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Solid phase microextraction of rhodamine B in cosmetic samples using ZnS@GO@WMCNTs Nanocomposite with Spectrophotometric Detection

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ABSTRACT

Rhodamine B dye (RhB) has carcinogenicity, genotoxicity, neurotoxicity and toxicity on living cells and therefore its use is prohibited. but it is still secretly used in cosmetics and foods. For this reason, it is important to develop analytical methods for accurate and sensitive analysis of trace levels of RhB dye in cosmetic and food samples. In this study, a new solid phase microextraction method (SPME) was developed for quick and cheap analysis of RhB in cosmetic samples. A new nanohybrid material including graphene oxide (GO), multi-walled carbon nanotubes (MWCNTs) and zinc sulfide nanoparticles (ZnS) was synthesized by hydrothermal synthesis method and the new ZnS@GO@WMCNTs nanohybrid material was used as sorbent in simultaneous separation and preconcentration of RhB from cosmetic products by SPME. ZnS@GO@WMCNTs material was characterized by Raman spectroscopy, scanning electron microscopy (SEM), SEM-Mapping and energy dispersive X-Ray fluorescence (EDX) techniques. The effects of experimental parameters such as amount of sorbent, pH of sample solution, sample volume, effects of matrix, eluent solutions on the recoveries of RhB were investigated. RhB dye adsorbed on ZnS@GO@WMCNTs was eluted with acetic acid–ethanol mixture (2:1) and determined by using UV–Visible spectrophotometer at 550 nm. The fact that RhB adsorbed quantitatively on the adsorbent at all pH values shows that strong Van der Waals interactions between the ZnS@GO@WMCNTs and RhB molecules are effective in adsorption. In optimal experimental conditions, the limit of detection (LOD) and preconcentration factor (PF) of the proposed MSPE-UV/Vis spectroscopy procedure were 4.74 and 44, respectively. The MSPE-UV/Vis procedure was successfully applied to the microextraction and determination of RhB in nail polishs ve lipstick samples with recoveries in the range 95–101 %.

1. Introduction

Paints, which are used almost everywhere today, have become an indispensable part of our lives with the impact of social media on people [1]. Dyes used in the food, beverage, cosmetics, textile, cleaning and pharmaceutical industries ensure that these products are preferred by customers and increase their market value [2]. However, these dyes decrease the quality of life by negatively affecting human health, for this reason, it is of great importance to develop analysis methods that can perform trace level analyzes of dyestuffs in different products.

The dyes are being formed five main groups according to their chemical structure and RhB dye is a member of the xanthenes family [3]. RhB which is easily soluble in water and used as a coloring in food, medicine and especially cosmetic products, finds a wide area of applications in the industry by easily bonding or joining many materials. However, irritant, carcinogenic, chronic, genotoxicity, neurotoxicity and toxicity effects of RhB dye on humans and animals were observed. Because of these serious adverse effects of RhB on humans and animals, its use in cosmetic and food products has been prohibited in many countries by Regulation (EC) No 1223/2009, published in the Official Journal of the European Union and the International Agency for Research on Cancer (IARC) [4–9]. Despite this, RhB dye is illegally used due to its low price, stability, chemical and light resistance and high efficiency. Therefore, accurate, sensitive and reliable analysis of RhB in

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cosmetic products is of great importance.

Until today, many analytical methods have been developed for the analysis of RhB such as high-performance liquid chromatography (HPLC), liquid chromatography-mass spectroscopy (LC-MS) UV–Vis spectroscopy, voltammetry, electrophoresis, fluorescent spectroscopy etc. or integrated devices [10–16]. UV–Visible spectrometry is an important instrument at this area due to its simplicity, available in almost every laboratory, does not require much expertise and lower cost than other instruments. In all these techniques, the target analyte must be subjected to pre-sample preparation in order to isolate and preconcentrate it from the complex matrix environment. In the sample preparation step of synthetic dyes, solid phase extraction (SPE), liquid–liquid extraction (LLE), cloud point extraction methods are frequently used [12,17–21]. Many of these methods involve high amounts of organic solvents, samples, and long experimental steps. Therefore, techniques that are simple, fast, cheap, efficient and comply with green chemistry principles are needed in cosmetic and food analysis. Microextraction methods, which is a new field of study, can both respond to these needs and show a new way for routine analysis.

Recently, nanoparticles have been the focus of analytical sample preparation studies due to their high surface areas, large extraction capacities, easily functionalizability, separation capacities etc. properties. Besides, by creating composites of these nanoparticles with different materials, extraction efficiency, selectivity and surface modification can be improved [22–27]. Especially, GO and MWCNTs which can be easily and quickly modification is often preferred sample preparation techniques. GO is a selective and/or effective material due to its large surface area, π decolized electron system, morphology and cheap synthesis process [28–31]. However, due to the tendency of GO layers to agglomerate easily, it greatly affects its adsorption capacity [32,33]. One of the most effective ways to overcome this problem is to modify it with different materials. Carbon nanotubes (CNTs) have been reported in different studies as suitable materials for this purpose. Therefore, in this study, GOs were modified with MWCNTs.

