

## A New Spectrophotometric Method for Determination of Tartrazine in Saffron Samples Based on Modified Magnetic Graphene Oxide Nanocomposite

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### Abstract

Quality control in agricultural products has always been noticed. In the present study, a new pre-concentration technique for the determination of Tartrazine (TZ) in saffron samples by employing Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide-COOH as an adsorbent is presented. Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide-COOH was prepared and characterized by scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FT-IR). After extraction, the TZ concentration was measured by the UV-Vis spectrophotometer. The important factors for pre-concentration such as sample pH, amount of adsorbent, contact time and eluent volume were examined and optimum conditions were obtained. The new proposed spectrophotometric method shows good dynamic range of 0.02 to 10 mg/L ( $R^2 > 0.996$ ) for TZ with a limit of detection (LOD) of 0.01 mg/L after pre-concentration. This method was applied to the analysis of TZ in saffron samples and recovery values and enrichment factor were found as 94% and 5, respectively. Finally, 5 saffron samples were spiked with TZ and analyzed with new spectrophotometric methods, and results compared by HPLC as a standard method. The results of the t-test showed that there is no significant difference between the two methods.

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### Keywords

Fe<sub>3</sub>O<sub>4</sub>

Food adulteration

Graphene Oxide-COOH

Pre-concentration

### Introduction

Saffron is one of the most expensive medicinal herbs used in the pharmaceutical and food industries. Saffron quality control is of paramount importance for consumers and producers (Karimi, Feizy, Mehrjo, & Farrokhnia, 2016). Inadvertent and intentional pollution could significantly

affect the quality of saffron. Moreover, the high cost of saffron is responsible for the great attention paid to its quality.

Azo dyes are important synthetic colorants widely utilized to improve food color which are compounds with the azo functional group and the aromatic ring.

These dyes could cause allergies and

jeopardize the health of consumers if used excessively (Ahlström, Sparr Eskilsson, & Björklund, 2005). Therefore, determining the level of azo dyes in food products of great importance for quality assurance purposes and protect consumers' health. Tartrazine (TZ) is one of the highly used azo dye in many food products. It should be emphasized that the Iranian national standards have banned TZ in foods and especially in saffron products.

Currently, the most common techniques for the determination of TZ are photometry (Al-Degs, El-Sheikh, Al-Ghouti, Hemmateenejad, & Walker, 2008; Kucharska & Grabka, 2010; Sorouraddin, Rostami, & Saadati, 2011), chromatographic methods, spectrophotometry (Hashim Al Sultani, Mohammed Al-Rashidy, & Al-Samrai, 2019; Pourreza & Ghomi, 2011), capillary electrophoresis (Del Giovine & Piccioli Bocca, 2003) and voltametric methods (Ghoreishi, Behpour, & Golestaneh, 2012; Karim-Nezhad, Khorablou, Zamani, Seyed Dorraji, & Alamgholiloo, 2017), which have been frequently applied for the individual or simultaneous measurement of the TZ. Many of the reported methods require skilled operators and expensive equipment, so they are not available in many common laboratories. The TZ has an efficient absorbing group in the visible region; therefore, spectrophotometry is a common method for quantitative analysis. Although spectrophotometric techniques are simple, the detection of colorants by using these techniques often interferes with the complex food matrix.

At first, TZ should be extracted from foodstuffs and then determined. There have been numerous methods for the extraction and pre-concentration of TZ like liquid-liquid extraction (Ma, Li, Wang, & Zhao, 2015; Tang *et al.*, 2015), membrane filtration (Soylak & Cihan, 2013), cloud point extraction (Aydiner, Kaya, Beril Gönder, & Vergili, 2010; Ostovan, Asadollahzadeh, & Ghaedi, 2018) and solid phase extraction (SPE) (El-Shahawi, Hamza, Al-Sibaai, Bashammakh, & Al-

Saidi, 2013; Tatara, Materna, Schaadt, Bart, & Szymanowski, 2005).

