Applied Chemistry Today **18(69)** (2023) 69-84

Semnan University

Applied Chemistry Today

Journal homepage: https://chemistry.semnan.ac.ir/

ISSN: 2981-2437

Research Article

Preconcentration and Measurement of Sudan IV Utilizing the UA-d-µ-SPE Method with a Smartphone as a Simple Measurement Tool in Food and Water Samples

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PAPER INFO

Article history:
Received: 11/Jul/2023
Revised: 27/Aug/2023
Accepted: 30/ Aug /2023

Keywords:
Smartphone, Bi_2O_3/ZnO/Pd adsorbent, Sudan IV color, Food and water sample, Ultrasonic-assisted dispersive micro solid phase extraction (UA-d-µ-SPE).

ABSTRACT

In analytical chemistry, the use of the simplest tool that provides the possibility of on-site measurement, low cost, and simple equipment has always been an area of interest for researchers. In recent years, the use of smartphones as an available tool can have these features. In this study, Bi_2O_3/ZnO/Pd adsorbent was used for preconcentration and measurement of Sudan IV color as one of the azo family colors in food and water samples, exploiting ultrasonic-assisted dispersive micro solid phase extraction (UA-d-µ-SPE) method along with a smartphone. The structure of this adsorbent was examined by XRD, SEM, and EDS analyses. Factors such as the amount of adsorbent (5.1 mg), sample solution pH (7.1), washing solvent volume (430.0 µL), and adsorption time (65 seconds) were optimized, utilizing central composite design (CCD) method. The type of washing solvent (methanol) and desorption time (45 seconds) were also optimized using the one-parameter-at-a-time method. In the best conditions, the limit of detection (LOD) was 5.58 ng mL^{-1}, and the linear detection range (LDR) for this color was 20-1100 ng mL^{-1}. The enrichment factor (EF) was also computed as 22.87. In addition, the relative standard deviation (RSD%) was acquired as 3.91 with n=5.

DOI: https://doi.org/10.22075/CHEM.2023.31190.2190

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How to cite this article: Haghgoo Qezelje, H., Rajabi, M., Asghari, A., & Bazregar, M. (2023). Preconcentration and Measurement of Sudan IV Utilizing the UA-d-µ-SPE Method with a Smartphone as a Simple Measurement Tool in Food and Water Samples. *Applied Chemistry Today*, 18(69), 69-84. (in Persian)

1. Introduction

Azobenzene dyes are a well-known class of artificial organic dyes containing the (-N=N) group, which are hydrophobic and used in various industrial applications, including textiles, plastics, pharmaceuticals, cosmetics, food products, biomedicine, and polymers. Despite their versatile applications, these dyes are known as environmental pollutants that may pose harmful risks to the health of living organisms. Sudan compounds, a type of azo dye, can cause cancer and genetic mutations that can accumulate in fatty liver tissues and lead to lipodystrophy. The International Agency for Research on Cancer (IARC) has categorized these dyes as unauthorized additives and class 3 carcinogens. However, due to their low cost, they are still used as color fixatives in some food products such as pepper, curry powder, etc. [1-3].

Sudan family colors have a wide variety of structures, and one of the most commonly used is Sudan IV. The toxic limit of Sudan IV depends on various factors such as the exposure time and dosage. Empirical studies have shown that this color has toxic effects, and the European Union (EU) has set a maximum limit of 0.5-1 mg per kg in food and cosmetic products to ensure consumer safety [4].

Despite significant advancements in analytical equipment, direct measurement of real samples is often not feasible, due to problems including the low concentration of analytes, the presence of interferents in complex matrices, and the incompatibility of some samples with analyzer devices and equipment [5, 6]. Thus, it is necessary to have a step called sample preparation. Classical procedures encompass solid phase extraction (SPE) and liquid-liquid extraction (LLE), with the former offering advantages such as high enrichment and selectivity factor, reduced organic solvent consumption, and shorter extraction time compared to the latter [7-11]. In recent years, the d-µ-SPE method has been introduced to address the limitations of SPE, including high sample volume and organic solvent requirements, high cost, and environmental incompatibility. Additionally, the d-µ-SPE method has gained widespread use owing to its capability to reduce extraction time by increasing the contact surface through the spread of the extractant phase in the sample solution [8].

The d-µ-SPE method requires the use of sorbents with high purity, lifetime, selectivity, and chemical or physical stability to ensure its efficiency. Three groups of sorbents have been utilized in this method: classical sorbents exploited for SPE, composites, and nanostructured sorbents like nanoparticles (NPs) [12]. In recent years, the use of nanostructured sorbents has gained attention, due to their high area-to-volume ratio which is very beneficial in the d-µ-SPE technique. However, the application of nanoparticles such as TiO_2, SiO_2, ZnO, Au, SnO_2, etc. in the d-µ-SPE method is challenging due to their high dispersion and instability in bulk sample solutions. To address this issue, recent literature has explored combining micromaterials with nanostructures to improve extraction capability and overcome the limitations of nanostructured sorbents [13]. Composites, which have high surface area ratio and porosity, have also been investigated as hybrid materials that bear both the advantages of the initial materials the collective advantages [14]. Among the various sorbents, zinc oxide nanoparticles have been widely employed due to their cost-effectiveness, nontoxicity, high surface area, abundance, and excellent chemical and thermal stability in various applications, including thin film transistors, food packaging, gas sensors, oil and gas sector, extraction metals, and solar cells [15]. To improve the performance of ZnO, various engineering strategies have been employed, such as synthesizing nanocomposites, developing heterostructures, and doping with suitable dopants [16]. Some recent studies have also focused on modifying the properties of ZnO coupled with Bi_2O_3, which may result in new materials with improved physicochemical properties [17, 18].