MWCNTs, on the other hand, has small diameter, specific surface area, hydrophobic property of the surface, large adsorption capacity and inner tube cavity etc. stands out with its properties [34–37]. Both materials or composites have taken their place as sorbents in the solid phase microextraction method, which is one of the trending microextraction methods [38–41].

In this study, ZnS@GO@WMCNTs nanohybrid material was synthesized by simple hydrothermal method and used as an adsorbent in the separation and enrichment of RhB from different cosmetic samples by SPME. RhB concentration in last phase was measured with UV–Vis spectrophotometer at 550 nm.

2. Experimental

2.1. Instrumental

RhB dye analyzes in the final phase after SPME was carried out by a UV–Vis spectrophotometer (UH 5300 Hitachi, USA) with micro quartz cell (10 mm). An ultrasonic water bath which has maximum 35 kHz ultrasound frequencies (Norwalk, CT, USA) and vortex (VWR International LLC, USA) were used to provide homogenization and preparation of micro-sized suspensions in the sample solutions. A Hettich Rotofix 32 centrifuge (Buckinghamshire, UK) was used in the separation of adsorbents from solution phase. The pH of all solutions were adjusted by a pH meter with Sartorius Pt-10 (Goettingen, Germany) model glass-electrode. The chemical and morphological analyses of the fabricated GO and ZnS@GO@WMCNTs materials were conducted by exploiting many characterization techniques including Raman spectroscopy, scanning electron microscopy (SEM), SEM-Mapping and energy dispersive X-Ray fluorescence (EDX) techniques.

2.2. Chemicals and reagents

All chemicals used were of analytical purity and any purification process wasn't applied. Ultra-pure water used throughout the entire study was obtained using a Milli-Q system (18.2 MΩ cm resistivity, Millipore Corporation, USA). $1x10^{-4}$ mol·L^{-1} stock solution of RhB (Merck, Darmstadt Germany) was prepared in ethanol. Phosphate buffer solutions (pH 2.0, 3.0, 4.0, 6.0 and 7.0) and acetate buffer solution (pH 5.0) were prepared for pH adjustments. Acetic acid and ethanol used as eluents were purchased from Merck (Darmstadt, Germany). Graphite powder, thioacetamide and zinc acetate dihydrate of used in the synthesis of ZnS@GO@WMCNTs nanohybrid material was obtained from Merck (Darmstadt, Germany). MWCNTs was provided by Sigma-Aldrich (St. Louis, MO, USA) was used.

2.3. Synthesis of ZnS@GO@WMCNTs nanohybrid material

GO used to obtain the nanohybrid material is produced from graphite powder. The modified Hummer method, which we used before, was used in the synthesis of GO from graphite powder [42].

The hydrothermal synthesis method is an effective method based on the formation of supercritical fluid at high temperature and pressure. Controlled production is possible by changing the temperature, pressure and the amount and values of the reacting species. This method, which is based on fragmentation and recombination reactions between components at high temperature and pressure, is one of the cheapest nanoparticle production methods. In our study, thioacetamide molecule breaks down and S atom in it becomes free, combines with Zn^{2+} ions to form ZnS nanoparticles, and simultaneously enables the formed ZnS nanoparticles to hybridize GO and MWCNTs. 0.5 g of synthesized GO in 25 mL of distilled water was sonicated for 1 h in ultrasonic water bath and then 0.25 g of MWCNTs was added on it (Mixture-I). 1.0 g of $Zn(CH_3COO)_2{\cdot}2H_2O$ dissolved in 15 mL of distilled water, then 3 g of thioacetamide dissolved in 15 mL of distilled water were solved (Solution-I). Mixture-I and Solution-I was mixed and homogeneous distribution of the resulting mixture was ensured by ultrasonic vibration for 30 min. Then the mixture was taken to the hydrothermal synthesis unit with a volume of 100 mL and the reaction was started at 200 °C. The reaction was stopped after 14 h. The transparent solution portion at the top of the synthesis unit was separated by decantation method. The product which solid portion at under of the synthesis unit was washed with 7 mL of ethanol and then three times with 5 mL of deionized water, then dried oven for 12 h at 60 °C.

2.4. MSPE-UV/Vis spectroscopy procedure

SPME method were performed in 10 mL of aqueous sample solutions at pH 3.0 containing 1×10^{-4} mol·L^{-1} of RhB. 4.0 mg of the synthesized hybrid material (ZnS@GO@WMCNTs) was added in the aqueous sample solution and then the obtained mixture was sonicated in an ultrasonic water bath for 15 min. At this stage, homogenization was provided and the RhB molecules was absorbed on ZnS@GO@WMCNTs. After the absorption process, the mixture was centrifuged to separate the aqueous phase from the solid phase (4000 rpm, 10 min). The aqueous phase was taken by using syringe and then 900 μL of acetic acid–ethanol solution at 2:1 vol ratio was added to on the ZnS@GO@WMCNTs with the aid of a micropipette. It was vortexed for 2 min to elute RhB molecules from ZnS@GO@WMCNTs. Then, the mixture was centrifuged at 4000 rpm for 10 min to separate the eluent phase from the ZnS@GO@WMCNTs. The eluent phase containing the RhB dye was separated by using a syringe. In the final stage, the eluent phase was transferred into a microcuvette with a volume of 1 mL and the RhB concentration was measured at 550 nm with a UV–Visible spectrophotometer.

