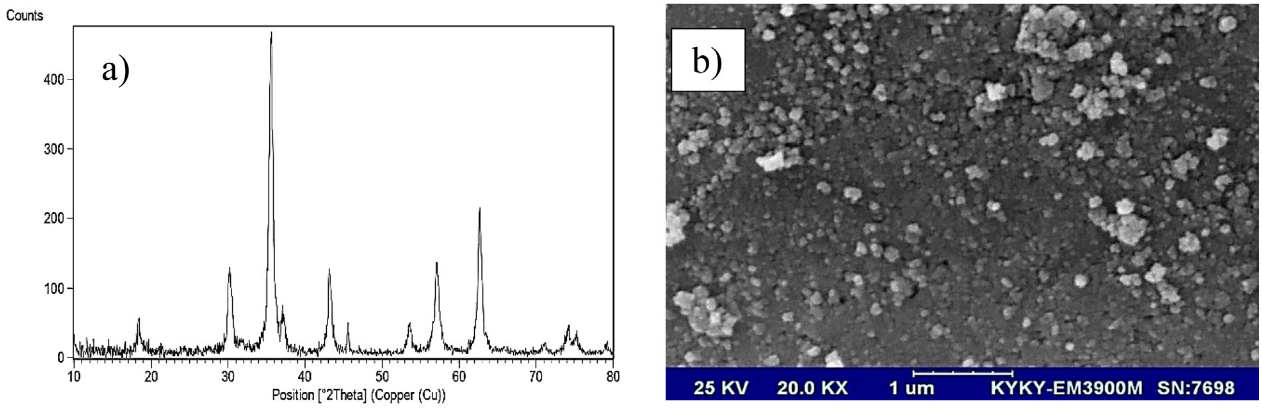

**Fig. 1** (a) XRD pattern and (b) SEM image of $CoFe_2O_4$ nanoparticles.

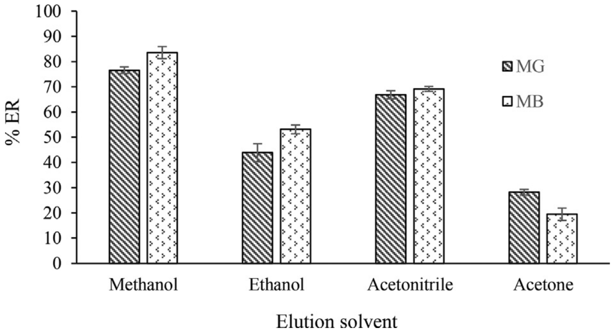

**Fig. 2** The effect of type of eluent on the recovery of dyes.

dyes). In fact, it shows that the results are not random and the terms in the models have a significant effect on the reaction. F-value less than 0.5 for non-compliance indicates that a pure trial error is acceptable and confirms the validity of the model. Using the experimental data, the final model for the extraction of MG and MB on $CoFe_2O_4$ was described using Equations (6) and (7), respectively.

$$
\begin{aligned}
ER\%_{MG} = {} & -225.2209 + 3982.1458 * \textit{Adsorbent amount} \\
& + 17.1617 * \textit{pH of solution} + 0.9259 \\
& * \textit{Eluent volume} + 13.0813 \\
& * \ \textit{Ultrasonication time} - 9.2187 \\
& * \textit{Adsorbent amount} * \textit{pH of solution} + 0.6762 \\
& * \textit{Adsorbent amount} * \textit{Eluent volume} \\
& - -32.3437 * \textit{Adsorbent amount} \\
& * \textit{Ultrasonication time} + 9.2187E - 003 \\
& * \textit{pH of solution} * \textit{Eluent volume} + 0.0410 \\
& * \textit{pH of solution} * \textit{Ultrasonication time} \\
& + 5.7437E - 003 * \textit{Eluent volume} \\
& * \textit{Ultrasonication time} - 47526.0416 \\
& * \textit{Adsorbent amount}^2 - 1.1625 \\
& * \textit{pH of solution}^2 - 2.0340E - 003 \\
& * \textit{Eluent volume}^2 - 0.8950 \\
& * \textit{Ultrasonication time}^2 \qquad (6)
\end{aligned}
$$