In analytical chemistry, the goal is to use simple equipment with appropriate accuracy and precision to measure various analytes in different samples. To achieve this goal, one method is to use smartphones which have gained a lot of attention due to their high-resolution and sensitive cameras, extensive storage space, powerful processors, portability, availability, low cost, and ability to install various applications and perform digital function analysis. Smartphones can be used to measure compounds that are inherently colored or can become colored under certain conditions [19]. Various color systems, including RGB (red, green, blue), CMYK (cyan, magenta, yellow, key), and LAB, can be used to measure color combinations. Among these, the LAB color system is commonly used due to its closer proximity to the human eye's color perception mechanism. By taking pictures of colored compounds and using image processing software, the amount of each constituent color can be determined using different color systems. The concentration of each colored analyte can then be determined by drawing the calibration curve of standard analyte solutions [20].

In this study, the efficiency, ease, and cost-effectiveness of the smartphone and LAB color system in Color Grab version 3.9.2 software were evaluated for measuring Sudan IV color in food and water samples. The Bi_2O_3/ZnO/Pd absorbent was used for preconcentration of the mentioned colors, and a designed camera chamber was used to take pictures of the samples. The results confirmed the effectiveness of this method for measuring colored analytes in food samples.

2. Experimental

2.1. Chemicals

A standard solution of Sudan IV color (Sigma Aldrich, Germany) with a concentration of 1.0 mg mL^{-1} was built by dissolving an appropriate amount of the color in methanol. To protect the color from heat and light-induced degradation, the solution was stored in a refrigerator at 4 °C. Working standard solutions were built by diluting the stock solution with deionized water. Acetonitrile, ethanol, acetone, chloroform, and methanol (Merck, Germany) with high-performance liquid chromatography (HPLC) grade purity were used as desorption agents from the adsorbent surface. HCl and NaOH with a concentration of 0.1 mol L^{-1} were used to adjust the pH of the sample solutions. For the synthesis of the nanocomposite, palladium chloride, hexahydrate zinc nitrate, bismuth nitrate pentahydrate, and sodium dodecyl sulfate (Merck, Germany) were used.

2.2. Apparatus

In order to capture images of the sample solutions, a newly designed imaging chamber was used. The chamber was made of wood and had dimensions of 85 × 97 millimeters, with a distance of 85 millimeters between the camera lens and the sample location, and its interior surface was covered with white paint. Four 10 × 40-millimeter LED lights were embedded inside the chamber, facing the sample location, to provide the necessary light source for photography. The measurement device utilized in this method was an iPhone 8 smartphone (Apple, USA) equipped with Color Grab version 3.9.2 software. The AEU-210 balance (Shimadzu, Japan) was used to measure the weight of the materials. The pH of the solutions was adjusted utilizing a Hanna HI 2211 pH meter (Woonsocket, RI, USA). The Hettich EBA 20 centrifuge (Tuttlingen, Germany) was used to separate the phases. The SW3-type ultrasonic bath with a power of 80 W and a frequency of 50/60 kHz at room temperature was used to synthesize the absorbent and disperse the absorbent particles in the solution (SONO SWISS, Switzerland). The Bruker D8 Advance XRD (Billerica, MA, United States) and Mira3 Detector SAMx EDS (Kohoutovice, Czech Republic) were used to confirm the synthesis of the nanocomposite. The TESCAN BRNO-Mira3 LMU FESEM microscope (Kohoutovice, Czech Republic) was used to determine the structure and morphology of the synthesized absorbent. The AFE1200L furnace (Qazvin, Iran) was used for calcination of the nanocomposite.

2.3. Synthesis of the adsorbent

The Bi_2O_3/ZnO/Pd nanocomposite was synthesized using a one-pot one-step ultrasound-assisted method. The synthesis process involved dissolving 7.27 grams of bismuth nitrate pentahydrate in 25 milliliters of deionized water and transferring it to an Erlinmeyer flask. Separately, 2.84 grams of zinc nitrate hexahydrate and 426 milligrams of sodium dodecyl sulfate were dissolved in 25 milliliters of deionized water and poured into the reaction vessel. In addition, 4.0 milligrams of palladium chloride were added and the mixture was subjected to sonication for one hour. The pH of the solution was then adjusted to 9 utilizing a 0.1 mol L^{-1} solution of sodium hydroxide and the nanocomposite synthesis was continued for another two hours in an ultrasonic water bath. The resulting precipitate was filtered using Whatman No. 40 filter paper and washed with deionized water until the pH reached a neutral state. It was then dried in an oven at 120 degrees Celsius for one hour. Finally, the precipitate was calcined in a furnace at 400 degrees Celsius for three hours to complete the synthesis process [21,22].