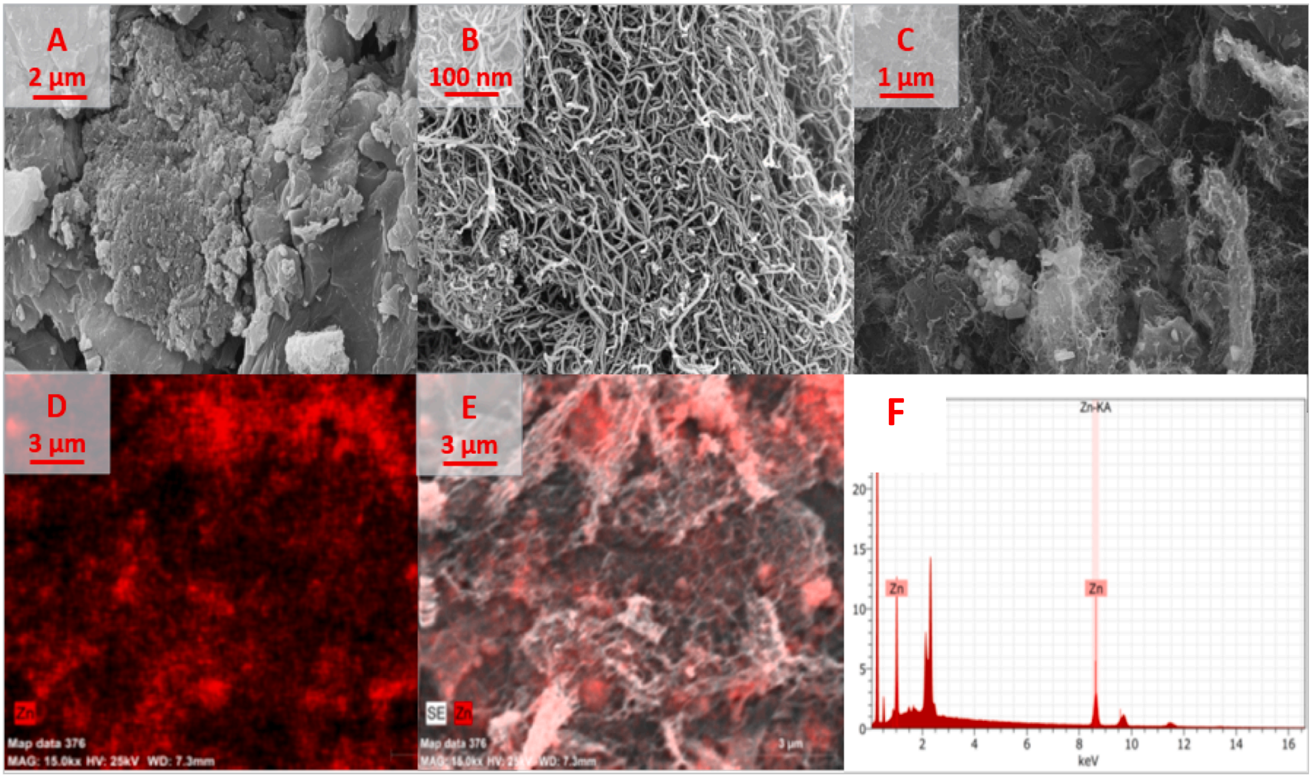

Fig. 1. (A) SEM image of GO, (B) SEM image of MWCNTs, (C) SEM image of ZnS@GO@WMCNTs hybrid material, (D, E,) SEM mapping photographs of ZnS@GO@WMCNTs hybrid material, (F) SEM-EDX analysis of ZnS@GO@WMCNTs hybrid material.

2.5. *Preparation of real samples*

The developed SPME method was applied for determination of the RhB concentration in two types of nail polish and a lipstick sample obtained from cosmetic markets served in Kayseri, Turkey. To apply the developed SPME method to nail polishes samples, 1.5 g of nail polish samples were taken and 10 mL of acetone was added. The resulting mixture was kept in the water bath for 10 min then shaken in the shaking bath for 30 min. In this process, RhB in the nail polish sample was passed into the acetone phase. Then, this mixture was centrifuged for 10 min. The solid phase at the bottom of the centrifuge tube was separated from the acetone phase containing RhB. A certain volume of this solution was taken, necessary dilutions and pH adjustments were made and subjected to the developed SPME method. To apply the developed SPME method to lipstick sample, 0.1 g of lipstick sample were taken and 10 mL of ethyl alcohol was added to the lipstick sample. The resulting mixture was kept in the water bath for 10 min then shaken in the shaking bath for 1 h, later then, this mixture was centrifuged for 10 min. The solid phase at the bottom of the centrifuge tube was separated from the ethyl alcohol phase containing RhB. Known volume of this solution was taken, necessary dilutions and pH adjustments were made and subjected to the developed SPME method.