$$
\begin{aligned}
ER\%_{MB} = {} & -257.5980 + 4365.5208 * \textit{Adsorbent amount} \\
& + 1.34857 * \textit{Eluent volume} + 17.8557 \\
& * \textit{pH of solution} + 17.6759 \\
& * \textit{Ultrasonication time} + 1.9037 \\
& * \textit{Adsorbent amount} * \textit{Eluent volume} \\
& + 40.9687 * \textit{Adsorbent amount} \\
& * \textit{pH of solution} - 62.7187 \\
& * \textit{Adsorbent amount} * \textit{Ultrasonication time} \\
& + 0.0106 * \textit{Eluent volume} * \textit{pH of solution} \\
& + 8.3187E - 003 * \textit{Eluent volume} \\
& * \textit{Ultrasonication time} + 0.2673 \\
& * \textit{pH of solution} * \textit{Ultrasonication time} \\
& - 65163.5416 * \textit{Adsorbent amount}^2 - 3.3795E \\
& - 003 * \textit{Eluent volume}^2 - 1.6122 \\
& * \textit{pH of solution}^2 - 1.3694 \\
& * \textit{Ultrasonication time}^2 \qquad (7)
\end{aligned}
$$

A reasonable agreement and high coefficient of determination of the graph of experimental values of recovery to the predicted value indicate the high efficiency of the equation mentioned for evaluating and explaining the experimental data (Fig. 3). Actual values, response data are based on measurements performed and predicted values are obtained from the model. According to Fig. 3a and 3b, the correlation between experimental data and predicted values shows the appropriateness of the model. Data were analyzed to check for normal residues (Fig. 3c and 3d). Residual analysis is the main diagnostic tool to check the adequacy of the proposed model so that for normal distribution of errors, the residues are either in a straight line or very close to the line. From Fig. 3c and 3d, it is obvious that the points are close to the straight line, indicating that the errors are normally and independently distributed and that the assumptions are not violated. Fig. 3e and 3f shows the run scheme to the residuals. According to the figure, the remaining stochastic pattern shows the adequacy of the model, and for integrated analysis, experimental data are required, assuming that the data have a normal distribution.