2.4. Preparation of real samples

Samples of hot chili sauce, turmeric, and saffron were purchased from a local store (Semnan, Iran). These samples were dried in an oven at 75 degrees Celsius. To extract the compounds present in the samples, 0.25 grams of each of them were weighed and placed in 2.5 milliliters of methanol solvent in an ultrasonic water bath for 20 minutes. The samples were filtered utilizing Whatman No. 40 filter paper and 1 milliliter of each of them was diluted to a volume of 10 milliliters with water, using fourfold distilled water [23].

A water sample from the tap water (Semnan, Iran) was also examined. This sample was filtered utilizing Whatman No. 40 filter paper and then stored in a matte glass at 4 degrees Celsius in the refrigerator [6].

Finally, the pH of all samples was adjusted to 7.1.

2.5. Extraction process

In this work, 10 milliliters of a solution containing a concentration of 100 ng mL-1 of Sudan IV dye, with a pH of 7.1, was introduced into a conical tube. For the extraction process, 5.1 milligrams of Bi_2O_3/ZnO/Pd absorbent were added to the solution as the extraction phase and subjected to an ultrasonic water bath for 65 seconds. Separation of the sample solution from the extraction phase was performed by centrifugation at 3500 rpm for 7 minutes. The absorption process was carried out by adding 430 microliters of methanol as a desorption solvent to the solid extraction phase and subjecting it to an ultrasonic water bath for 45 seconds. Centrifugation at 3500 rpm was used for 5 minutes to separate the desorption solvent from the extraction phase. The extraction phase containing the analyte was poured into a quartz microcell of 300 microliters and placed in the photometric chamber to be measured using a smartphone.

Afterwards, the efficiency of the devised sample preparation method was appraised by calculating the extraction recovery (%ER) and the enrichment factor (EF).

$$EF = \frac{C_{final}}{C_{initial}}$$

$$ER\% = \frac{n_{final}}{n_{initial}} \times 100 = EF \times \frac{V_e}{V_s} \times 100$$

Where C_{final} and $C_{initial}$ are the concentrations present in the desorption solvent (final) and the sample solution (initial), respectively. $n_{initial}$ and n_{final} are the respective moles of sample solution and desorption solvent. V_s is sample solution's volume and V_e is desorption solvent's volume.

The stages of this process are shown in Figure 1.

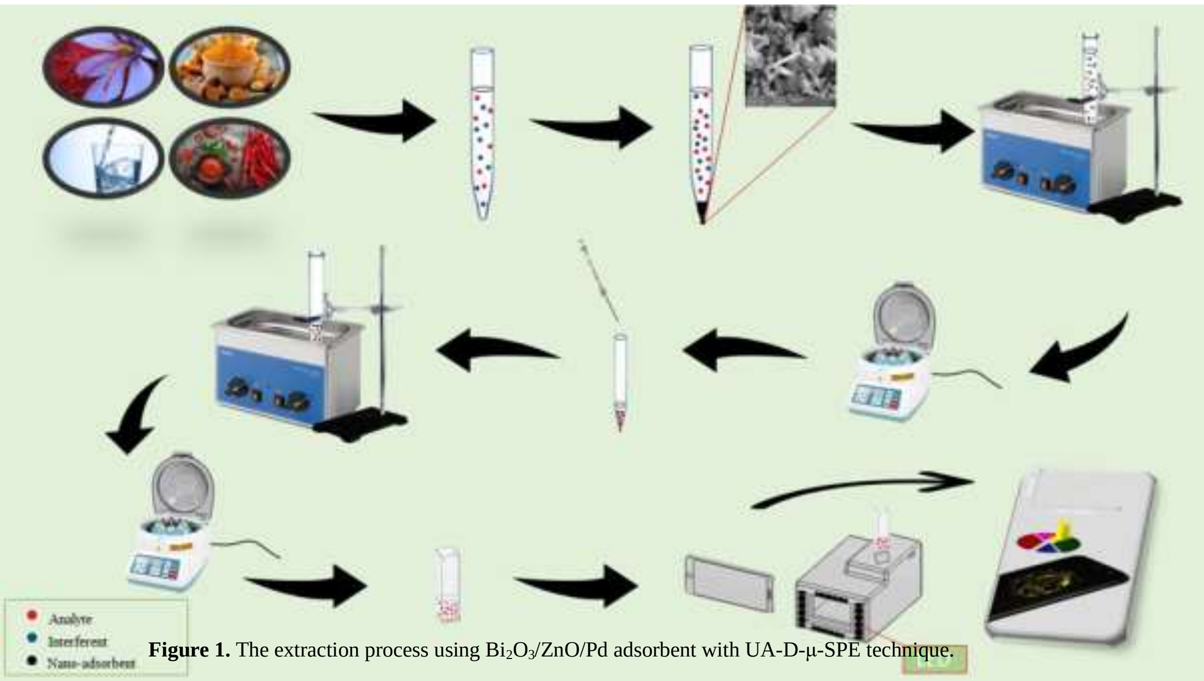

Figure 1. The extraction process using Bi_2O_3/ZnO/Pd adsorbent with UA-D-μ-SPE technique.

