A solid phase extraction based UPLC-ESI-MS/MS method using surfactant-modified clay as extraction sorbent for the removal and determination of rhodamine B in industrial wastewater samples

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ABSTRACT

A fast and sensitive solid phase extraction based on ultra-performance liquid chromatography electrospray ionization tandem mass spectrometry method has been established for determining basic colorant, rhodamine B. This method is based on the extraction of rhodamine B from aqueous solution on surfactant (cetyltrimethylammonium bromide) intercalated montmorillonite (clay k10) followed by elution. The modified material was found to be highly efficient extracting target dyes even at trace levels. The basic methanol solution was used as an eluent for the effective desorption of the dye. The chromatographic separation of analyte was achieved on the Acquity® BEH C_{18} reversed phase column using a binary mobile phase (a mixture of CH_3OH and 0.1% aqueous formic acid solution (75:25, v/v) in isocratic mode at a flow rate of 0.3 mL/min. Both the detection and quantitation of rhodamine B were achieved with a spectrometer of mass operating in positive electrospray ionization mode in less than 1.0 min run time with sharp and excellent peak symmetry. The described method provides excellent quality parameters including linearity ($r > 0.998$), precisions (day-to-day and run-to-run) (RSD < 3.3%), and sensitivity. Both detection and quantification limits were calculated as signal-to-noise (S/N) ratios of 3 and 10, and were found to be 0.24 and 0.82 ng/mL, respectively. Industrial wastewater samples including the printing press, paper industry, textile industry, processed food industry, and laundry have been analyzed and the quantities of rhodamine B were found to be from 0.45–1.78 µg/mL. The percentage recovery values were obtained in the range of 99%–103% depending on sample matrices.

Keywords: Cetyltrimethyl ammonium bromide; Montmorillonite; Chromatography, mass spectrometry, Rhodamine B; Industrial wastewater

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1. Introduction

Synthetic colors have globally been used to avoid the original color discoloration of various processed foods and to make them more attractive in drawing attention of the consumers [1]. They have been considered superior over natural food colors in terms of their uniformity and applicability. Hence, the applications of such colorants have been increased daily in various industries, including paper, plastic, laundry, textile, paint, cosmetics, and food. Among the various synthetic dyes, rhodamine B (RhB) has been most commonly used as coloring agents in those industries. It is highly water soluble dye and belongs to the class of xanthene. It has been used as a very useful chemical for the detection and determination of metals and organic components [2–6]. However, the use of this dye as a food color has been discontinued since long time due its suspected carcinogenic properties [7]. In addition, when the dye molecule released directly or indirectly into the aqueous streams it triggers a serious warning to the aquatic environment. It has shown harmful effects toward human beings and animals in terms of irritation to the respiratory tract, skin, and eyes once it enters into the body [8,9]. Considering its serious health concern, various agency has set certain regulation for the uses of such dye [10–12]. Therefore, for all the researchers all over the universe are providing lots of efforts to remove RhB from industrial waste before it can be discharged into the environment.

Many methods have been reported earlier for the removal of dye which include adsorption [11–13], chemical coagulation–flocculation [14,15] photocatalytic degradation [16,17], chemical oxidation [18], and membrane filtration [19,20]. It was obvious from the reported data that adsorption is the most efficient technique for dye removal from various wastewater. Many research works have been proposed to check the feasibility of different adsorbent for the removal of RhB from aqueous solution [21–27]. The limitation of adsorbent separation of adsorption technique for some extent was overcome by introducing magnetic adsorbent where the separation of adsorbents are quite easier than traditional centrifugation and other techniques [28–32]. Interestingly, there are many literatures have been reported for determining RhB including UV-visible spectrophotometry [33,34], dispersive liquid–liquid microextraction, and high-performance liquid chromatography–ultraviolet (HPLC–UV) [35], solid-phase extraction (SPE) and UV-VIS spectrophotometry [36] and HPLC coupled with fluorescence detection [37] as far as we know, no methods were informed for the quantitative analysis of RhB based on ultra-performance liquid chromatography-electrospray ionization tandem mass spectrometry (UPLC-ESI-MS/MS) and SPE technique. The Improved stationary phases of UPLC implied gains in analysis throughput and sensitivity compared to other conventional methods. Additionally, UPLC coupled with the MS that provides superior confirmatory capability has made it a method of choice. Therefore, in this study the determination of RhB in industrial wastewater using SPE based UPLC-ESI-MS/MS method has been developed. Montmorillonite (MMT) clay modified with cetyltrimethylammonium bromide (CTAB) was used as an SPE adsorbent. The proposed solid-phase extraction based reversed-phased UPLC-ESI-MS/MS is a new method for the extraction, enrichment, and determination of RhB from various industrial wastewater samples and offered advantages in terms of extraction and quantitation of target dye at trace level.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were of analytical reagent grade or as specified. Sigma-Aldrich chemical company (Germany) was supplied MMT K10 clay. A surfactant, CTAB was obtained from Sigma, US. The RhB dye was obtained from Sigma-Aldrich as well. Methanol (CH_3OH) and diethyl ether ($C_2H_5OC_2H_5$) were procured from Fisher Scientific (UK). Ethanol (C_2H_5OH) and acetone (CH_3COCH_3) were provided by Sigma-Aldrich and WinLab (UK chemical company), respectively. Milli-Q water purification system manufactured by Millipore Corporation (Bedford, MA, USA) was used for preparing milli-Q water. Extrelut-20 was employed as an extraction column collected from (Darmstadt, Germany). The coupling pieces and stopcocks were obtained from Varian supplier (Harbor City, California, USA). Visiprep™ and Visidry™ vacuum manifolds were used in the SPE method for pre-concentration purpose, (Supelco, Gland, Switzerland). High purity argon gas of purity 99.999% was used as collision gas and was procured from Specialty Gas Centre, Jeddah, Saudi Arabia.