Magnetic solid phase extraction (MSPE) is one of the attractive techniques used for the extraction of residue of contaminants in food samples. In this method, the adsorbed analyte on the magnetic substrate is completely eluted using one or more suitable solvents.

MSPE extremely simplifies the SPE technique and has some advantages such as enhancing the extraction efficiency, high selectivity and low cost (Aguilar-Arteaga, Rodriguez, & Barrado, 2010). Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPS) are one of the important magnetic nanoparticles owing to their low cost and being eco-friendly. Modification of the surface of Fe<sub>3</sub>O<sub>4</sub> NPS nanoparticles can prevent their accumulation and oxidation and increase their selectivity for interaction with specific analytes. According to the application, different coatings such as conductive polymers, biopolymers, carbon nanoparticles, and metal nanoparticles are used for modifying the surface of magnetic nanoparticles. Recently, Fe<sub>3</sub>O<sub>4</sub>/Graphene Oxide (GO) nanocomposites have attracted the attention of researchers due to their excellent performance and wide applications (Wierucka & Biziuk, 2014).

In addition,  $\pi$ -Stacking of aromatic rings in GO can cause the adsorption of aromatic dyes through the  $\pi$ - $\pi$  interactions of aromatic rings (Jafarian Asl, Niazmand, & Jahani, 2020; Tang *et al.*, 2015). Furthermore, improving the azo dye adsorption is very important in separation applications. The modification of Fe<sub>3</sub>O<sub>4</sub>/GO with the carboxyl groups increases its selectivity for the separation of azo dyes. Also, the sorption of the carboxyl group on the Fe<sub>3</sub>O<sub>4</sub>/GO nanocomposite enhances the sorption of the TZ because the negative charge of the carboxyl group improves adsorbing the TZ with a positive charge.

Therefore, the aim of this study is to propose a new, rapid and sensitive pre-concentration method for the determination of TZ in saffron samples. Fe<sub>3</sub>O<sub>4</sub>/GO-COOH nanocomposite adsorbent was used for the

extraction and pre-concentration of TZ, with advantages of a rapid and highly efficient separation using an external magnetic field. In addition, the saffron sample matrix has no effect on the recovery percentage.

## Materials and methods

### Reagents and materials

Tartrazine (E 102) (99% purity), Graphite powder, Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), potassium permanganate ( $\text{KMnO}_4$ ), hydrochloric acid (37%), and  $\text{H}_2\text{SO}_4$  (98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Methanol and ammonia solution (25%) were purchased from Merck (Darmstadt, Germany).

### Apparatus

Fourier transform infrared (FTIR) spectra of nanocomposite were recorded by an AVATAR 370 FT-IR spectrometer (USA). The surface morphology and microstructure of the nanocomposite were studied by a field emission scanning electron microscope (FESEM) model S-4160 (Hitachi, Japan). A Cintra 101 UV-Vis spectrophotometer (GBC, USA) used to record ultraviolet and visible spectra (200-800 nm).

## Experimental

### $\text{Fe}_3\text{O}_4/\text{GO}-\text{COOH}$ synthesis

GO was synthesised from pure graphite powder by using Hummers method with slight modification (Hummers Jr & Offeman, 1958). Briefly, 2 g graphite powder was added to a beaker containing  $\text{H}_2\text{SO}_4$  (46 mL) and stirred in the ice bath (5 °C) for several min. Then, 6.0 g of potassium permanganate ( $\text{KMnO}_4$ ) was gradually added to the mixture under ice cooling and stirring until the solution becomes dark green. Then, 360 mL of deionized water (DW) was added to the mixture and it was kept at 35 °C for 120 min and then refluxed for 15 min at 95 °C. After that, the reaction was stopped by adding 6 mL  $\text{H}_2\text{O}_2$  (30%) and 280 mL DW yielding a color change to bright yellow and the yellow mixture was centrifuged. Then,

the reaction was stopped by adding 6 mL of  $\text{H}_2\text{O}_2$  (30%) and 280 mL of DW by changing the color to light yellow. The yellow mixture was centrifuged. To remove sulfate ions ( $\text{SO}_4^{2-}$ ) and neutralize the precipitate, it was washed several times with HCl (5%) and DW. Finally, the product was sonicated for 60 min for the preparation of GO and subsequently used for the preparation of the  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposites (Aboobakri & Jahani, 2020; Chandra *et al.*, 2010).