2.6. Optimization process

The investigation of effective parameters and their interactions is carried out using the central composite design (CCD) as one of the most commonly used methods in response surface methodology. By using this method, we can obtain empirical polynomial equations that have the ability to predict the extraction efficiency under different conditions. The effective factors and their interactions for the preconcentration of Sudan IV dye in food and water samples using Bi_2O_3/ZnO/Pd absorbent and CCD were investigated. For this purpose, the Design Expert version 13.0.1.0 software was used to design the experiments.

A five-level CCD was used for a one-block experiment with four main effective factors, including the solution pH, adsorbent dose, desorption solvent volume, and absorption time. For this purpose, 30 experiments (16 for factorial points, 8 for axial points, and 6 for central points) were designed. The levels of the main factors of the designed experiments and their responses are shown in Tables 1 and 2, respectively.

3. Discussion and Conclusion

3.1. Investigation of the structure and morphology of Bi_2O_3/ZnO/Pd adsorbent

3.1.1. SEM image of the adsorbent

FESEM was used to investigate the morphology and structure of the synthesized adsorbent. According to the reports on the morphology of each of the constituent parts of the absorbent synthesized by this method, it can be noted that Bi_2O_3 nanoparticles have a rod-like morphology [24], while ZnO/Pd nanoparticles have a spherical morphology [21].

In Figure 2, we can observe the structure of the Bi_2O_3/ZnO/Pd nanocomposite. The results indicate that the synthesized adsorbent has a rod-like morphology with spherical nanoparticles on its surface. It can be noted that the use of sodium dodecyl sulfate as a stabilizer prevents particle aggregation and therefore

Table 1. A one-block five-level CCD with four main effective factors in UA-D-μ-SPE for the absorption of Sudan IV dye.

Independent variables	Ranges and levels				
	-α	-1	0	+1	+α
Initial pH (A)	2	5	8	11	14
Nano adsorbent dosage (mg) (B)	2	4.5	7	9.5	12
Eluting solvent volume (μL) (C)	200	300	400	500	600
Adsorption time (s) (D)	30	60	90	120	150

Table 2. Experimental conditions of the central composite design experiment.

Run	Factors				Extraction Recovery of Sudan IV
	A	B	C	D	ER%
1	8	7	600	90	69
2	8	7	400	90	96
3	8	7	400	90	94
4	5	4.5	500	120	65
5	5	9.5	300	60	67
6	5	9.5	500	60	75
7	8	12	400	90	46
8	2	7	400	90	89
9	8	7	200	90	46
10	11	9.5	500	120	55
11	11	4.5	500	60	78
12	11	4.5	300	120	56
13	8	7	400	90	97
14	5	4.5	300	60	77
15	8	7	400	30	82
16	5	4.5	500	60	87
17	11	4.5	500	120	69
18	11	9.5	500	60	69
19	8	7	400	90	96
20	5	4.5	300	120	64
21	8	7	400	150	59
22	8	7	400	90	95
23	14	7	400	90	72
24	5	9.5	500	120	56
25	11	4.5	300	60	55
26	11	9.5	300	120	45
27	8	7	400	90	94
28	8	2	400	90	68
29	11	9.5	300	60	43
30	5	9.5	300	120	56

increases the contact surface area of the adsorbent [25]. In general, FESEM analysis confirmed the successful synthesis of the Bi_2O_3/ZnO/Pd nanocomposite.

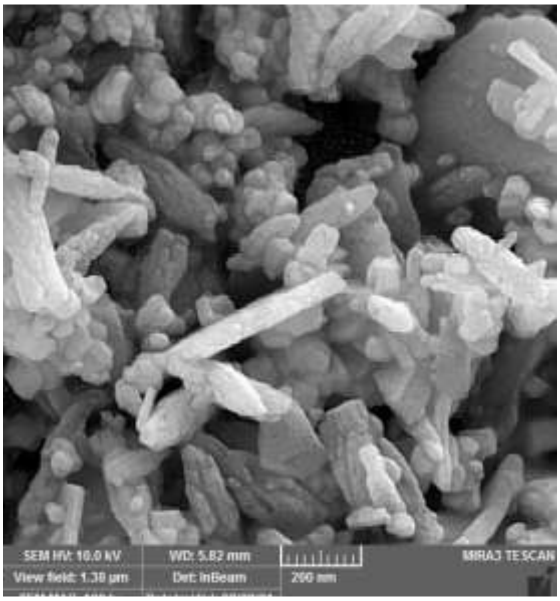

Figure 2. FESEM image of the surface of Bi_2O_3/ZnO/Pd nano adsorbent.

3.1.2. XRD pattern of the adsorbent

According to the XRD pattern obtained, which is visible in Figure 3, the desired crystalline combination of ZnO, Bi_2O_3, and Pd has been formed. The peaks located at 2θ values of 27.61 and 28.00 indicate the presence of Bi_2O_3, the peaks located at 2θ values of 34.54 and 63.08 indicate the existence of ZnO, and the peaks located at 2θ values of 46.34 and 67.75 indicate the presence of palladium in the desired combination.