2.2. Sample preparation

The stock solution of RhB (100 mg/mL) was prepared in methanol and diluted as required for further studies. To construct the calibration curve of RhB, a series of the working standards with concentration from 0.0005 to 5.0 mg/mL were prepared prior to analysis. All the solutions and real samples were injected into the UPLC-MS/MS system after being filtered through a 0.22 μm PTFE (polytetrafluoroethylene) syringe filter (Chromafil® Xtra, Macherey–Nagel, Duren, Germany). The RhB quantitation was acquired using the standard addition at various concentration levels.

2.3. Instrumentation

A Acquity® UPLC system coupled to a Quattro Premier triple quadrupole mass spectrometer (Waters, Milford, MA, USA) was used for the UPLC-ESI-MS/MS analysis of all standards and samples. The separation of the target dye was accomplished on a reversed phase Acquity® BEH C18 column (50 mm × 2.1 mm id and a 1.7 μm particle size) manufactured by Waters (Milford, MA, USA). The Quattro Premier triple quadrupole mass analyzer (Micromass, Milford, MA, USA) of the UPLC system consisted of an electrospray ionization source (ESI, Z-spray) which can operate both in positive and negative ionization mode. A nitrogen generator was used to produce high purity nitrogen (NM30LA, Peak Scientific, Inchinnan, United Kingdom). An Oerlikon rotary pump (SOGEVAC SV40 BI, Cedex, France) was used to deliver primary vacuum to the MS detector. All the data acquisition and analyses were performed using MassLynx

V4.1 software (Waters, Milford, Massachusetts, USA). The characterization of surface functionality of the CTAB modified clay materials was performed using Fourier transform infrared (FTIR) spectra of in the range of 4,000–600 cm^{-1} of model Varian 3100 spectrometer (USA). The surface crystallinity properties of the modified clay was determined via X-ray diffraction (XRD) analysis using Philips Xpert X-ray diffractometer (Baltimore, MD).

2.4. Sample analysis

2.4.1. MMT intercalation

The SPE method has been extensively used to separate the target compounds from a variety of matrices, such as water, beverages, and biological samples [38–40]. Different adsorbents have been prepared and applied for this purpose and the modification of adsorbents with various functional groups have also been performed to change the extraction properties of the adsorbents [41]. In the current research, CTAB modified MMT clay were prepared and adopted as the SPE adsorbent according to our previous report [41]. To intercalate MMT clay by CTAB, 50 g of MMT was suspended in 600 mL and 1% CTAB solution under continuous stirring at 400 rpm for 24 h. Thereafter, it was filtered by Whatman filter paper No. 1 and was washed several times with D.I water until near to neutral pH was achieved. The intercalated MMT (CTAB-MMT) was successfully synthesized and dried at 50°C under vacuum for 24 h.

2.4.2. Sample extraction procedure

The contaminated wastewaters were acquired in glass bottles of 500 mL from different parts of the industries located in Saudi Arabia, including printing press (Arabian Printing and Publishing House, Lana Printing Press), paper (Gulf Paper Industries Factory Co., Ltd.), textile (FPC Industrial Company), processed food (ARASCO Foods Processing Plant), and laundry (Al Rahdan, Al Jaber). The collected water samples were then filtered through Whatman grade no. 42 filter paper (Maidstone, United Kingdom), and were stored in refrigerator at 4°C until their analysis to avoid any microbial adulteration. The filtration and storage of real samples were made according to the reported paper [13]. To minimize the chances of adsorbing target dye in the filter paper, we had passed a few mL of the real sample through the filter paper before collecting them for experiments. A certain amount of CTAB-MMT clay adsorbents were weighed and packed into the empty Extrelut column of volume 6 mL. To avoid leaking of the adsorbents, two microporous blockers were fitted inside the Extrelut one before pouring the adsorbents and other after pouring the materials. Then the packed adsorbents were washed with Milli-Q water (40 mL) allowing the adsorbent to settle inside the column. Finally, the washed column was dried for 8–10 min under vacuum and it was ready to be used. The stored wastewater samples (20 mL) were taken out from the refrigerator and through the column passed at controlled flow rate. Maintenance of lower flow rate is an important parameter as the adsorption may varied with the contact time of the dye with the adsorbent.