Magnetic  $\text{Fe}_3\text{O}_4/\text{GO}$  nanoadsorbent were achieved by means of chemical co-precipitation reaction.  $\text{FeCl}_2$  (0.032 g), and  $\text{FeCl}_3$  (0.082 g) were dissolved in 25 mL of DW and GO ( $1.0 \text{ gL}^{-1}$ ) was dispersed in this solution by sonication (60 min). Ammonia solution was added slowly to the solution at 80 °C under vigorous stirring to precipitate iron oxides on the surface of the GO. After regulation of pH (10-11), the solution was heated at 80 °C for 1 h (Fooladi, Razavizadeh, Noori, & Kakooei, 2020).

Upon the completion of reaction, the  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposite was separated from the mixture using permanent magnet and washed with DW. Then, prepared material was dried in a vacuum at 60 °C, and finally  $\text{Fe}_3\text{O}_4/\text{GO}$  was obtained (Sadeghi, Fooladi, & Malekaneh, 2014).

For  $\text{Fe}_3\text{O}_4/\text{GO}-\text{COOH}$  preparation, 100 mg  $\text{Fe}_3\text{O}_4/\text{GO}$  was dispersed in 100 mL DW and sonicated for 60 min. Then 25 mL of NaOH (3 mol/L) was added to the mixture and sonicated for 180 min. Finally, chloroacetic acid (2.5 gr) was gradually added to the suspension to transform hydroxyl groups to carboxylic acid at the surface of  $\text{Fe}_3\text{O}_4/\text{GO}$  nanocomposite. The  $\text{Fe}_3\text{O}_4/\text{GO}-\text{COOH}$  was gained and washed with DW and then dried in an oven at 60 °C (Park & Jung, 2012).

### Magnetic solid-phase extraction procedure

The MSPE procedure was carried out as follows. Initially, 6 mg of  $\text{Fe}_3\text{O}_4/\text{GO}-\text{COOH}$  nanocomposite was added to a 50 mL container. It was then sonicated (30 min). Then, 10 mL of standard solution or saffron sample was added and shaking for

10 min. The nanocomposite was then separated from the liquid phase with a strong magnet at the bottom of the container. The collected nanocomposites containing the TZ were stirred with 2 mL of methanol: ammonia (5:95) for 5 min. Finally, the elution solution containing TZ was measured at 430 nm.

### Sample preparation

5 samples of saffron were used from 5 various local markets during the same year of their harvest. Saffron powder (1 g), was weighed and mixed with 20 mL water. The solution was vortexed for 10 min, and kept away from light for 24 h. Consequently, the precipitate was getting rid of the supernatant liquid. Then, the solvent was evaporated at room temperature under vacuum condition. In the following, the residue was redissolved in 2 mL water; the aqueous was vortexed for 2 min and stored in a stoppered glass bottle for further analysis (Moradi-Khatoonabadi, Amirpour, & AkbariAzam, 2015).

## Results and discussion

### Nanocomposite characterization

To ascertain the successful synthesis and carboxylation,  $\text{Fe}_3\text{O}_4/\text{GO}$  and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  were compared through FT-IR and FE-SEM characterization. FT-IR was used to identify different oxygen-containing functional groups in  $\text{Fe}_3\text{O}_4/\text{GO}$  and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$ . The strength vibrations of O-H at  $3425\text{ cm}^{-1}$ , the carbonyl group vibrations (C=O) at  $1730\text{ cm}^{-1}$  and the aromatic carbon-carbon double bond (C=C) at  $1627\text{ cm}^{-1}$  are the main groups for detecting graphene-to-GO conversion. Fig. (1) displays the FT-IR spectra of the  $\text{Fe}_3\text{O}_4/\text{GO}$  (a) and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  (b).