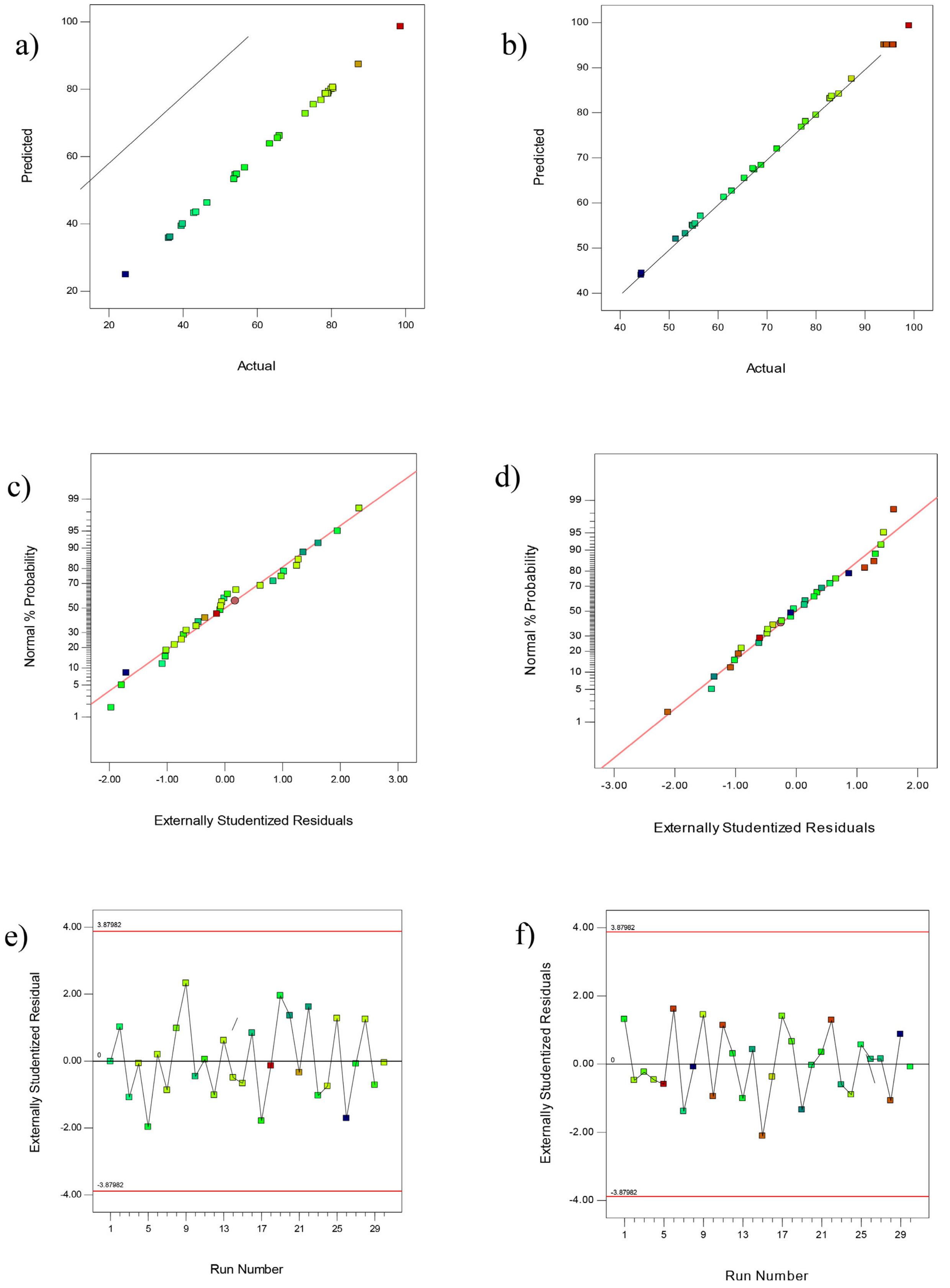

**Fig. 3** Experimental versus predicted values for the %ER (a) MG (b) MB onto $CoFe_2O_4$; normal probability plots of residuals for the % ER (c) MG (d) MB by $CoFe_2O_4$; Plot of residuals versus run number (e) MG and (f) MB obtained using CCD.

### 3.4. Effects of process variables

The interaction between different variables and their corresponding effect on the response was investigated by scattering analysis by three-dimensional (3D) plots. It is useful to visualize the relationship between response and experimental levels of each factor. For graphical interpretation of interactions, the use of 3D model functions is highly recommended. In these functions, the response is placed against two experimental factors, while other factors remain constant at the central level. Fig. 4a and 4c show the effect of $CoFe_2O_4$ adsorbent amount on MG and MB extraction. As it is clear from the figures, the amount of adsorbent has affected the extraction and increasing the amount of adsorbent has been beneficial for the extraction of MG and MB. As can be seen, for both dyes, recoveries have increased with the increasing amount of absorbent. Because by increasing the amount of adsorbent, the number of places available for the interaction of adsorbent and dye molecules increases, hence the amount of dye extraction from the solution increases (Liu et al., 2022; Aigbe et al., 2021).

Also, Fig. 4a and 4c graphically show the effect of pH on the amount of MG and MB extraction. The pH of the solution is very effective on the speed of the process as well as the amount of extraction. For each system, the best conditions in terms of pH must be determined by conducting experiments. At low pH values, due to the presence of electrostatic repulsions between the positive charge of the adsorbent and the analyte, the opportunity and conditions for dye extraction are not provided. But in the alkaline pH range, the electrostatic interactions between the adsorbent with a negative charge and the dye with a positive charge are increased for optimal extraction and recovery (Samadi et al., 2021; Asfaram et al., 2016).