After that, 20–30 mL of Milli-Q water was passed through the column to rinse the adsorbent followed by vacuum dry for 10 min. The adsorbed target dye was then eluted from the Extrelut packing by passing 20 mL basic methanol solution (0.1 N NaOH solution of methanol) at an equal flow rate of 1 mL/min. The eluted sample was evaporated until dryness under nitrogen flow and reconstituted in methanol–aqueous formic acid (75/25, v/v). Finally, the eluted mixture was filtered using 0.22 μm PTFE syringe filter before their injection to the UPLC-MS/MS system. To evaluate the effectiveness of extraction method in terms of RhB recovery, and to investigate the influence of matrix effects, two without-spiked and three spiked wastewater samples, 50% (50 ng/mL), 200% (200 ng/mL), and 500% (500 ng/mL) were analyzed by the standard addition quantification procedure. The percentage indicating the increase of RhB in sample after spiking. The spiking of the RhB was done at the starting of the SPE process.

3. Results and discussion

3.1. Characterization of CTAB-MMT

3.1.1. Fourier transforms infrared spectroscopy

The FTIR spectra of unmodified CTAB modified MMT clay before and after RhB adsorption were studied (Fig. 1). The FTIR spectra of both unmodified and CTAB modified MMT (CTAB-MMT) clay show absorption bands at 462 and 511 cm^{-1} ascribed to bending frequencies of Si–O–Mg and Si–O–Al, respectively. While, band found at 1,071 cm^{-1} was associated with characteristic stretching vibrations of Si–O group [42,43]. The absorption peak at 801 cm^{-1} was confirmed the presence of amorphous silica in the clay materials [44]. A peak at 1,661 cm^{-1} was associated with the H–O–H bond deformation [45]. A broad peak in between the region 3,330 and 3,580 cm^{-1} was ascribed to –OH stretching vibrations of water molecules present in MMT [46].

The CTAB-MMT-RhB presents three new absorption bands in the FTIR spectrum. The peaks located at 2,922 and 2,852 cm^{-1} are ascribed to C–H asymmetric and symmetric stretching vibrations. The third peak that was appeared at 1,480 cm^{-1} ascribed to flexural vibrations of CH$_3$. The CTAB-MMT-RhB also showed a peak at 3,620 cm^{-1} attributed to OH stretching, a typical band for the smectite group [46]. The absorption band of –OH bending vibration of MMT (1,661 cm^{-1}) was moved to 1,710 cm^{-1} for the CTAB-MMT-RhB indicating the increase in hydrophobicity of the modified materials and confirms the incorporation of surfactant cations (mainly hydrophobic) into the clay structure [47]. Additionally, the changes in peak positions of RhB adsorbed CTAB-MMT confirm the adsorption of dyes.

3.1.2. XRD analysis

The diffraction patterns of the powdered MMT and MMT nanocomposite samples were recorded (Figure not shown). The pure MMT clay was clearly shown 2:1 layered structure of smectite class and the peaks at 2θ equals to 19.860° and 27.950° confirms the presence of beidellite in MMT [48]. The addition of CTAB leads to the disappearance of the peak at 2θ = 17.870° which is might due
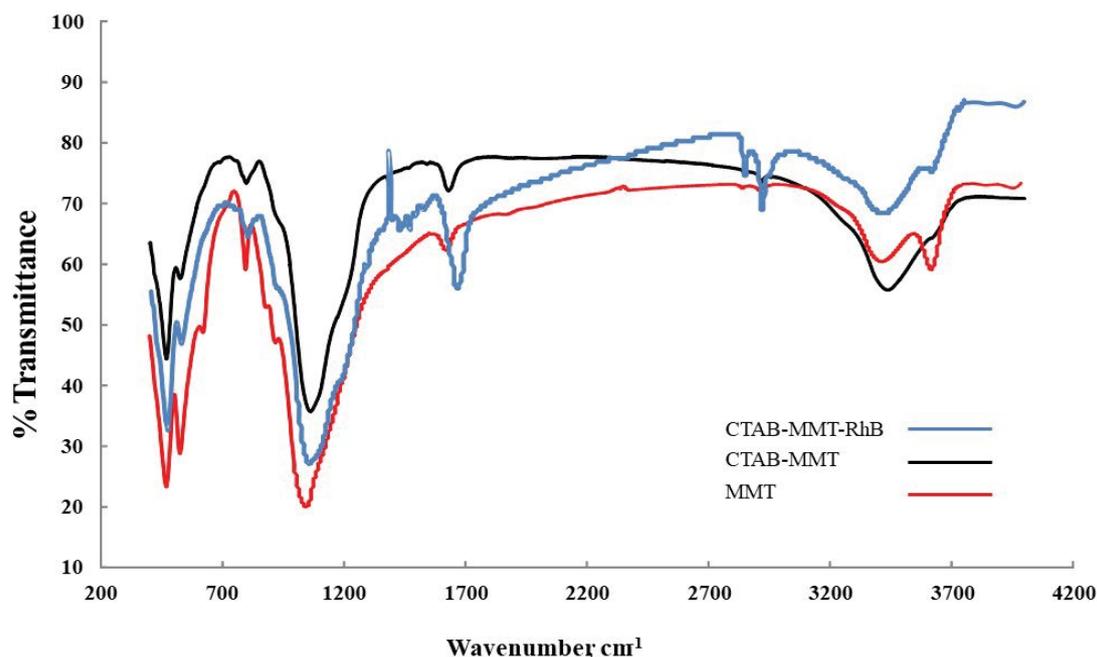
Fig. 1. FTIR spectra of clay (MMT), red color; CTAB modified MMT, black color; and CTAB modified MMT after adsorption of RhB, blue color. FTIR: Fourier transform infrared; CTAB: cetyltrimethylammonium bromide.