3. Results and discussion

3.1. *Characterization of ZnS@GO@WMCNTs nanohybrid material*

Morphological and structure analysis of GO, MWCNTs and

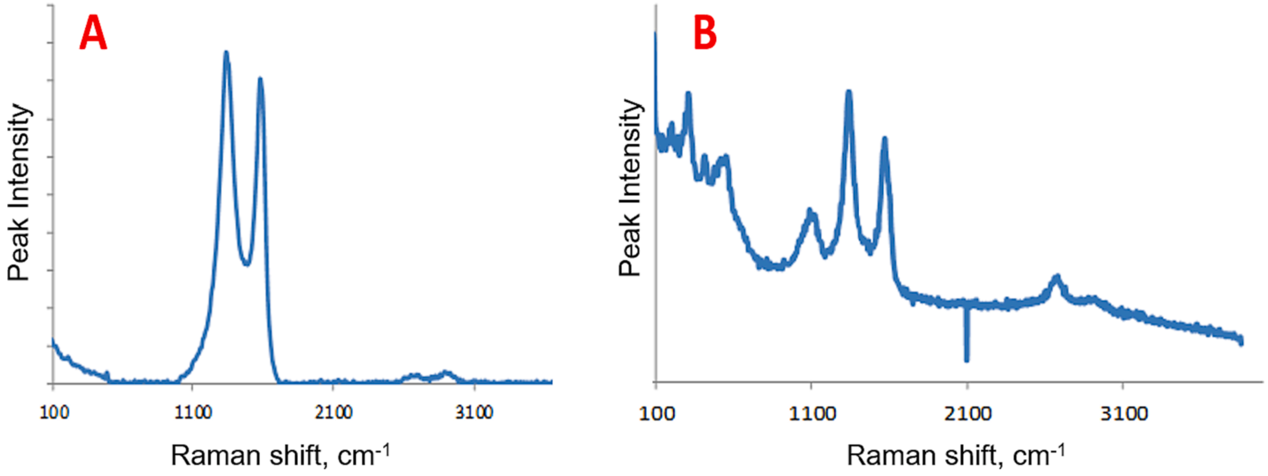

Fig. 2. (A) Raman spectra of GO and (B) Raman spectra of ZnS@GO@WMCNTs hybrid material.

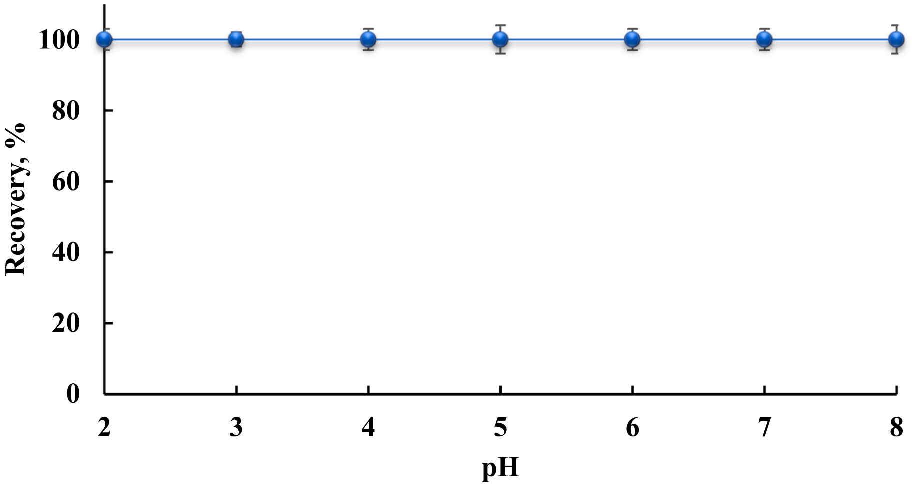

Fig. 3. Effect of sample solution pH on the recovery of RhB (Amount of ZnS@GO@WMCNTs: 5 mg, ultrasonic irridation time: 15 min, eluent: 900 μL of acetic acid–ethanol solution at 2:1 vol ratio, sample volume: 25 mL, N = 3).

ZnS@GO@WMCNTs nanohybrid materials were performed by SEM analysis. SEM images of GO, MWCNTs and ZnS@GO@WMCNTs were presented in Fig. 1. When Fig. 1A is examined, layers of GO can be seen. This demonstrates the successful production of less-layered GO from graphite powder. Successful production of single and/or less-layered GO layers means providing surfaces with large surface areas that can interact more with the analyte. The moss-like structure of the MWCNTs is clearly visible in the hybrid material (Fig. 1B–1C). SEM mapping photographs of ZnS@GO@WMCNTs were shows ZnS nanoparticles are uniformly and homogeneously dispersed in the GO@MWCNTs matrix (Fig. 1D–1E). SEM analysis showed that there are important morphological differences for GO, MWCNTs and ZnS@GO@WMCNTs. Hence, the surface of ZnS@GO@WMCNTs is seen different than that of GO and MWCNTs. SEM-EDX analysis of ZnS@GO@WMCNTs hybrid material also confirms the SEM mapping images and shows the presence of ZnS nanoparticles in the structure (Fig. 1F).