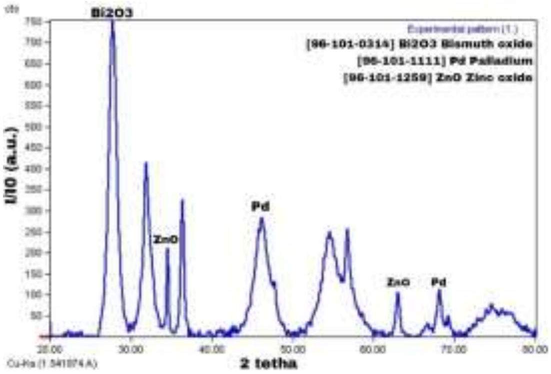

Figure 3. XRD pattern of Bi_2O_3/ZnO/Pd nano adsorbent.

3.1.3. EDS spectrum of the adsorbent

EDS X-ray diffraction spectroscopy was used to analyze the elemental composition of the Bi_2O_3/ZnO/Pd adsorbent. According to the results obtained in Figure 4, the amount of main elements present in this adsorbent is 0.10%, 19.03%, 11.91%, and 68.96% for Pd, Bi, Zn, and O, respectively. The results indicate the success of the synthesis of the adsorbent used.

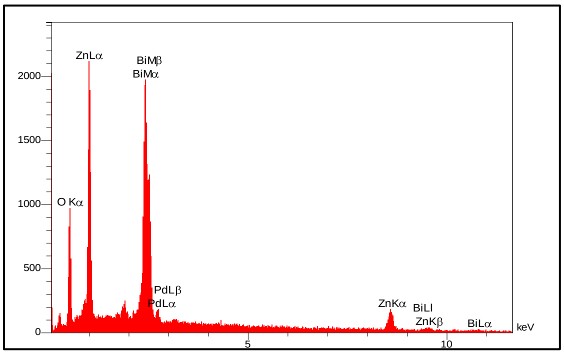

Figure 4. EDS spectrum of Bi_2O_3/ZnO/Pd nano adsorbent.

3.2. Statistical evaluation of the method

The analysis of variance (ANOVA) table was used to investigate the significance of the studied parameters and to achieve a suitable model, based on using criteria such as the F-test and p-value. The results of the analysis of variance are shown in Table 3. Considering that at a 95% confidence level, the p-value for the proposed model is less than 0.05, and the critical F-value is less than the calculated F-value, it can be concluded that the proposed model is significant and acceptable. Additionally, the large p-value for lack-of-fit, which is greater than 0.05, indicates that the error associated with the unmodeled part is not significant, and the remaining errors are due to randomness. The values of R^2, R^2-adj., and R^2-pred., which are close to one and each other, can prove the validity of the model and its high predictive power. The encoded model for Sudan IV dye can be seen in

Table 3. ANOVA summary for CCD method in UA-D-μ-SPE for the adsorption of Sudan IV dye.

Source of variance	Sum of squares	Degree of freedom	Mean squares	F-value	P-value
Sudan IV					
Model	8451.23	11	768.29		<0.0001
Residual	71.44	18	3.97		
Lack-of-fit	64.10	13	4.93		0.0943
Pure error	7.33	5	1.47		
$R^2 = 0.9916$	Adj. $R^2 = 0.9865$	Pred. $R^2 = 0.9675$	Adeq Precision = 40.57		

the following equation, in which Y represents the percentage of yield.

$$Y = 95.33 - 4.62\,A - 5.38\,B + 5.71\,C - 5.46\,D + 3.31\,AC + 2.81\,AD - 2.69\,CD - 4.18\,A^2 - 10.05\,B^2 - 9.93\,C^2$$

Moreover, by examining Figure 5, it can be observed that the data follows a normal distribution in acceptable ranges, there is no systematic error, and there is good agreement between the experimental and predicted data by the model, which confirms the reliability of the proposed model.