to the interruption of the crystallite structure of the clay. In addition, the peak at $2\theta = 26.680°$ of MMT was changed to $2\theta = 26.660°$ of CTAB modified MMT nanocomposite indicating the insertion of CTAB cations between the layers of MMT clay [49]. From the Scherer equation, the mean crystallite sizes of MMT was calculated and found to be changed the size from 80 to 66 nm in the modified MMT nano composite [41].

3.2. Optimization of SPE

Since there are, no earlier studies reported relating to the determination of RhB from wastewater samples using UPLC-MS/MS procedure and SPE. The preliminary studies were performed on standard dye solutions. Once the solution was passed through the CTAB-MMT clay packed Extrelut column, clear physical changes in color of the adsorbents were clearly noticed indicating the adsorption of dye materials (Fig. 2). Various parameters including sample flow and adsorbent dose were optimized to achieve best extraction of the dye. The optimum flow was 0.1 mL/min, and the adsorbent dose was 0.05 g. The desorption of the adsorbed RhB dye was then performed by testing various solvents including, ethyl acetate, acetone, dichloromethane, ethanol, methanol, and the basic solutions of methanol. Among all the tested solvents, basic methanol was successfully desorbed the dye molecules from the SPE sorbents and showed excellent recovery values (98.6%) (Fig. 2) than other eluents. Hence, it was selected as elution solvents. The organic eluents prefer over the inorganic for the easy pre-concentration of the target analyte. The elution of RhB using formic acid as sample modifier to the aforementioned solvents were also checked and the results demonstrated that most of the aforementioned solvents

with formic acid were failed to elute RhB from the sorbent with almost negligible recovery. In the same way, the adsorption–desorption studies for wastewater sample was carried out by passing the samples through the CTAB-MMT packed Extrelut column followed by desorption. Finally, the elutes were injected into the UPLC-MS system.