An absorption band at  $580\text{ cm}^{-1}$  is dedicated to stretching vibration of Fe-O-Fe. Spectral changes related to  $\text{Fe}_3\text{O}_4/\text{GO}$  carboxylation, and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  formation were observed as follows: dual bond vibration shift from  $1627$  to  $1600$  and one peak of COH groups at  $1249\text{ cm}^{-1}$ .

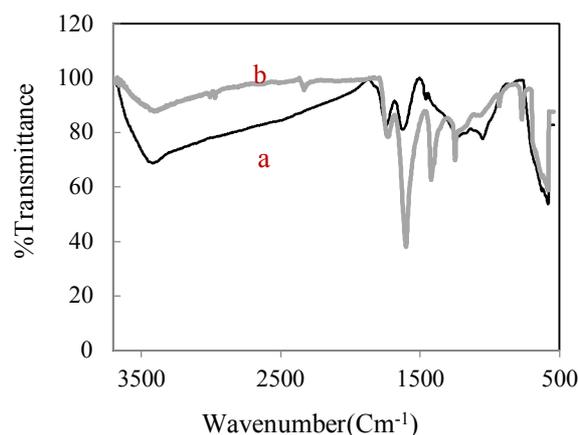


Fig. 1 FT-IR spectra  $\text{Fe}_3\text{O}_4/\text{GO}$  (a) and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  (b)

The morphology of  $\text{Fe}_3\text{O}_4/\text{GO}$  and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  was characterized via by SEM images. It is obvious from Fig. (2), when the nanocomposite is functionalized with the carboxyl group, the aggregation of nanoparticles is observed.

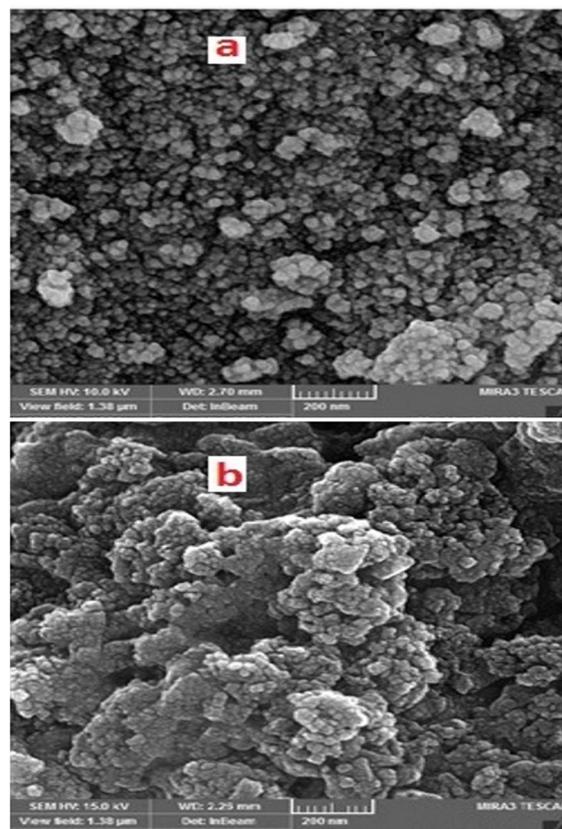


Fig. 2. FESEM images of  $\text{Fe}_3\text{O}_4/\text{GO}$  (a) and  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  (b)