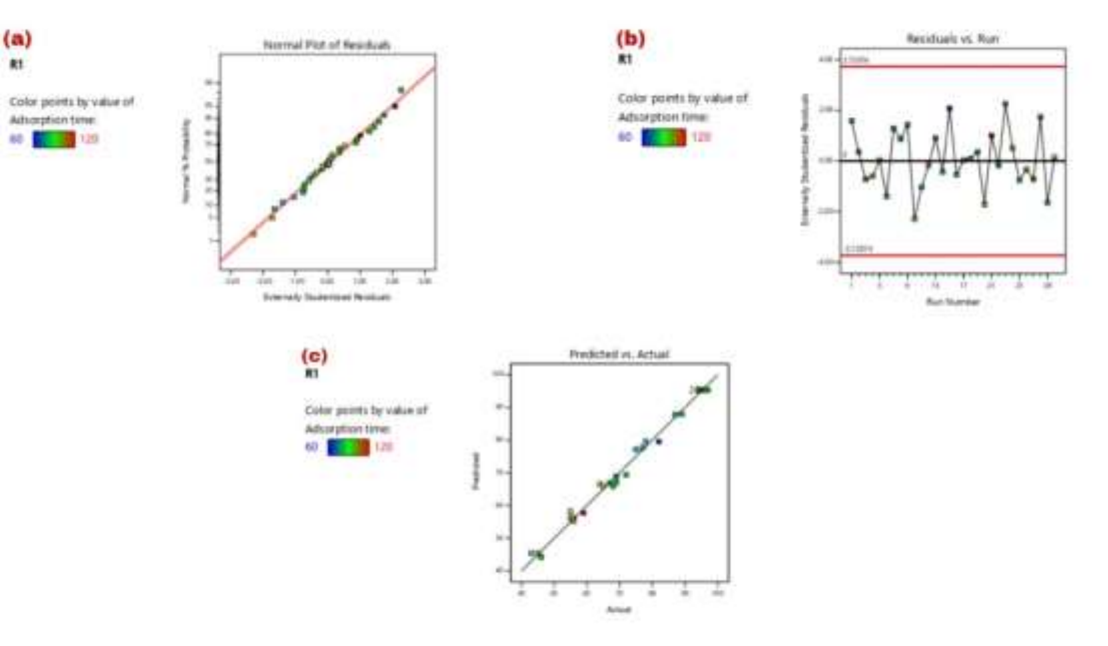

Figure 5. Two-dimensional plot of (a) normal distribution of residuals, (b) random error values for each experiment, and (c) predicted response of the model versus experimental values.

3.3. Parameter optimization

3.3.1. Optimization of the type of eluting solvent using a one-variable method

The type of eluting solvent has an imperative impact on the extraction and adsorption of the analyte by the adsorbent, and it should have the ability to separate and dissolve the analyte from the surface of the adsorbent. To this end, various eluting solvents were studied based on their polarity. These solvents included methanol, ethanol, acetonitrile, chloroform, and acetone. According to the results obtained in Figure 6, it can be concluded that methanol has the highest recovery for Sudan IV dye due to its higher polarity compared to other organic solvents studied.

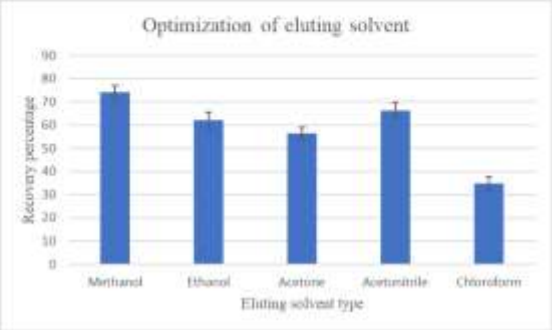

Figure 6. Optimization of the eluting solvent type under the following conditions: 10 mL of a solution containing Sudan IV dye with a concentration of 100 ng mL^{-1}, 9.5 mg of adsorbent, solution pH of 5, adsorption time of 60 s, 500 µL of eluting solvent volume, and 30 s of extraction time (n=3).

3.3.2. Optimization of the extraction time using a one-variable method

Among the effective parameters in preconcentration and measurement of Sudan IV dye in the UA-D-µ-SPE method, the extraction time can be mentioned. The analyte adsorbed on the surface of the adsorbent should have enough time to be separated from the adsorbent surface by the eluting solvent. Therefore, extraction times of 15, 30, 45, 60, 75, and 90 seconds were studied. Based on the results obtained in Figure 7, it can be concluded that the highest amount of extraction occurs at 45 seconds, and after that, the recovery rate becomes constant with increasing time. Therefore, the optimal extraction time was selected as 45 seconds.

3.3.3. Optimization of effective parameters in the adsorption step using the central composite design method

The interaction effect betwixt the amount of adsorbent and the volume of eluting solvent is shown in Figure 8 (a). According to the observations, the extraction efficiency percentage increases with an augmentation in the volume of eluting solvent up to about 430 µL, which can be due to the sufficient volume of eluting solvent to separate the analyte from the adsorbent surface. With an increase in the volume of eluting solvent beyond about 440 µL, we observe a decrease in the extraction efficiency, which can be due to the dilution of the analyte. With an increase in the amount of adsorbent, we observe a decline in the recovery rate, which can be attributed to the aggregation of the adsorbent particles with an increase in their amount, leading to a decline in the effective contact surface area.

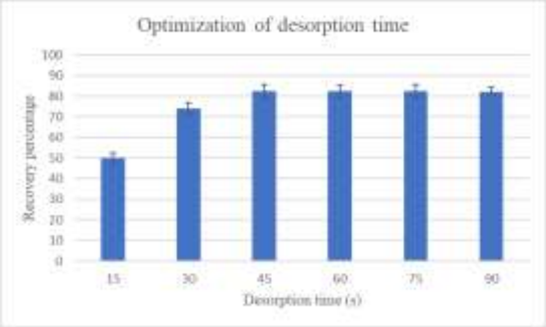

Figure 7. Optimization of the extraction time under the following conditions: 10 mL of a solution containing Sudan IV dye with a concentration of 100 ng mL^{-1}, 9.5 mg of adsorbent, solution pH of 5, 60 s of adsorption time, 500 µL of eluting solvent volume, and methanol as the eluting solvent type (n=3).