3.3. Optimization of chromatographic separation

The development of a high-throughput UPLC-ESI-MS/MS based method has been described in the current study. The optimization of chromatographic parameters was performed to avoid the peak tailing and to achieve the best chromatogram with high symmetric peaks. The different chromatographic conditions including columns type, composition of mobile-phase, and flow rate were investigated. Among the tested reversed-phase UPLC columns (Acquity® UPLC BEH C_8, C_{18}, from Waters) better results were obtained with BEH C_{18} columns. The main advantages of selecting the BEH columns, it can produce stability even at lower pH and provide negligible column bleed due to their special built on materials. All these advantages allow the 1.7 μm BEH column to provide extreme performance even in harsh operating condition and is very useful for MS applications [50]. In addition to these, the specially designed new proprietary end-capping of BEH columns was delivered higher efficiencies, sharp peaks, and highest MS sensitivities during the analysis. Rather than BEH column, Acquity® UPLC HILIC (hydrophilic interaction liquid chromatography) column was also investigated and better separation was achieved with BEH column. Hence, in the current studies BEH C_{18} column was selected for the analysis of RhB. The influence of mobile phase was also optimized to achieve best separation with maximum peak intensity. For the same, mobile
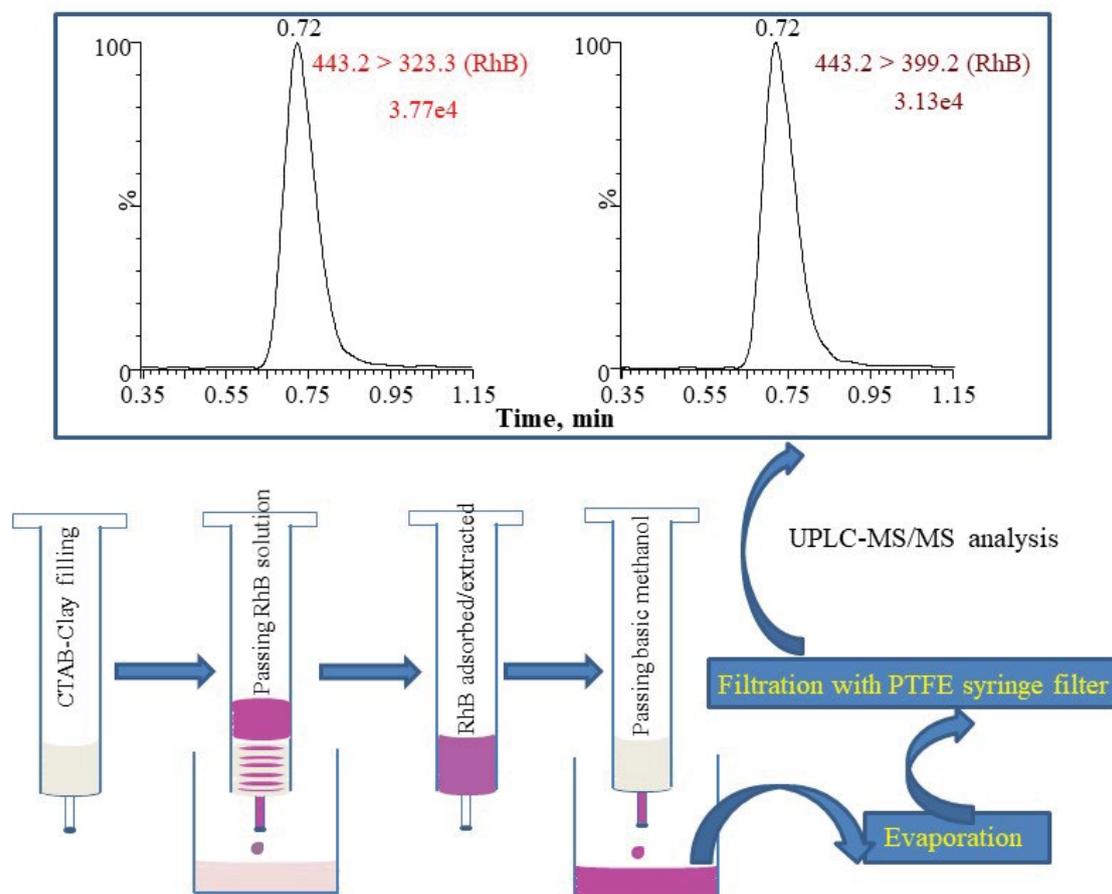
Fig. 2. Proposed methodology for the proposed SPE based UPLC-ESI-MS/MS method.

phases comprising of methanol, water, and acetonitrile individually and as well as with different proportions were tested. It was found that the binary mixture of methanol–aqueous formic acid with the ratio 75/25 (v/v), was provided best results.

The effect of addition of organic modifier such as formic acid (0.2%–0.05%) into the mobile phase was also investigated to see the improvement in the peak shape and its symmetry [50]. The binary mobile phases was flowed both in isocratic and gradient modes and best separation with excellent peak symmetry, good reproducibility, and low detection limit were obtained for target dyes when using mobile phase in isocratic elution mode. The temperature effect of column on the separation of dye was also tested and room temperature was chosen for further experiment. The flow of mobile phase ranging from 0.15 to 0.5 mL/min were tested as well and low mobile phase flow rate of 300 µL/min was selected for the analysis of target compound. Under the optimal experimental conditions, the analysis run time was less than 1 min. The injection volume for all the samples were 1.0 µL.

3.4. Optimization of MS detection parameters

MS conditions for the proposed method were optimized by the direct infusion of standard RB solutions of 20 µg/mL. Comparatively higher concentration of 20 µg/mL was infused to achieve better ionization and detection of the target dye. Both the positive and negative ionization modes were tested in order to receive highest intensity MS signal. The MS full scan analysis was conducted to select the primary precursor ion and optimum cone voltage. Optimum peak response was achieved with highest signal intensity and peak symmetry in the ESI +ve mode. Although, the proton (H$^+$) was not added to the target compounds due to the positive nature of the RB, but the positive ionization helps mainly to build up intensive precursor ions ([M]$^+$) [50]. As a result, the ESI +ve mode was selected for the studied compounds during the experiments. The ESI conditions in terms of source temperature from 100°C to 150°C, desolvation temperature from 150°C to 500°C, desolvation gas flow from 400 to 700 L/h; capillary voltage, 2.5–4.5 kV; collision gas flow from 0.10 to 0.50 L/h; and cone voltage from 1 to 100 V were investigated using direct infusion of target RhB dye. The optimum conditions to achieved best intensity and superior peak symmetry using the following conditions: source temperature, 120°C; desolvation temperature, 300°C; desolvation gas flow, 500 L/h; capillary voltage, 3.2 kV; collision gas flow, 0.20 l/h; and cone voltage, 1–100 V.