Fig. 4b and 4d show the effect of solvent volume on the extraction rate of MG and MB. Experiments were performed using different volumes of methanol in the range of 100–300 μL. The results showed that with the increase in the volume of the solvent, the amount of recovery of MG and MB from the surfaces of nanoparticles increased, which could be due to the greater interaction of the solvent with the dye

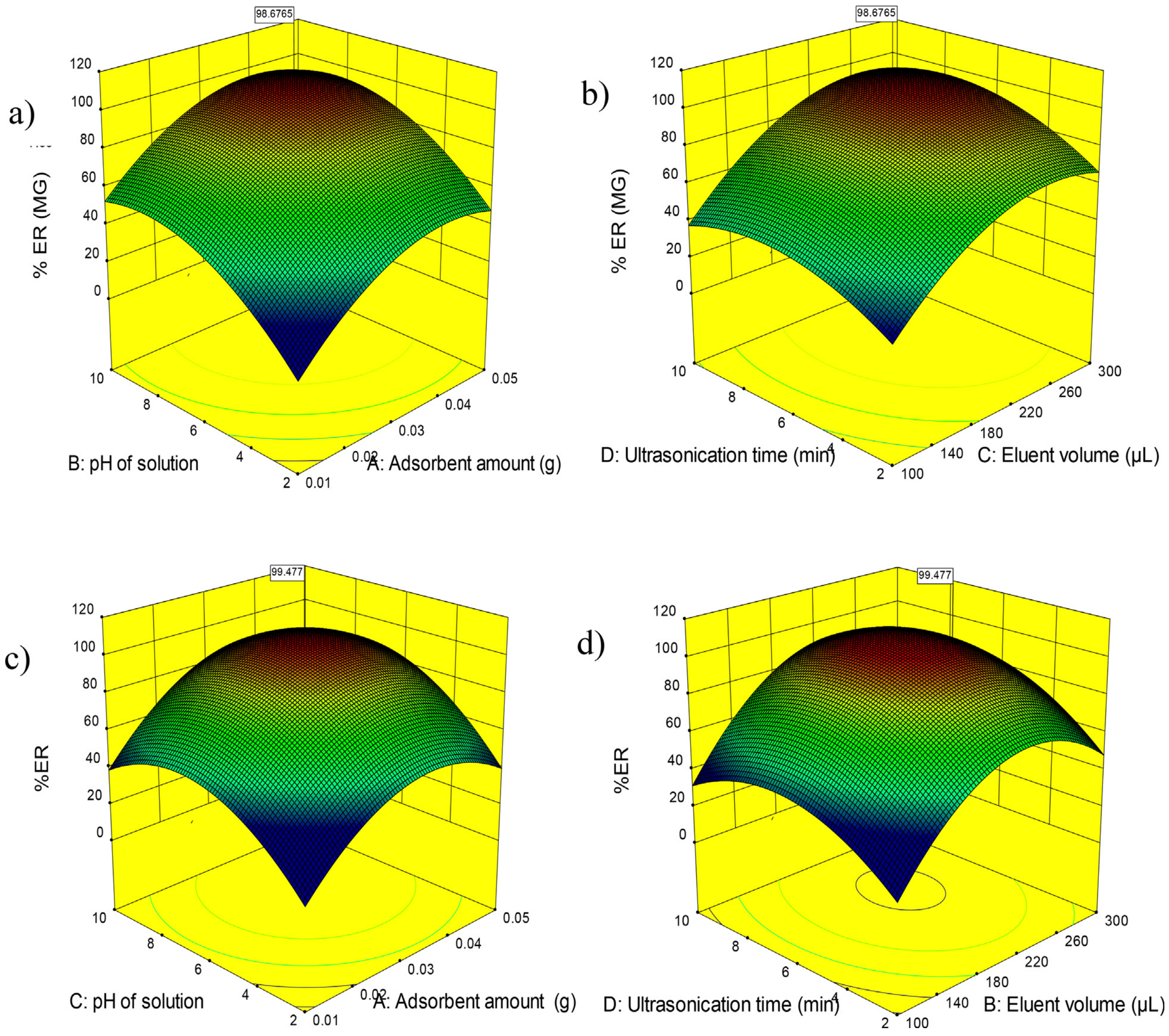

**Fig. 4** 3D surface plots indicating interaction effects of independent variables on variation of ER% a), b) MG and c), d) MB using $CoFe_2O_4$.

molecules Aramesh et al., 2021). As can be seen, the value of 251 μL for MG and 248 μL for MB was chosen as the optimal volume.