### Optimization of the MSPE procedure

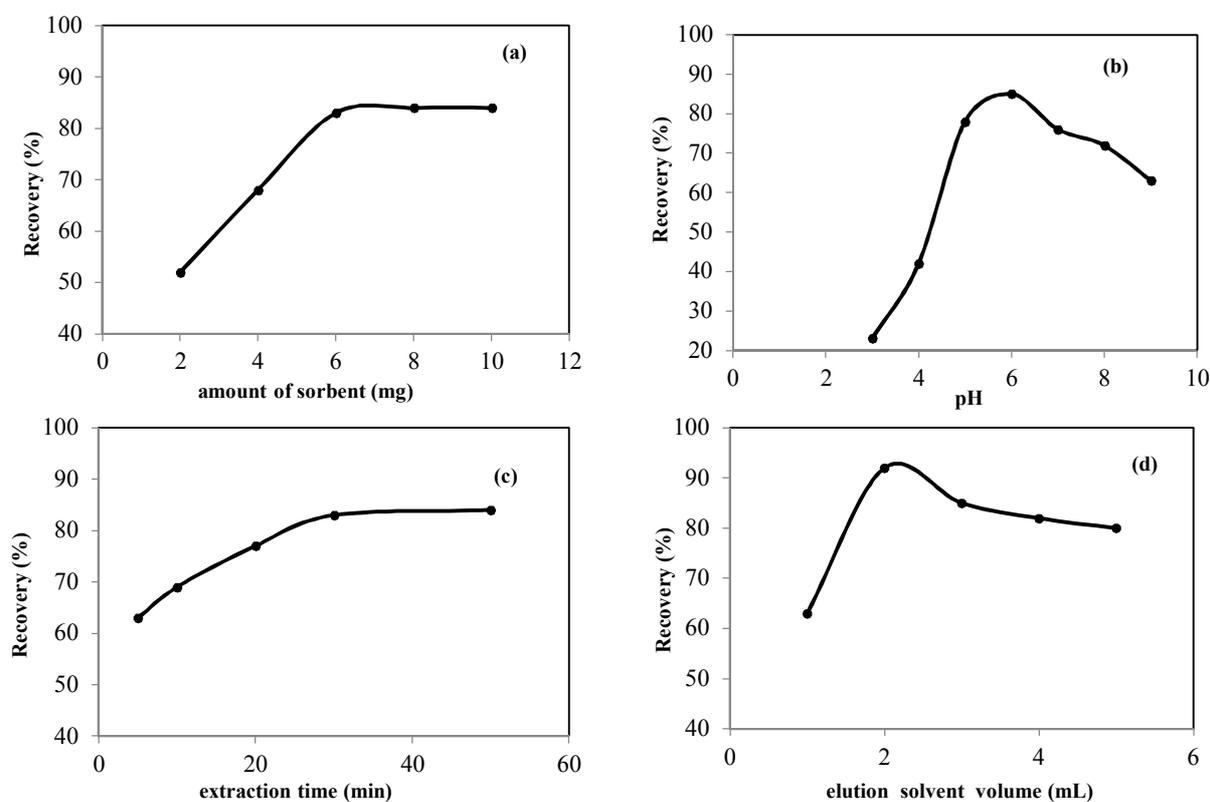
For the SPE procedure, the adsorbent amount presents a significant feature in the enrichment of analytes. Fig. (3a) shows the

effect of the adsorbent amount on the extraction efficiency. The influence of this parameter was calculated in the range of 2-10 mg of the adsorbent. The results illustrated that the recovery percent enriched with increasing the amount of  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  from 2 to 6 mg and after that, the recoveries percentage are remained constant due to saturation of the  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  surface with TZ (Iranmanesh, Jahani, Nezhadali, & Mojarrab, 2020). Eventually, 6 mg of the sorbent was selected as the optimum volume for our work. The pH effect of the aqueous solution on the adsorption capacity of  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  for TZ was studied in different pH ranging from 3 to 9. Fig. (3b) demonstrates that the amount of adsorbed TZ increased when the pH reached 6 from 3 but reduced at higher pH values (Zhang *et al.*, 2018).