To achieve better analysis with quantitation and confirmation, the multiple reaction monitoring (MRM) mode was selected where the acquisition of precursor ions and minimum of two daughter ions were performed [51].

The daughter with higher intensity was chosen for quantification and the daughter with relatively low peak intensity was used for the confirmation of the target dye. The most favorable conditions for MRM analyses are provided in Table 1. The transitions of precursor ion selected in the positive ionization mode were 443.2 > 399.2, 443.2 > 323.3, and the collision energy applied were 38 and 60 V, respectively. The mass spectra and possible fragmentation pattern of RhB dyes have been illustrated in Fig. 3. The high purity nitrogen (99.99%) was produced using a nitrogen generator model NM30LA (Peak Scientific, Inchinnan, United Kingdom) and the argon gas was used as collision. The optimum vacuum for the detector was achieved operating an Oerlikon rotary pump, (model SOGEVACSV40 BI, Cedex, France). For quantification of RhB, the highly intense daughter ion (443.2 > 323.3) was selected between the two transitions and other one was chosen (443.2 > 399.2) for qualitative analysis. All the data analysis was carried out using MassLynx V4.1 software (Waters, Milford, USA).

3.5. Validation of method

The validation of the proposed SPE based UPLC-ESI-MS/MS method was performed using the optimized UPLC-MS/MS parameters. The linearity range, limit of detection (LOD) and limit of quantification (LOQ), run-to-run (repeatability), and day-to-day (reproducibility) precision and recovery values were tested. The linearity was studied over a range of RhB concentrations and it was found to be 2.5–1,000.0 ng/mL. The calibration plot was constructed using the peak area and the concentration of RhB with correlation coefficient (r) value greater than 0.998.

The LOD and LOQ data of the proposed method were calculated based on S/N ratio of 3 and 10, respectively. Both LOD and LOQ parameters for the developed method were found to be 0.24 and 0.82 ng/mL, respectively.

The repeatability (run-to-run precision) experiment of the described UPLC-ESI-MS/MS method was established by injecting six replicate of RhB standard (200.0 ng/mL)

Table 1
MRM conditions applied with the MS/MS system*

Analyte	Precursor ion (m/z)	Quantification		Confirmation	
		Collision energy (V)	Daughter ion (m/z)	Collision energy (V)	Daughter ion (m/z)
RhB	443.2	60	323.3	38	399.2

*Dwell time = 0.025 s, in all cases.
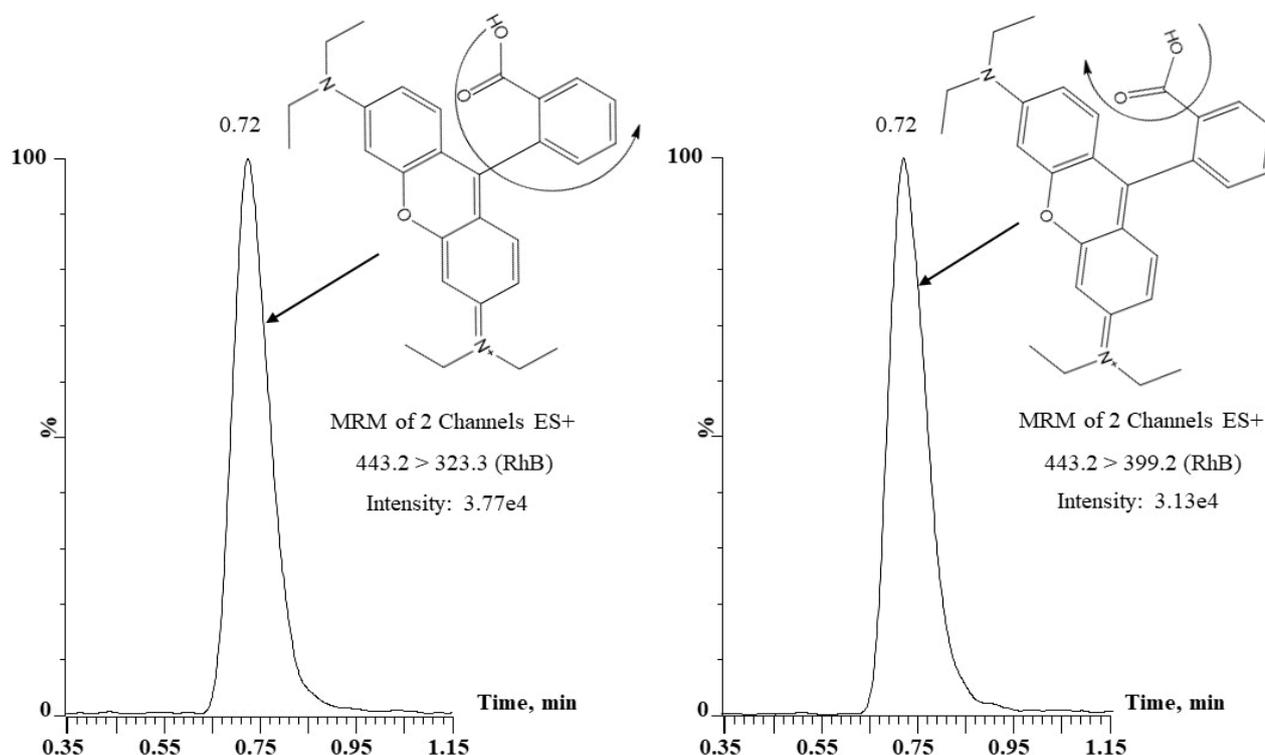
Fig. 3. UPLC-ESI-MS/MS chromatogram of RhB fragmentations (m/z 443.2 > 323.3) and (m/z 443.2 > 399.2) with possible fragmentation pattern.