The effect of ultrasonication time on MG and MB extraction are shown in Fig. 4b and 4d. Ultrasonication time, compared to other selection indicators, plays a minor role in the extraction value and indicates that the performance can be obtained in a short time. According to the studies, the absorption operation is carried out in two stages. The first stage is the fast absorption stage of the absorbent surface and the second stage is the slow stage of internal mass transfer. In the first case, it causes that the absorbent sites are empty, absorption is carried out on the absorbent, and with the passage of time and the speed of the sites becoming faster, the penetration of dye molecules into the empty absorbent sites causes the transformation of the absorption process (Sharifpour et al., 2022; Sheibani et al., 2022).

### 3.5. *Optimization of variables on the extraction of MG and MB dyes*

In order to increase the extraction efficiency of MG and MB dyes by $CoFe_2O_4$, it is necessary to optimize the variables affecting the process. Effective factors included amount of adsorbent, ultrasonication time, pH, and eluent volume. For this purpose, the possibility of predicting the response level method was used and experiments were conducted under optimal conditions. The results showed recovery in the range of 96.94–99.79% for MG and MB dyes (Table 2).

### 3.6. *Analytical figures of merit*

Considering the importance of analyte determination in low concentration in samples, preconcentration and separation before analysis are of great importance. The calibration curve was obtained from the analysis of MG and MB using a UV/Vis spectrophotometer by plotting the signal intensity against the dye concentration. Absorption increased linearly with the concentration of MG and MB, and linear calibration equations were obtained in the range of 70–550 ng $mL^{-1}$ and 40–450 ng $mL^{-1}$ for MG and MB, respectively. A major challenge in mining exploitation is choosing test conditions that provide reliable response and an acceptable limit of detection. Experiments were performed under optimal extraction conditions to check the coefficient of determination ($R^2$) and limit of detection (LOD of the proposed method for $CoFe_2O_4$ adsorbent, and the results are given in Table 3. Also, in order to show the reusability of $CoFe_2O_4$ for the extraction of MG and MB, the adsorption-washing cycle was repeated 10 times. According to Fig. 5, no noticeable change was observed in the extraction rate of MG and MB up to five times, and then a further decrease in the extraction percentage of dyes was observed. Therefore, $CoFe_2O_4$ sorbent can be used five times to extract MG and MB.

### 3.7. *Analysis of real samples*

In order to check the feasibility and reliability of the developed and optimized method, fish, tap water, wastewater, and fish farming water samples containing MG and MB were used for testing (Table 4). The samples were examined by UAMSPE-UV/Vis method under optimal conditions. The validity of the model was checked by predicting the concentration of MG and MB in real samples to obtain extraction with recovery and RSD. The results showed that the proposed method has excellent values and its efficiency does not change with the presence of the matrix, and there is also a good agreement between the determined and specified. The recovery showed that the UAMSPE-UV/Vis method is an efficient method for the detection of complex samples containing MG and MB.

**Table 2** Optimum conditions derived by RSM for extraction of dyes.

| Optimal conditions | | | | | Recovery (%) | |
|---|---|---|---|---|---|---|
| Dyes | Adsorbent amount (g) | pH of the solution | Eluent volume (μL) | Ultrasonication time (min) | Experimental | Predicted |
| MG | 0.038 | 8 | 251 | 7.8 | 99.67 | 98.68 |
| | 0.038 | 8 | 251 | 7.8 | 96.94 | 98.68 |
| | 0.038 | 8 | 251 | 7.8 | 98.05 | 98.68 |
| MB | 0.034 | 7 | 248 | 5.7 | 98.12 | 99.47 |
| | 0.034 | 7 | 248 | 5.7 | 99.79 | 99.47 |
| | 0.034 | 7 | 248 | 5.7 | 97.84 | 99.47 |