To determine the appropriate contact time of the  $\text{Fe}_3\text{O}_4/\text{GO-COOH}$  with TZ, the percentage of TZ recovery at different extraction times was investigated. It was established that 20 min was enough to obtain higher recoveries of TZ (Fig. 3c). This observation can be explained when the

extraction process started, there were many adsorption sites on the surface of composites and the target could be easily extracted. Through the passage of time, more adsorption sites were employed (Taghizade, Ebrahimi, Fooladi, & Yoosefian, 2021). Extraction equilibrium was achieved when all the adsorption sites were occupied. Accordingly, 20 min were selected as the optimal extraction time.

In the SPE method, elution solvent selection is one of the main factors. It is reliant on sorbent and target interaction. Here, 4 types of solutions of ammonia-water (5:95, v/v), ammonia-methanol (5:95, v/v), acetic acid-methanol (5:95, v/v) and acetic acid-water (5:95, v/v) were compared as eluent. Under the same extraction and elution conditions, the ammonia-methanol (5:95, v/v) desorption power was better than other candidates. Besides, the influence of the volume of eluent (from 1 to 5 mL) on the desorption efficiency of the TZ was optimized. The results indicated that desorption equilibrium was attainable after about 2 mL (Fig. 3d).



**Fig. 3.** Effect on enrichment efficiency of MSPE: (a) amount of sorbent, (b) pH, (c) extraction time, (d) elution solvent volume

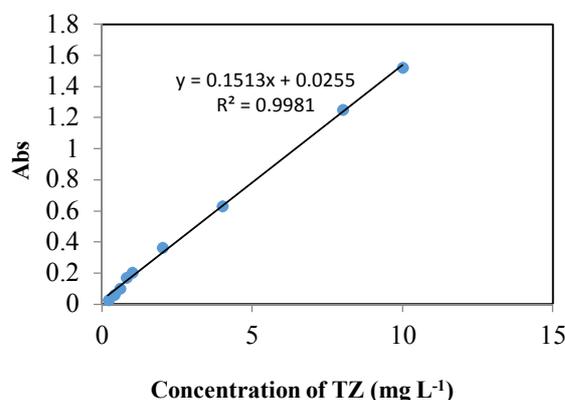
**Table 1.** Detection of TZ in spiked saffron samples

Sample	Spiked concentration of TZ (mg L <sup>-1</sup> )	proposed method TZ (mg L <sup>-1</sup> )	HPLC method (mg L <sup>-1</sup> )	t <sub>exp</sub>
1	1.00	0.95±0.05 <sup>a</sup>	0.98±0.01 <sup>a</sup>	0.96
2	1.00	0.94±0.06 <sup>a</sup>	0.96±0.02 <sup>a</sup>	0.55
3	1.00	0.95±0.05 <sup>a</sup>	0.97±0.02 <sup>a</sup>	0.64
4	1.00	0.95±0.08 <sup>a</sup>	0.93±0.04 <sup>a</sup>	0.39
5	1.00	0.98±0.02 <sup>a</sup>	0.95±0.01 <sup>a</sup>	2.32

<sup>a</sup> Mean value ± standard deviation, n=3; t<sub>critical</sub>=3.18, P≤0.05.

### Method validation

The quantitative results including, linearity, the limit of detection (LOD), precision, and recovery of the developed method was verified under the optimum experimental conditions. The results showed responses were linear in the range of 0.02 to 10 mg L<sup>-1</sup> (Fig. 4). For the newly developed method, the LOD was 0.01 mg L<sup>-1</sup> based on 5 repetitive blank determinations. Based on repeatability study, extractions of an aqueous solution of 0.2 mg L<sup>-1</sup> of TZ with Fe<sub>3</sub>O<sub>4</sub>/GO-COOH were developed, resulting in a RSD of 4.3% for the intra-day repeatability and 6.4% for the inter-day repeatability. Under optimized conditions, the recoveries for the TZ at the 3 concentrations of 0.05, 1.00 and 5.00 mg L<sup>-1</sup> were 93.5, 98.6 and 96.4%, respectively.