Raman spectroscopy is widely used in the characterization of metal-based materials and carbon products containing conjugated and double carbon–carbon bonds. Raman spectrums of the GO and ZnS@GO@WMCNTs hybrid material are presented in Fig. 2. The peak at around 1580 cm^{-1} and the peak at around 1360 cm^{-1} are specific D and G band Raman peaks for the GO. The Raman spectrum of ZnS@GO@WMCNTs hybrid material were compared with GO Raman spectrum. Significant differences were seen between Raman spectrums. The new six peaks between 250 cm^{-1} and 700 cm^{-1} correspond to formation of ZnS nanoparticles. These six Raman peaks are compatible with the literature [43]. It is also seen that the peaks seen in at around 1580 cm^{-1} and 1360 cm^{-1} for GO shift and the Raman densities decrease.

3.2. *Effect of pH*

Analyte adsorption and solubility properties are primarily dependent on the pH of the sample solution [38–40]. Therefore, the first analytical parameter to be optimized is the pH of the sample solution. The effect of sample solution pH on the recovery of RhB were scanned in the range of pH 2.0–8.0 by using buffer solution. As shown in Fig. 3, the quantitative recoveries (100 %) of RhB were obtained at all studied pH values. The results show that the adsorption of RhB is independent of pH. This can be explained by the fact that Van der Waals interactions between ZnS@GO@WMCNTs and RhB molecules are primarily effective in the adsorption of RhB molecules [41]. So, Optimum pH was selected as 3.0.

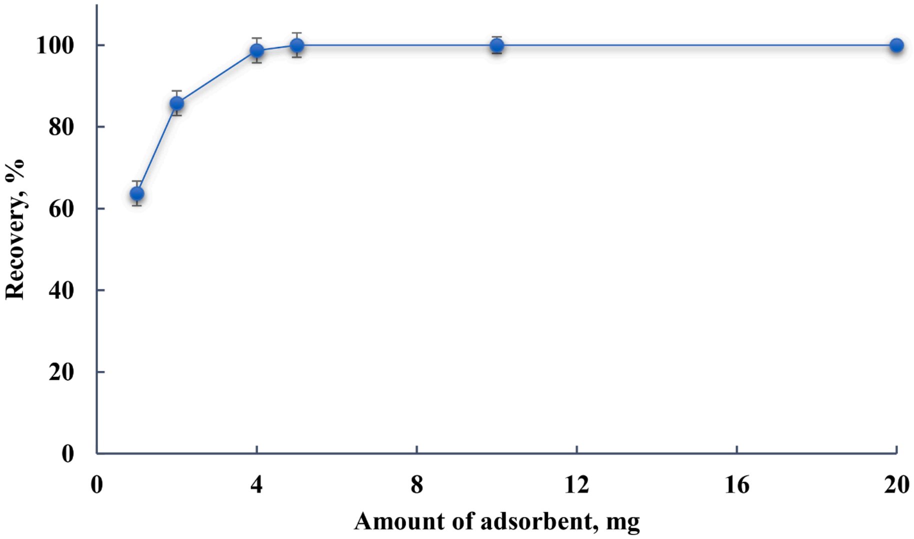

Fig. 4. Effect of amount of adsorbent on recovery of RhB (pH of sample solution: 3.0, ultrasonic irridation time: 15 min, eluent: 900 μL of ethanol-acetic acid mixture at volume ratio 1:2, sample volume: 25 mL, N = 3).

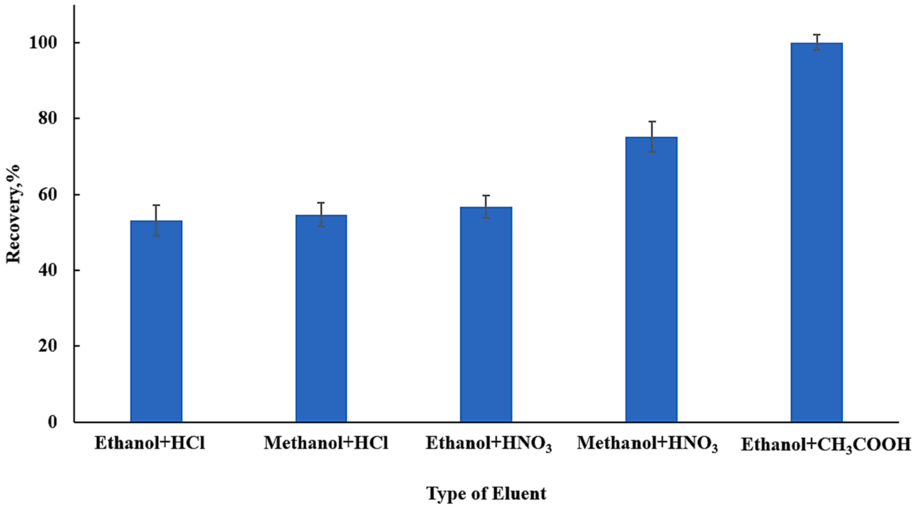

Fig. 5. Effect of type of eluent on recovery of RhB (pH of sample solution: 3.0, ultrasonic irridation time: 15 min, amount of adsorbent: 4.0 mg, eluent volume: 900 μL, sample volume: 25 mL, N = 3).