and a waste sample of known concentration (0.5 mg/mL) on the same day. The repeatability was evaluated using relative standard deviation (RSD, %) of the peak area values and was found to be 2.06% in the analysis of the standard and 2.32% in the analysis of waste sample. In addition, the reproducibility precision was performed by injecting six replicates of the same solutions along six consecutive days. The RSD values found for reproducibility were 2.59% for the standard and 3.88% in the analysis of the waste sample. All these values of the proposed UPLC-MS/MS method indicates that it can be applied for the quantification of trace levels of target analytes in standard and as well as in real samples.

The standard addition methodology was adopted for evaluating the effect of sample matrix on the S/N ratio of RhB. For the same, five real samples were tested and the obtained recovery for RhB were found to be in the range of 99% and 103% (Table 2). The effect of the negligible matrix on the signal of RhB can be attributed to the special Z-spray configuration of the MS ionization source, which restrict the entry of other species into the MS detector.

3.6. Real sample analysis

To authenticate the applicability of the described SPE based UPLC-MS/MS method, it was applied for the analysis of RhB in various wastewater samples collected from waste stream of different industries of Riyadh, Saudi Arabia. The desorption of the RhB from the adsorbent was achieved using basic methanol solution. The obtained experimental results for the quantitative screening of RhB indicated that negligible effects were observed by the investigated sample matrices. The obtained quantities of RhB have been demonstrated in Table 2. The highest level of the dye was found (1.99 μg/mL) in Processed food industry sample. The lowest amount of RhB was found in the paper industry sample. The recovery values were found from 99% to 103% in all of the analyzed waste samples. To avoid any contamination during analysis, the blanks samples were consistently analyzed and negligible contamination was noticed. Fig. 4 represents the UPLC-ESI-MS/MS chromatograms of three processed food industry samples. The proper optimizations of SPE and chromatographic parameters and shape (Z) of ESI source provided a negligible matrix effect. The chromatogram of the real samples indicate that the sample matrix does not modify the target dye signal when analyze in the wastewater samples. The analytical parameters of the proposed method in view of LOD and RSD (%) are compared with other studies [52,53] and are given in Table 3.

4. Conclusions

A fast, sensitive, cost-efficient, green, and dependable technique based on SPE and UPLC-ESI-MS/MS has been established and applied for the quantitative determination of RhB in various wastewater samples collected from different industries. The method is found to be matrix free as a negligible matrix effect was noticed during analysis and it required minimum pre-treatment of the sample without the loss of any target dyes. The extraction of the RHB from aqueous solution was performed using the low-cost SPE method with significant advantages in terms of lower analysis time and lower solvent consumption volume. Additionally, the probability of minimal losses of the target dye helps to deliver better sensitivity to the system. Surfactant CTAB intercalated MMT clay k10 as SPE adsorbent has shown excellent extraction capability for RhB. The proposed method offers higher sensitivity, wide linearity range, good precision, and very rapid analysis with minimal sample pretreatment steps. All the validation data and obtained results using the proposed method confirm the applicability of the method as a new and novel technique for the regular analysis of RhB in industrial waste discharges. Additionally, the described method was found to be more sensitive than the other reported results. In the future, the proposed SPE based UPLC-ESI-MS/MS method could comprehensively be utilized in the efficient extraction and quantitation of various colored pollutants to save all the living creatures from their exposure providing green environment.

