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Comparison of preconcentration and determination methods of a textile dye by spectrophotometry: cloud point extraction and solid-phase extraction

Yavuz Sürme[a,*], A. Taner Bişgin[a], Mustafa Uçan[a], İbrahim Narin[b]

[a]*Faculty of Arts and Sciences, Department of Chemistry, Niğde University, Nigde 51240, Turkey, Tel. +90 3882254048; Fax: +90 3882250180; email: ysurme@nigde.edu.tr (Y. Sürme), Tel. +90 3882254054; email: atbisgin@nigde.edu.tr (A. Taner Bişgin), Tel. +90 3882254222; email: ucan@nigde.edu.tr (M. Uçan)*
[b]*Faculty of Pharmacy, Erciyes University, Kayseri 38039, Turkey, Tel. +90 3522076666-14273; email: narin@erciyes.edu.tr*

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ABSTRACT

This study deals with the preconcentration, determination, and removal of Lanaset Blue 2R textile dye from aqueous medium by two different methods. For this purpose, cloud point extraction (CPE) and solid phase extraction (SPE) methods were optimized. Amberlite XAD-1180 resin was used as adsorbent for SPE while Tergitol NP-7 non-ionic surfactant was used as surfactant rich phase for CPE. The common optimization steps were determined as initial solution pH, linear dynamic range, sample volume, equilibrium time and limits of detections were characterized for both SPE and CPE techniques while specific optimization steps such as temperature and surfactant concentration were also determined for CPE. The results showed that the CPE and SPE of dye were quantitative at pH 6. Detection limits were 21-μg L^{-1} for CPE and 9-μg L^{-1} for SPE. The enrichment factors were 40 and 10 for SPE and CPE, respectively. The real sample analysis was successfully performed with both techniques. The strengths and weaknesses of the methods were highlighted.

Keywords: Lanaset dyes; Cloud point extraction; Solid-phase extraction; Tergitol NP-7

1. Introduction

Textile dyes are classified into: acid, basic, disperse, direct, and reactive dyes according to their bounding mechanism between dyes and fibers [1]. Industrial textile effluents are important sources of water pollution and environmental contamination because of their huge discharged wastewater volumes [2,3]. The wastewater of textile industry is known to contain strong color. So, the treatment of these waters has been a problem [4]. The discharge of dyes in the water causes the bioaccumulation by organisms in water which may affect human health by transportation of food chain. Therefore, determination and/or removal of dyes from waters are of prime importance for environment and human health.

There are several methods in the literature for the determination of dye molecules from waters such as adsorption [5,6], cloud point extraction (CPE) [7,8], and removal such as biological treatment [9,10], coagulation [11,12], oxidation [13,14] techniques.

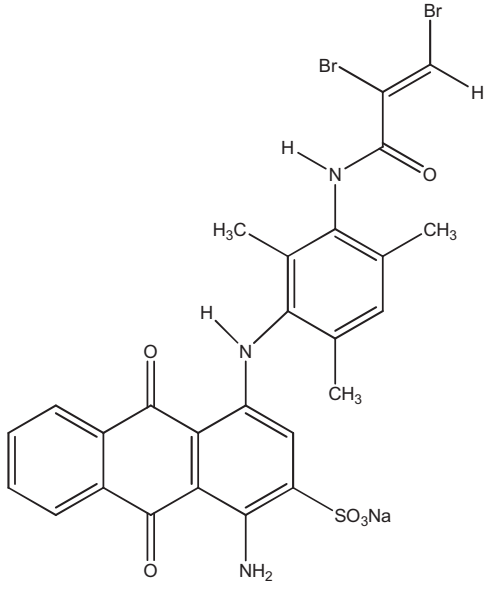
Among these pretreatment options, adsorption and CPE appear to have significant potential for the extraction, determination, and removal of color from waters. The CPE can also be considered as a green analytical technique by limiting the use of toxic organic solvents [15,16].

*Corresponding author.