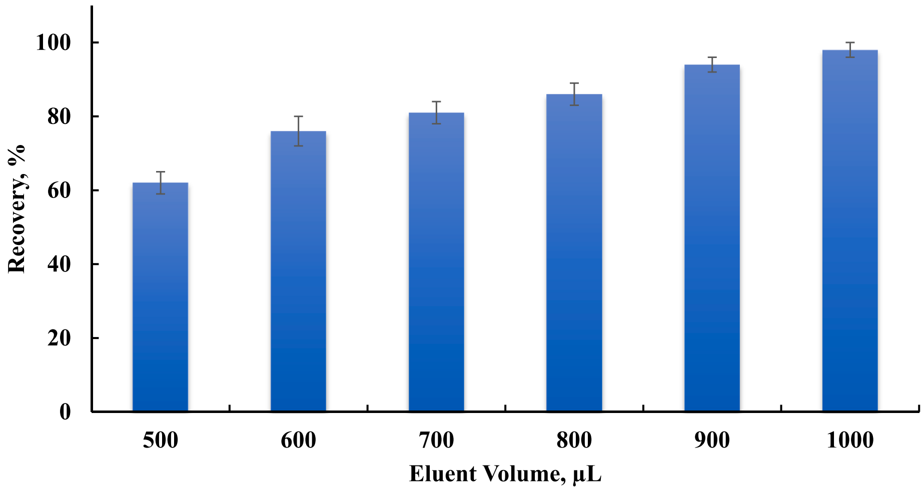

Fig. 6. Effect of volume of eluent on recovery of RhB (pH of sample solution: 3.0, ultrasonic irridation time: 15 min, amount of adsorbent: 4.0 mg, eluent: ethanol-acetic acid mixture at volume ratio 1:2, sample volume: 25 mL, N = 3).

The pH independence of RhB adsorption is the most important advantage of the developed method, as no effort will be made for pH adjustment.

3.3. Effect of adsorbent amount

For solid phase microextraction methods, it is important to optimize the amount of adsorbent so that all analyte molecules can be adsorbed on the minimum amount of sorbent [41]. Hence, the different amounts of ZnS@GO@WMCNTs between 1 and 20 mg were tested to find the optimum amount. The results given in Fig. 4 showed that 4.0 mg of adsorbent was sufficient for the quantitative analysis of RhB. Thus, 4.0 mg of adsorbent was identified as optimum amount and used in subsequent studies. In addition, it was observed that the hybrid material used can be used repeatedly after the elution process.

3.4. Effect of eluent type

Different eluents were tested to re-desorb the RhB molecules adsorbed to ZnS@GO@WMCNTs. For this purpose, ethanol, methanol and their acidic solutions were used. The elution efficiency was lower than 20 % when pure ethanol and methanol were used as eluents, and in this case, the combinations of ethanol and methanol with hydrochloric acid, nitric acid and acetic acid were tested, respectively. The results shown in Fig. 5 showed that the highest recovery efficiency was obtained with the ethanol-acetic acid mixture at 2:1 vol ratio. Therefore, ethanol-acetic acid mixture at 2:1 vol ratio was used as the optimal eluent for further experiments.

3.5. Effect of eluent volume

The effect of eluent volume on the recovery of RhB dye was investigated by changing eluent volume from 500 μL to 1000 μL. Quantitative results were obtained 900 μL and above volume of acetic acid–ethanol solution at 2:1 vol ratio. The optimum eluent volume was determined as 900 μL and this volume was used in subsequent studies (Fig. 6).

3.6. Effect of sample volume

For the sample preparation methods, the maximum applicable sample volume is important in order to determine the lowest analyte concentration that can be detected by obtaining a higher preconcentration factor [43–46]. While examining the effect of sample volume on the method, other conditions were kept constant and different volumes