Table 2
Amounts of RhB obtained from various industrial wastewaters and recovery results

Sample type	Sample	RhB (μg/mL ± s*)	Recovery values (%)
Laundry	1	1.72 ± 0.44	100
	2	1.28 ± 0.25	102
	3	1.39 ± 0.54	100
	4	1.02 ± 0.14	100
Printing press	1	0.87 ± 0.30	99
	2	0.47 ± 0.12	100
	3	0.69 ± 0.25	100
	4	1.09 ± 0.52	99
Paper industry	1	0.88 ± 0.12	100
	2	0.60 ± 0.07	99
	3	0.45 ± 0.08	101
	4	0.69 ± 0.02	100
Textile industry	1	1.78 ± 0.09	101
	2	0.99 ± 0.10	103
	3	1.08 ± 0.21	101
	4	1.55 ± 0.19	102
Processed food	1	1.99 ± 0.50	103
	2	1.28 ± 0.21	102
	3	1.75 ± 0.59	101
Plastic	1	0.59 ± 0.20	99
	2	1.01 ± 0.15	100
	3	1.25 ± 0.29	101

*Standard deviation attained from standard addition calibration.
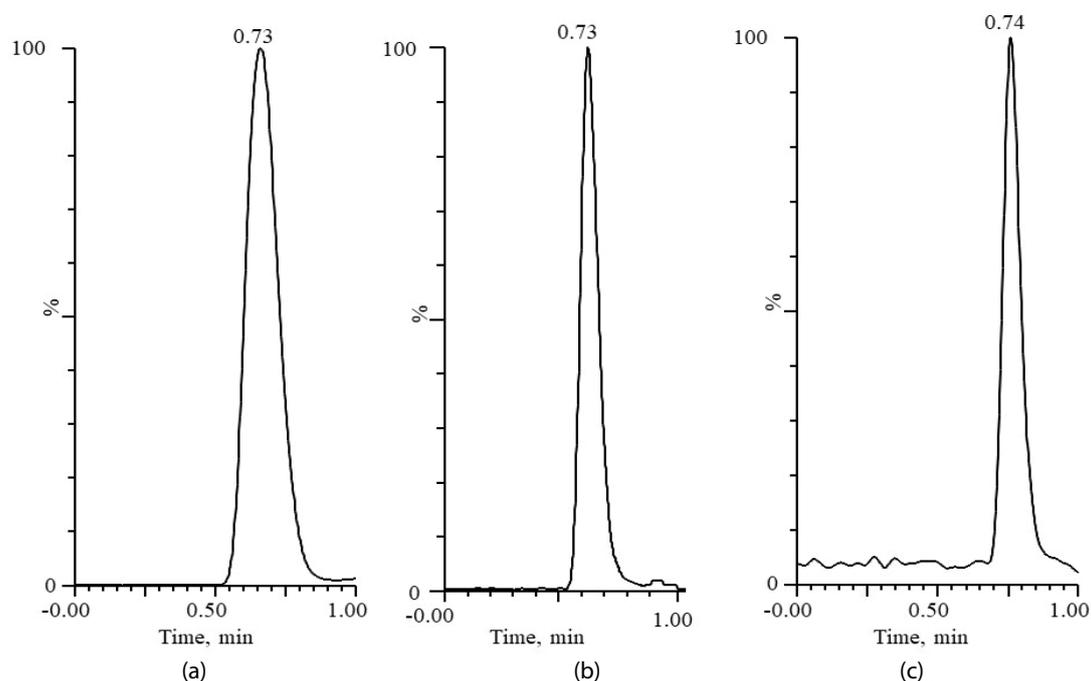
Fig. 4. UPLC-ESI-MS/MS chromatograms of dominant fragmentation (443.2 > 323.3) of RhB in processed food industry sample, (a) sample 1, (b) sample 2, and (c) sample 3.

Table 3
Performance comparison of the proposed method with recent studies on the determination of RhB

Detection method	Preconcentration method	Matrix	Linearity (ng/mL)	LOD, ng/mL	RSD, %	Recovery, %	Reference
UV-Vis	Cloud point/SPE	Industrial, cosmetic, and water	50–5,000 and 100–4,000	0.70/1.20	6.0/5.0	94–106	52
UV-Vis	Dispersive liquid-liquid micro-extraction	Zlack tea, red wine, and chilli powder	5–450	1.93	4.7	88.1–111.6	53
UV-Vis	SPE	Soft drink, wastewater, and lipstick	250–3,000	3.14	5.0	>95	36
HPLC-Vis	Dispersive liquid-liquid microextraction	Environmental waters, soft drink, and cosmetics	5–1,000	1.15	<4.5	100	35
HPLC-FLD	SPE	Wastewater and surface water	2–50 and 50–1,000	0.5	<4	83–85	37
UPLC-ESI-MS/MS	SPE	Waste water	2.5–1,000	0.24	<3.3	99–103	Current paper

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