**Table 3** Analytical performances of the proposed method for CoFe2O4 adsorbent for extraction of dyes.

| Analytes | MG | MB |
|---|---|---|
| Regression equation | A = 0.0027C−0.0124 | A = 0.0032C + 0.0388 |
| Coefficient of determination | 0.9977 | 0.9983 |
| Linear range (ng $mL^{-1}$) | 70−550 | 40−450 |
| LOD (ng $mL^{-1}$) | 16.5 | 11 |
| RSD (%) (n = 5) | 2.9 | 2.3 |
| Recovery (%) | 98.69 | 99.24 |
| Enrichment factor | 30 | 40 |

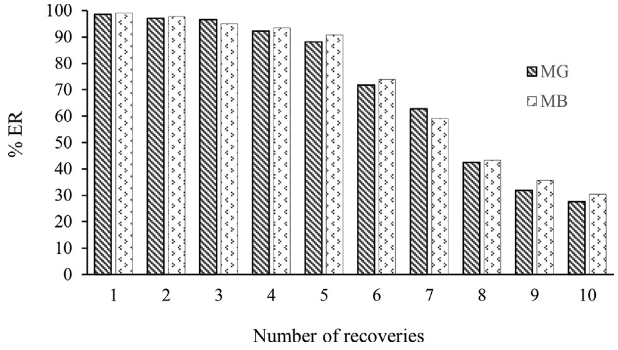

**Fig. 5** Effect of number of recoveries on $CoFe_2O_4$.

### 3.8. Comparison of the proposed UAMSPE-UV/Vis with other methods

Table 5 shows a comparison between the results obtained by some measurement methods to determine MG and MB with the present method. As it is clear from Table 5, the proposed method is comparable to or has superior behavior compared to the mentioned methods. Because no cleaning step was necessary for biological matrices. Also, in the present research, the amount of organic solvent used was very low. It should be noted that the most important advantage of UAMSPE-UV/Vis is the easy separation and reversibility of the process. Because the adsorbent can be easily separated from the liquid environment by a magnet and can be used again for the next tests. High sensitivity and selective analysis devices such as HPLC or MS have been used in most aforementioned methods. It is costly to use these devices, and their widespread use for dyes determining is not possible in developing countries. Therefore, the present method combined with spectrophotometry, which has high sensitivity, simplicity, speed, and reproducibility, is suitable for pre-concentrating and extracting small amounts of dyes from aqueous samples.

## 4. Conclusion

In this study, CoFe2O4 nanoparticles were synthesized and used as absorbers in UAMSPE-UV/Vis method to extract MG and MB. RSM was used to optimize the extraction parameters. This model achieved higher accuracy through the analysis of fewer samples and focused more on the ability to predict capacity and mining conditions, and was an excellent complement to real samples. Under optimal conditions, the ER percentage of MG and MB was obtained in the range of 96.94–99.79%. According to the results, the proposed method is

**Table 4** Extraction of MG and MB in real samples.

| Sample | Spiked concentration (ng $mL^{-1}$) | | Found (ng $mL^{-1}$) | | Recovery (%) | | RSD (%) (n = 5) | |
|---|---|---|---|---|---|---|---|---|
| | MG | MB | MG | MB | MG | MB | MG | MB |
| Tap water | 200 | 150 | 197.6 | 147.9 | 98.80 | 98.60 | 3.8 | 2.2 |
| | 400 | 300 | 395.9 | 298.1 | 98.97 | 99.36 | 3.0 | 3.2 |
| Wastewater | 200 | 150 | 195.9 | 148.7 | 97.95 | 99.13 | 2.7 | 3.9 |
| | 400 | 300 | 399.3 | 291.5 | 99.82 | 97.16 | 3.1 | 3.5 |
| Fish | 200 | 150 | 190.6 | 147.3 | 95.30 | 98.20 | 3.3 | 4.2 |
| | 400 | 300 | 388.8 | 289.4 | 97.20 | 96.46 | 5.3 | 3.6 |
| Fish farming water | 200 | 150 | 199.4 | 148.4 | 99.70 | 98.93 | 3.7 | 3.3 |
| | 400 | 300 | 396.4 | 297.3 | 99.00 | 99.10 | 4.2 | 4.1 |