The interaction effect between the amount of adsorbent and the extraction time is shown in Figure 8 (b). According to the results obtained, an increase in the extraction time leads to a decrease in the recovery rate, which can be due to the detachment of the adsorbed analytes from the adsorbent surface due to the excessive ultrasonic wave intensity applied to the solution containing the sample and adsorbent. Again, we observe a decrease in the recovery rate under the influence of an increase in the amount of adsorbent.

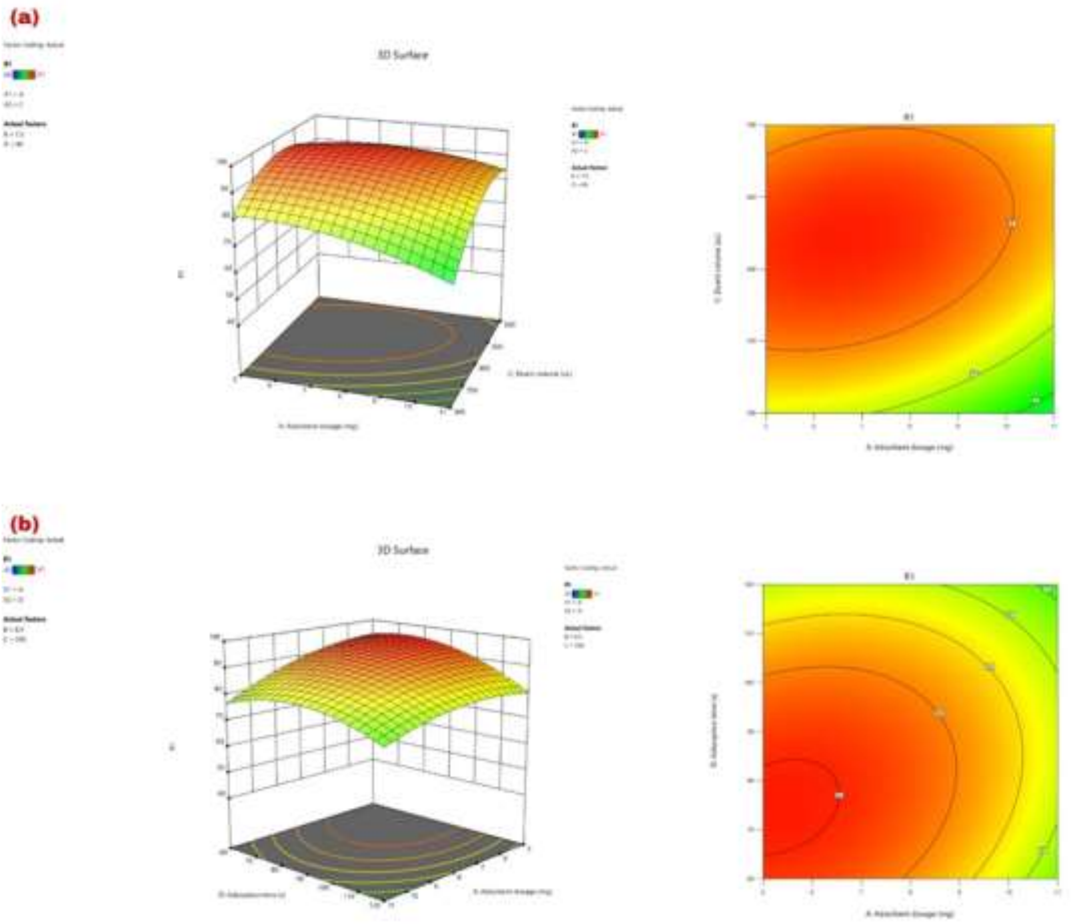

Figure 8. The interaction effect between the amount of adsorbent and the volume of eluting solvent (a), and the interaction effect between the amount of adsorbent and the extraction time (b) on the adsorption of Sudan IV dye.

According to the results of the desirability function, the optimal conditions for the adsorption of Sudan IV dye are an adsorbent amount of 5.1 mg, a sample solution pH of 7.1, an eluting solvent volume of 430.0 µL, and an extraction time of 65 s, which lead to the highest recovery rate. The desirability function value for the optimal conditions was 1.00.

3.4. Figures of Merit

According to the optimal conditions obtained, the analytical characteristics of the method are shown in Table 4. In the best extraction conditions for Sudan IV dye, the extraction recovery rate was 98.37%, the limit of detection (LOD) was 5.58 ng mL^{-1}, the linear dynamic range (LDR) was 20-1100 ng mL^{-1}, the enrichment factor (EF) was 22.87, and the relative standard deviation percentage (RSD%) was 3.91 for n = 5. Additionally, this adsorbent has the ability to extract metals up to 8 times without a significant decrease in the extraction percentage.

Table 4. Figures of merit of the UA-D-µ-SPE method for Sudan IV dye.

Parameter	Sudan IV
EF[a]	22.87
LDR[b]	20-1100
LOD[c]	5.58
ER%[d]	98.37%
Intra-day precision (RSD[e]%)	3.91
Inter-day precision (RSD%)	5.23

[a] Enrichment Factor.
[b] Linear dynamic range.
[c] Limit of detection.
[d] Extraction recovery.
[e] Relative standard deviation.