In CPE, the amphiphilic surfactant molecules, whose head is hydrophilic and tail is hydrophobic are used for preconcentration [17]. Two important properties for CPE are the critical micellar concentration where the surfactant molecules become associated to form micelles [18,19] and the cloud point temperature above which the solution becomes turbid [20]. When the temperature of the solution rises above the cloud point, it is possible to separate into two phases: a surfactant rich phase including the target analytes and an aqueous phase. High enrichment factors can be gained by CPE because of the small volumes of surfactant rich phase [21]. So, it is suitable for preconcentration of dye molecules in waters.

On the other hand, solid phase extraction (SPE) is a separation, purification, and preconcentration method based on adsorption of target analytes onto different resins [22,23] There are two phases in the technique: stationary and mobile phases. Aqueous sample containing target analyte passes through the chromatographic column gravitationally after providing specific conditions for retention of analyte on the resin. Retained analyte is eluted from the resin using appropriate eluents and diluted to desired volume. Therefore, high preconcentration factors can be obtained [24]. This phenomenon makes the method suitable for the enrichment of dyes in waters [25,26].

In this study, Lanaset Blue 2R (LB2R) (Fig. 1) was extracted and determined as a target analyte. The main parameters, affecting extraction, determination, and removal of dye were investigated in detail. The analytical performances of two methods were compared in this work. The characteristics and performance parameters of the methods SPE and CPE and were described and evaluated below.



sodium (*Z*)-1-amino-4-(3-(2,3-dibromoacrylamido)-2,4,6-trimethylphenylamino)-9,10-dioxo-9,10-dihydroanthracene-2-sulfonate

Fig. 1. Chemical structure of LB2R textile dye.

2. Experimental

2.1. Materials

Tergitol NP-7 commonly described as an alkylaryl polyether alcohol (Sigma-Aldrich, USA) is a non-ionic surfactant with a low cloud point of 20°C at 1 wt.%, was used in CPE. LB2R textile dye was provided from a textile factory and used directly. Other chemicals were all analytical grade supplied from Sigma-Aldrich, USA and used without further purification. Amberlite XAD-1180 is a cross-linked, non-ionic, hydrophobic, and polymer adsorbent containing both a continuous polymer phase and a continuous pore phase with a surface area of 450 $m^2 g^{-1}$ purchased from Sigma-Aldrich, USA was used in SPE experiments.

2.2. Methods

CPE experiments were carried out using a 50-mL polyethylene tube with a screw cap containing different concentrations of Tergitol NP-7 surfactant, 5 μg LB2R dye, and/or several auxiliary ions in Nuve BM-402 model thermostatic water bath (Nuve, Turkey) for 30 min of incubation times. After complete phase separation, solution was centrifuged for 5 min with a Nuve NF-400 model centrifuge (Nuve, Turkey) dilute phase was removed and surfactant rich phase was transferred into a 5-mL volumetric glass and dissolved with methanol using a Velp RX3 model vortex mixer (Velp, Italy).

SPE experiments were conducted using 5-μg LB2R dye and auxiliary ions containing aqueous sample solution which were prepared in 50-mL aliquots and passed through the column packed with Amberlite XAD-1180 gravitationally. The retained LB2R was eluted with 5 mL of 1 M HCl in ethanol.

2.3. Analysis

The LB2R concentrations of samples, gained from both methods, were determined by Shimadzu UV-160 A model spectrophotometer (Shimadzu, Japan) at 625 nm. LB2R was initially calibrated separately for different concentrations in terms of absorbance units, which were recorded at wavelength of 625 nm, at which maximum absorption occurred. The presence of Tergitol NP-7 did not significantly affect the λ_{max} of