**Table 5** Comparison of the proposed method with other reported methods for MG and MB determination.

| Analyte | Extraction method | Detection method | Linear range (ng $mL^{-1}$) | LOD (ng $mL^{-1}$) | Enrichment factor | References |
|---|---|---|---|---|---|---|
| MG | CPE | Spectrophotometry | 9.9–800 | 2.9 | 20 | An et al., 2010 |
| | MIP- SPE | HPLC | 10–600 | 1.23 | * | Hu et al., 2015 |
| | RDSE | Spectrophotometry | 10–1000 | 1.4 | * | Richter et al., 2011 |
| | SPE | Spectrophotometry | 320–5000 | 67 | 90 | Al-Degs & Sweileh 2012 |
| | SPE | UPLC/EITMS | 2.5–100 | 1 | * | Xu et al., 2012 |
| | UAMSPE | Spectrophotometry | 70–550 | 16.5 | 30 | This work |
| MB | SPE | LC-MS/MS | 10–5000 | 0.1 | * | Khan et al., 2014 |
| | SPE | Liquid chromatography | 1000–5000 | 300 | * | Memon et al., 2014 |
| | SPE | Spectrophotometry | 8–2212 | 2.5 | 135 | Ramandi & Shemirani 2015 |
| | SALLME-BE | Spectrophotometry | 2–170 | 0.5 | 173 | Ahmadi et al., 2019 |
| | UAMSPE | Spectrophotometry | 40–450 | 11 | 40 | This work |

Abbreviations: CPE: Cloud point extraction, MIP-SPE: Molecularly imprinted polymer- solid phase extraction, RDSE: Rotating disk sorbent extraction, SPE: Solid phase extraction, UPLC/EITMS: Ultra-Performance Liquid Chromatography with Electrospray Ionization Tandem Mass Spectrometry, UAMSPE: Ultrasonic-assisted magnetic solid phase extraction, LC-MS/MS: Liquid chromatography-tandem mass spectrometry, SALLME-BE: Shaker-assisted liquid–liquid microextraction combined with back-extraction, *Not report.

applicable for determining MG in the concentration range of 70–550 ng mL$^{-1}$ and for MB in the range of 40–450 ng mL$^{-1}$. The LOD for MG was 16.5 ng mL$^{-1}$ and for MB was 11 ng mL$^{-1}$. Also, the RSD value for the measurement of MG and MB was less than 4%. Also, methanol was considered an optimal eluent solvent. In the end, successful experiments were conducted to extract MG and MB from fish, tap water, wastewater, and fish farming water samples, which showed the effectiveness of the proposed method in extracting MG and MB from real complex samples with a very small amount in a short period of time. The real samples analysis results showed that the recovery efficiency of MG and MB dyes were in the range of 95.30–99.82%. The results of investigating the reusability of $CoFe_2O_4$ in MG and MB measurements showed that the $CoFe_2O_4$ adsorbent can be used for up to 5 absorption and desorption cycles, and no significant decrease in the extraction speed of MG and MB dyes was observed. One of the most important advantages of this method is its simplicity, low cost, and high preconcentration factor. On the other hand, its low LOD is a significant advantage compared to the low cost of the measurement equipment. All these results prove the suitability of the developed method in terms of simplicity, sensitivity and easy efficiency for the determination of MG and MB in real samples.

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## Author contributions

M.R. conceived and planned the experiments. S.Sh., and A. A. carried out the experiments, experimental design, and contributed to the interpretation of the results. S.Sh., and M.Kh. had a significant contribution for technical checking, validation and programming language checking of the manuscript in terms of grammar checking and writing. All authors discussed the results and contributed to the final manuscript.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.104868.

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