3.5 Interferences effects

The selectivity of the proposed method for the analyte was investigated against potential interferences with Sudan family dyes that may cause interference in the extraction and determination of analyte. The effect of these dyes is shown in Table 5. The results indicate that no interference is observed in the extraction of analyte in the presence of Sudan family dyes.

Table 5. Impact of interfering species on recoveries of Sudan (IV) in optimal condition.

Dye	Ratio of interfering dyes to analyte[1]	Sudan (IV) recovery (%)
Sudan (I)	30	97.16
Sudan (II)	30	93.97
Sudan (III)	30	94.52
Sudan orange G	30	95.81
Sudan red G	20	93.67

[1]Concentration of Sudan (IV): 50 ng mL^{-1}.

3.6. Measurement of Sudan IV dye in various real samples

To investigate the accuracy of the devised procedure in different food and water samples, the standard addition method was used. Food samples including hot pepper sauce, turmeric powder, saffron, and tap water prepared according to section 2.4, were evaluated at three concentration levels of 0, 50, and 100 ng mL^{-1} of Sudan IV dye. The accuracy assessment was performed using the relative recovery percentage (%RR) acquired for food and water samples according to the equation RR%=[(C_{found}–C_{real})/C_{added}]×100, where C_{found}, C_{real}, and C_{added} are the concentrations acquired after the pre-concentration process, the actual level in the sample solution, and the added concentration, respectively. The outcomes acquired are shown in Table 6. As can be seen, the %RR values spanned from 94.97 to 101.26 with RSD% values less than 3.84. These %RR values are valid and reproducible, confirming the excellent ability of the proposed UA-D-µ-SPE method for effective pre-concentration and accurate measurement of Sudan IV dye in complex real samples.

Table 6. Pre-concentration and measurement of Sudan IV dye in food and water samples using the UA-D-µ-SPE method under optimal conditions (n=3).

Real sample	C_{added}	C_{found})	RR% (RSD%)
	Sudan IV dye		
Hot chilli sauce	zero	N.D.	-
	50	47.49	94.98 (3.39)
	100	96.13	96.13 (2.75)
Turmeric powder	zero	N. D.	-
	50	48.14	96.27 (3.42)
	100	97.86	97.86 (3.67)
Saffron	zero	N. D.	-
	50	47.55	95.10 (2.23)
	100	96.46	96.46 (2.88)
Tap water	zero	N. D.	-
	50	50.63	101.26 (2.73)
	100	99.84	99.84 (2.93)

3.7. Comparison with previous studies

The comparison of the figures of merit of the present study with other methods for measuring Sudan IV dye in various real samples is presented in Table 7. As can be seen, the proposed method has a lower limit of detection, a suitable linear range, and a comparable relative standard deviation compared to other methods.

4. Conclusion

The current study demonstrates the high capability of the Bi_2O_3/ZnO/Pd adsorbent for effective pre-concentration and measurement of Sudan IV dye in different food and water samples. The use of this adsorbent, which is considered as a green, inexpensive, abundant, and chemically stable material, can indicate its high value in measuring Sudan IV dye. Additionally, the use of this adsorbent alongside the smartphone measurement method, which can provide features such as simplicity in measurement tools, low cost, easy portability, availability, and the ability to store extensive data, demonstrates the high potential of this method for pre-concentration and measurement of Sudan IV dye. Furthermore, having a low limit of detection, wide linear range, high repeatability, and suitable enrichment factor, it enables successful measurement of Sudan IV dye in food and water samples.

Acknowledgment

We want to take this opportunity to appreciate the support of Semnan University Chemistry Faculty for supporting this work.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript. In addition, the authors have entirely observed the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy.

Table 7. Comparison of different methods for measuring Sudan IV dye.

Extraction method	Real sample	LOD (ng mL^{-1})	LDR (ng mL^{-1})	RSD%	References
Micellar electrokinetic chromatography-MS/MS	chilli powder	6.0	20-500	-	[26]
Solvent extraction HPLC-DAD	Chilli sauce	8.5	40-2000	-	[27]
UA-SLME-HPLC-UV[1]	some spices	270	2500-100000	3.17	[28]
Modified QuEChERs Extraction-UFLC-UV[2]	chilli powder	40	-	3.836	[29]
VA-DLLME-HPLC-UV[3]	Chilli powder, chilli sauce, ketchup	1.0	3-1000	1.4	[30]
MSPE-HPLC-UV[4]	water	5	100-300000	-	[31]
UA-D-µ-SPE-Smartphone	Turmeric, Saffron, hot chilli sauce, tap water	5.58	20-1100	3.91	This work

[1] Ultrasonic assisted solid-liquid microextraction high performance liquid chromatography-ultraviolet.
[2] Modified QuEChERs Extraction ultrafast liquid chromatography-ultraviolet.
[3] Vortex-assisted dispersive liquid-liquid microextraction high performance liquid chromatography-ultraviolet.
[4] Magnetic solid-phase extraction high performance liquid chromatography-ultraviolet.

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