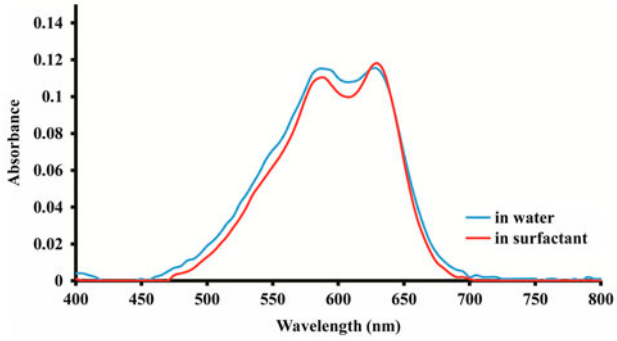


Fig. 2. The UV–vis spectra of LB2R dye in water and surfactant solution.

the dye. Fig. 2 shows the UV–vis spectra of LB2R dye in water and surfactant Tergitol NP-7 solution. Standard calibration curves were used to determine the dye concentrations.

3. Results and discussions

This section is evaluated in two parts. The first part discusses the effects of various operating conditions on the extraction efficiency of LB2R for both CPE and SPE. The second part discusses individual operating conditions of the methods. The results were defined as extraction efficiency of dye (%).

3.1. Effect of pH

The effect of solution pH on the recovery of the LB2R dye for CPE and SPE is shown in Fig. 3. The recovery values were not quantitative at acidic and basic pH values while the recoveries were over 90% when the pH of the sample solution ranged from 5.0 to 7.0 for CPE and SPE methods according to obtained results.

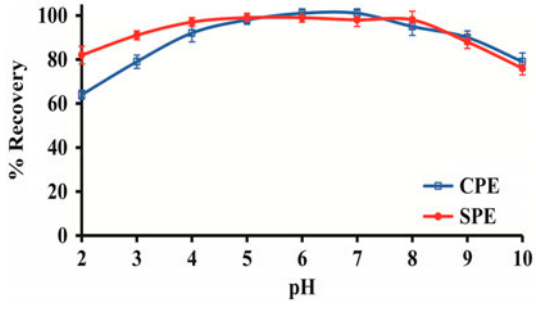


Fig. 3. Effect of solution pH on the recovery of LB2R for CPE and SPE (CPE: temperature: 30°C, dye: 5 μg, surfactant concentration: 0.3%, 5 min of centrifugation, eluent methanol. SPE: dye: 5 μg, eluent 1-M HCl in ethanol, $N = 4$).

These results can be explained by the characteristics of the dye molecules in solution. The adsorption and retention of the dye molecules were negatively affected at acidic and basic pH values at SPE method so the recoveries decreased while the reactivity and micelle formation mechanism were also affected at acidic and basic pH values at CPE method. On the other hand, these mechanisms and electrostatic interactions between dye and adsorbent were not significantly affected from the pH at neutral range. So, the optimal pH of 6 was chosen at which the recovery values were up to 95% for both methods.

3.2. Linear dynamic range

In a SPE or CPE analysis, it is prime important to determine the linear dynamic range to ensure the capability of extraction method. The linear dynamic range can be defined as the concentration range over which absorbance and concentrations remain directly proportional to each other. For this purpose, LB2R solutions were prepared at pH 6.0 and proposed CPE and SPE methods were applied. The results showed that the linear dynamic ranges for CPE and SPE were obtained as linear between 1 and 25 μg mL^{-1} concentrations with the regression equation of $A = 0.0073C + 0.0012$, $R^2 = 0.9997$ for CPE and 1–10 μg mL^{-1} $A = 0.0103C + 0.0007$, $R^2 = 0.9993$ for SPE (A: absorbance, C: concentration). Wide linear dynamic range allows the analysis of a wide range of sample concentrations and reduces sample preparation requirements. In our experiments, CPE allowed a wider detection range than the SPE.

3.3. Effect of interfering ions

The effects of some common ions which may interfere the CPE and SPE were investigated (Table 1).

3.4. Other optimization parameters for CPE and SPE

Extraction efficiency parameters of CPE technique were evaluated by equilibrium time, surfactant volume, effect of temperature, and sample volume. All experiments were conducted on the basis of changing one variable at one time while the others were used as fixed amounts and/or values. The results are given in Fig. 4.