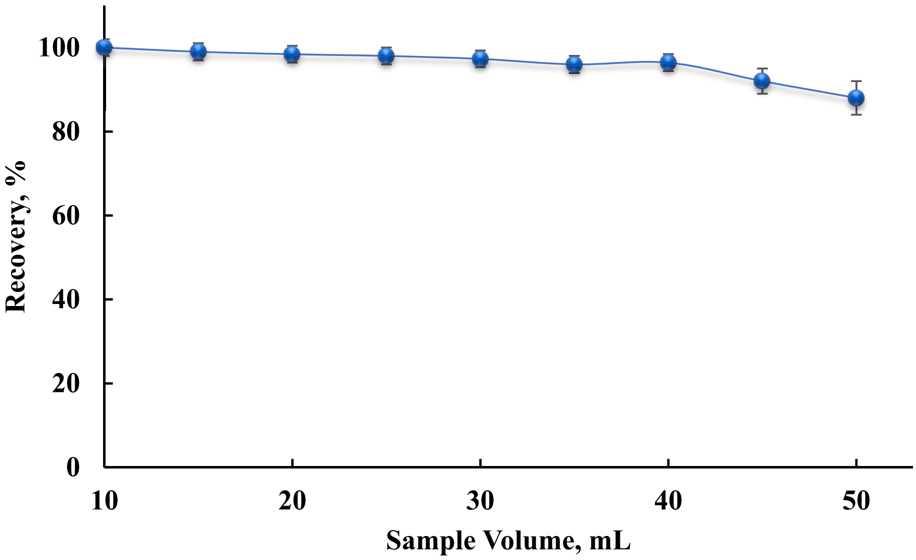

Fig. 7. Effect of Sample Volume on Recovery of RhB (pH of sample solution: 3.0, ultrasonic irridation time: 15 min, amount of adsorbent: 4.0 mg, eluent: 900 μL of ethanol-acetic acid mixture at volume ratio 1:2, N = 3).

Table 1
Effect of matrix species on recovery of RhB (pH of sample solution: 3.0, ultrasonic irritation time: 15 min, amount of adsorbent: 4.0 mg, eluent: 900 μL of ethanol-acetic acid mixture at volume ratio 1:2, sample volume: 40 mL, N = 3).

Ion	Added as	Concentration, $mg \cdot L^{-1}$	Recovery, %
F-	NaF	2500	100 ± 1
K^+	KCl	2500	101 ± 3
SO_4^{2-}	Na_2SO_4	2500	99 ± 1
CO_3^{2-}	Na_2CO_3	2500	102 ± 3
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	500	97 ± 2
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	10	99 ± 2
Mn^{2+}	$MnSO_4$	10	98 ± 1
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	10	99 ± 1

of the sample solution were tested between 10 and 50 mL. When the results shown in Fig. 7 were examined, it was seen that the increase in sample volume started to affect the RhB recovery after 40 mL. Above 40 mL of sample volume, the recovery values appears to be not quantitative. When the sample volume is 40 mL and the final volume is 0.9 mL, the preconcentration factor of the developed method was calculated as 44.

3.7. Effect of matrix species

Matrix species that may be found in the natural assay environment are likely to interfere with the determination of trace analytes [47–51]. Therefore, the effects of these species should be investigated. The influences of some ions on the recovery of RhB on the developed SPME procedure were investigated. The obtained recoveries results were presented in Table 1. The results showed that the specified matrix ions have no significant influence on the extraction efficiency and the developed SPME/UV–Vis spectroscopy procedure could be used for these matrix mediums.

3.8. Analytical performance of MSPE-UV/Vis spectroscopy procedure

Analytical performance parameters for the developed SPME/UV–Vis procedure was studied under the optimum experimental conditions (pH of sample solution: 3.0, ultrasonic irritation time: 15 min, amount of adsorbent: 4.0 mg, eluent: 900 μL of ethanol-acetic acid mixture at volume ratio 1:2, sample volume: 10–40 mL). Limit of detection (LOD), limit of quantification (LOQ), precision as the relative standard deviation (RSD, %), preconcentration factor (PF), robustness and correlation coefficient (R^2) parameters were studied to evaluate the developed SPME/UV–Vis spectroscopy procedure based the ZnS@GO@WMCNTs nanocomposite. The results are given in Table 2. Calibration graph and equation was created by applying the developed procedure to 40 mL standard solutions containing increasing concentrations of RhB under optimized analytical conditions. The calibration graph was created by plotting the UV–Vis spectrophotomer absorbances corresponding to the RhB concentrations in the standard solutions. The RSD% was obtained by applying the developed method to 100 $\mu g \cdot L^{-1}$ of RhB solution for 10 replicates. The LOD and LOQ values were obtained by applying the SPME/UV–Vis spectroscopy procedure to 10 replicates of blank samples. As LOD was defined to be three times the standard deviation of blank samples divided by the slope of the calibration curve, LOQ was defined to be ten times the standard deviation of blank samples divided by the slope of the calibration curve. In order to check robustness of the developed SPME/UV–Vis procedure, the pH of the sample solution was changed between 2.0 and 8.0, and other experimental parameters were kept at optimum conditions. When the results obtained were examined, it was observed that there was no statistically significant change in the recovery values with the pH change.

Table 2
Analytical performance parameters of the developed ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure.

Parameter	Value
Relative standard deviation, % (N = 10)	4.7
LOD, 3 s/m, $\mu g \cdot L^{-1}$ (N = 10)	4.8
LOQ, 10 s/m, $\mu g \cdot L^{-1}$ (N = 10)	15.8
Calibration equation	$y = 0.1612x + 0.0077$
Regression coefficient, R^2	0.9995
PF	44

3.9. Comparison of ZnS@GO@WMCNTs based SPME/UV–Vis spectroscopy procedure with other studies in the literature

The proposed ZnS@GO@WMCNTs based SPME/UV–Vis spectroscopy procedure was compared with different extraction/microextraction methods which have been reported recently in the literature. As can be seen in Table 3, it is evident that the LOD, LOQ, PF and RSD values were lower or comparable with the other extraction/

Table 3
Comparison of ZnS@GO@WMCNTs-based SPME/UV–Vis Spectroscopy Procedure with Other Studies in the Literature.