**Fig. 4.** Calibration curve of TZ concentration obtained in optimized condition

### Analysis of the saffron samples

To figure out the suitability of the developed method to real samples, representative saffron samples were used from 5 different local markets and then analyzed.

Firstly, analysis of the samples provided the absence of the TZ and then the accuracy of the mentioned method was evaluated by analyzing the samples spiked with the known amount of the TZ. Satisfactory spiked recovery results illustrated that the matrix effects were unimportant for determining the TZ in the studied saffron samples (Table 1). By comparing the results of TZ measurements with the proposed method and HPLC and evaluating them with T-test, it was found that there is no significant difference. These results characterized that the new pre-concentration method for TZ is appropriate for the quality control and determination of TZ in saffron samples.

### Conclusions

In this work, Fe<sub>3</sub>O<sub>4</sub>/GO-COOH as a magnetic adsorbent was synthesized. The magnetic properties of the substrate allow for rapid separation with an external magnetic field. The optimized conditions for the pre-concentration and spectrophotometric determination of TZ were 6 mg nanoadsorbent, 10 mL initial sample volume, at pH 6, and eluted with 2 mL methanol: ammonia (95:5, v/v) solvent for 5 min. The results show that the proposed new method can be used for the determination of TZ in saffron sample

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## یک روش اسپکتروفتومتری جدید برای تعیین تارترازین در نمونه‌های زعفران بر اساس نانوکامپوزیت گرافن اکساید مغناطیسی اصلاح شده

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### چکیده

کنترل کیفیت در محصولات کشاورزی همیشه مورد توجه بوده است. در مطالعه حاضر، یک روش پیش‌غلظت جدید برای تعیین رنگ تارترازین از نمونه‌های زعفران با استفاده از نانوکامپوزیت گرافن اکسایدی کربوکسیل‌دار مغناطیسی به‌عنوان جاذب ارائه شده است. در ابتدا نانوکامپوزیت گرافن اکسایدی کربوکسیل‌دار مغناطیسی تهیه و با میکروسکوپ الکترونی روبشی (SEM) و طیف‌سنجی مادون‌قرمز تبدیل فوری (FT-IR) شناسایی شد. پس از استخراج، غلظت تارترازین در زعفران توسط اسپکتروفتومتر UV-Vis اندازه‌گیری شد. فاکتورهای مهم برای پیش‌غلظت از قبیل pH، مقدار جاذب، زمان تماس و حجم حلال شست‌وشو مورد بررسی قرار گرفت و شرایط بهینه به‌دست آمد. روش اسپکتروفتومتری جدید پیشنهاد شده یک پاسخ خطی به غلظت تارترازین در محدوده ۰/۰۲-۱۰ میلی‌گرم بر میلی‌لیتر با حد تشخیص ۰/۰۱ میلی‌گرم بر میلی‌لیتر را نشان می‌دهد. این تکنیک برای اندازه‌گیری کمی و کیفی تارترازین در نمونه‌های زعفران مورد استفاده قرار گرفت و مقادیر بازیابی و فاکتور تغلیظ آن به ترتیب ۹۴ درصد و ۵ به‌دست آمد. در پایان ۵ نمونه مختلف زعفران با تارترازین آلوده و با روش پیشنهادی اندازه‌گیری شد و نتایج آن با روش استاندارد کروماتوگرافی مایع با کارایی بالا (HPLC) مقایسه شد. نتایج آزمون T-test نشان می‌دهد که هیچ‌گونه اختلاف معنی‌داری بین دو روش وجود ندارد.

**واژه‌های کلیدی:** اکسید آهن، پیش‌غلظت، تقلب در زعفران، گرافن اکساید کربوکسیل‌دار