The cloud point temperature of Tergitol NP-7 surfactant is one of the smallest values among the non-ionic surfactants. In our experiments, the best recovery values were gained at 30°C of solution temperature at which the values were higher than

Table 1
Influences of some ions on the recoveries of LB2R in the presence of 5 μg LB2R dye ($N = 4$)

Ion/dye	Added as	Concentration (μg mL^{-1})		% Recovery	
		SPE	CPE	SPE	CPE
Ni^{2+}	$Ni(NO_3)_2{\cdot}6H_2O$	100	100	94 ± 3	95 ± 2
Cd^{2+}	$Cd(NO_3)_2{\cdot}6H_2O$	100	100	103 ± 5	101 ± 2
Pb^{2+}	$Pb(NO_3)_2$	100	100	101 ± 2	99 ± 3
Co^{2+}	$Co(NO_3)_2{\cdot}6H_2O$	100	100	97 ± 1	98 ± 2
Cu^{2+}	$Cu(NO_3)_2{\cdot}5H_2O$	100	100	101 ± 1	99 ± 2
Cr^{3+}	$Cr(NO_3)_3{\cdot}3H_2O$	100	100	106 ± 3	102 ± 3
Al^{3+}	$Al(NO3)_3{\cdot}9H_2O$	1,000	1,000	94 ± 2	95 ± 1
Na^{+}	$NaNO_3$	2,000	2,000	95 ± 4	96 ± 2
K^{+}	KNO_3	2,000	2,000	99 ± 0	100 ± 1
Ca^{2+}	$CaCl_2$	2,000	2,000	100 ± 2	98 ± 2
Mg^{2+}	$Mg(NO_3)_2{\cdot}6H_2O$	2,000	2,000	99 ± 5	99 ± 2
Zn^{2+}	$Zn(NO_3)_2$	100	100	97 ± 1	95 ± 3
NO^{3-}	$NaNO_3$	2,000	2,000	98 ± 2	98 ± 2
SO_4^{2-}	Na_2SO_4	500	500	97 ± 3	96 ± 2
Cl^{-}	NaCl	2,000	2,000	95 ± 4	95 ± 2

95%. Above 30˚C, the recovery values decreased. This may be attributed that the temperature affected the equilibrium between micelles and monomers to the monomers side. The concentration of the Tergitol NP-7 is another important parameter for optimization of dye extraction. The Fig. 4 showed that 0.30% of final surfactant concentration (from 2% stock solution) was enough for quantitative extraction. Because of centrifugation step, volume of the test solution was the only limitation for CPE procedure. A concentration of 10, 15, 25 mL and a maximum of 50 mL of test solutions were prepared and the CPE was performed.