Extraction method	Analysis technique	LOD, μg·L^{-1}	LOQ, μg·L^{-1}	RSD, %	PF	Ref.
Magnetic solid phase extraction	UV–Vis spectroscopy	3.94	13.13	1.16	26	[51]
Micro-cloud point extraction (MCPE)	UV–Vis spectroscopy	2.2	7.3	6.75	28.4	[52]
Supramolecular solvent-based dispersive liquid–liquid microextraction (tetrahydrofuran and decanoic acid.)	UV–Vis spectroscopy	0.49	1.47	5.8	30	[53]
Dispersive liquid–liquid microextraction (DLLME)	UV–Visible spectroscopy	6.1	20.4	4.06	51	[54]
Dispersive liquid–liquid microextraction	UV–Vis spectroscopy	7	23	3.2	23	[55]
Ionic liquid-based matrix solid-phase dispersion homogeneous liquid–liquid microextraction	HPLC–UV detector system	8.8 (g·kg^{-1})	17.6 (g·kg^{-1})	1.4–5.7	–	[56]
Deep eutectic solvent based liquid phase microextraction	UV–Vis spectroscopy	2.2	7.3	2.3	25	[57]
Heat-induced homogeneous liquid–liquid microextraction	UV–Vis spectroscopy	14	47	1.03	10	[58]
Solid phase microextraction (ZnS@GO@WMCNTs)	UV–Vis spectroscopy	4.8	15.8	4.7	44	This study

Table 4
Analyte addition and recovery test for ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure for RhB in cosmetic samples (pH of sample solution: 3.0, ultrasonic irridation time: 15 min, amount of adsorbent: 4.0 mg, eluent: 900 μL of ethanol-acetic acid mixture at volume ratio 2:1, N = 3).

Added, μg·g^{-1}	Lipstick		Nail polish 1		Nail polish 2	
	Found, μg·g^{-1}	Recovery, %	Found, μg·g^{-1}	Recovery, %	Found, μg·g^{-1}	Recovery, %
0.0	0.31 ± 0.02	–	0.40 ± 0.02	–	2.12 ± 0.10	–
0.8	1.1 ± 0.06	95	1.15 ± 0.07	96	2.85 ± 0.12	98
1.6	1.9 ± 0.05	97	2.05 ± 0.10	102.5	3.70 ± 0.08	99

microextraction techniques. In addition, low cost, simple and fast preparation of sample solution and high recovery values are other advantages of our method compared to other methods.

3.10. . *Real sample application of the proposed ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure*

In order to check the accuracy and applicability of the developed ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure for real samples, analyte addition-recovery experiments were performed on lipstick and nail polish samples. Cosmetic products were prepared as described in the sample preparation section. The proposed method was applied to the prepared samples. In the application step, RhB at the concentration levels changing from 0.4 to 1.6 μg·g^{-1} were added in the lipstick and nail polish samples and then these samples subjected to the ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure under the optimum experimental conditions. The standard addition-recovery experiments for the samples were carried out in triplicate and independently. As shown in Table 4, the recoveries for RhB in lipstick and nail polish samples ranged from 95 to 103 %. These quantitative recovery values proven that the developed method worked correctly in lipstick and nail polish samples without matrix interference.

4. Conclusions

In this study, a procedure based on the combination of SPME and UV–Vis spectroscopy analysis technique as very simple, fast, cheap and environmentally friendly was developed for the simultaneous separation/preconcentration and determination of RhB dye in cosmetic products. ZnS@GO@WMCNTs nanohybrid material as a new SPME sorbent was synthesized by using a simple hydrothermal mehtod. The developed ZnS@GO@WMCNTs-based SPME/UV–Vis spectroscopy procedure provided advantages mentioned below;

- Due to strong Van der Waals interactions between ZnS@GO@WMCNTs and RhB molecules at all pH values, its high affinity for RhB at all pH values without adjusting the pH of any solution provides a significant convenience for the use of this material in routine analyses.
- The synthesized hybrid material can be used repeatedly.
- It allows analysis of RhB dye using a small amount of hybrid material and a minimum amount of solvent.
- Instead of expensive devices such as HPLC and LC-MS used in the analysis of RhB dye, UV–Vis spectrophotometer can be used that are cheap, not seeking expertise and available in almost every laboratory.
- The ZnS@GO@WMCNTs-based SPME/UV–Vis procedure has the potential to be used as a commercial kit in routine analysis for the determination of RhB dye in cosmetic samples as well as food and environmental samples.

CRediT authorship contribution statement

Seda Duman: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Erkan Yilmaz:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation. **Mustafa Soylak:** Writing – review & editing, Writing – original draft, Validation, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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