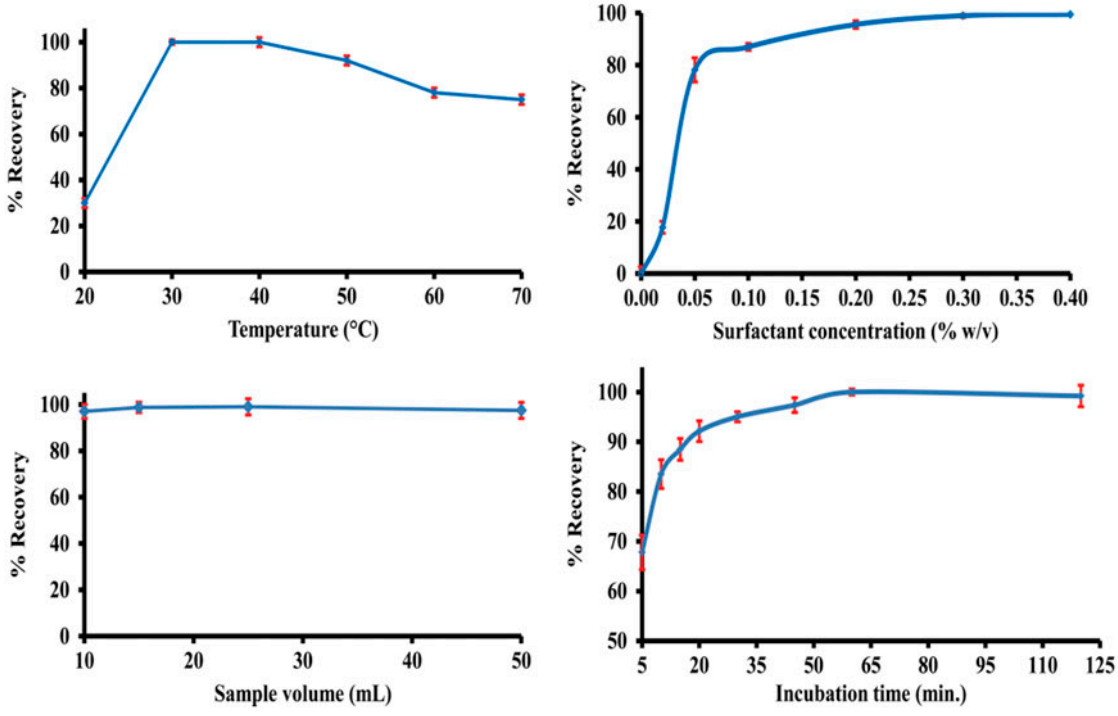


Fig. 4. Effect of temperature, surfactant volume, sample volume, and equilibrium time on the recovery of LB2R dye. (Dye: 5 μg, surfactant concentration: 0–0.4%, 5 min of centrifugation, eluent methanol, $N = 4$).

The results showed that the recovery values were up to 95% at experimented volumes. Another important parameter for the optimization was the equilibrium time. According to the results, the recoveries were higher than 90% after 25 min of incubation and 30˚C bath temperature. As a result, the optimal values of CPE were 30˚C, 0.3% of Tergitol NP-7 surfactant concentration, 50 mL sample solution, and 30 min of incubation time.

Four important optimization steps were performed for SPE. The optimal sample solution volume, sample flow rate, eluent flow rate, and eluent type were investigated in order to obtain recovery as high as possible. Experiments were conducted by changing one variable at a time basis.

The results are given in Fig. 5.

As it is showed in Fig. 5, the recovery values were quantitative up to 200 mL of sample volume. The solution was passed through the column at 1–10 mL min^{-1} to determine the sample flow rates and the values were quantitative at 1, 2, and 3 mL min^{-1}. The recoveries decreased after 3 mL min^{-1} because some of the dye molecules had left the column before reaching the adsorption equilibrium between dye and solid phase Amberlite XAD-1180. Different eluents were used to collect the adsorbed dye molecules. Among these eluents given in Fig. 5, 1-M HCl in ethanol was the only successful eluent whose recovery value was 99% ± 3. The flow rate of this eluent was also studied and found that 1 and 2 mL min^{-1} flow rates were quantitative for elution of LB2R dye from the adsorbent. Consequently, 200-mL sample solution volume, 2-mL min^{-1} sample flow rate, 1-M HCl in ethanol, and 2-ml min^{-1} eluent flow rate values were chosen as optimal values.

3.5. Detection and quantitation limits

Detection limits (DL) and quantitation limits (QL) of LB2R for CPE and SPE methods were calculated after application of the procedures to blank solutions under optimal conditions. DL and QL are used to describe the smallest concentration of an analyte that can be reliably measured by an analytical procedure [27]. These limits were calculated as the concentration equivalent to 3 and 10 times the standard deviation (n = 20) of the blank solutions for DL and QL, respectively. DL of the proposed preconcentration methods were calculated as 21 and 9-μg L^{-1} while the QL values were found as 58 and 21-μg L^{-1} for CPE and SPE, respectively. Analytical characteristics of the methods are given comparatively in Table 4.

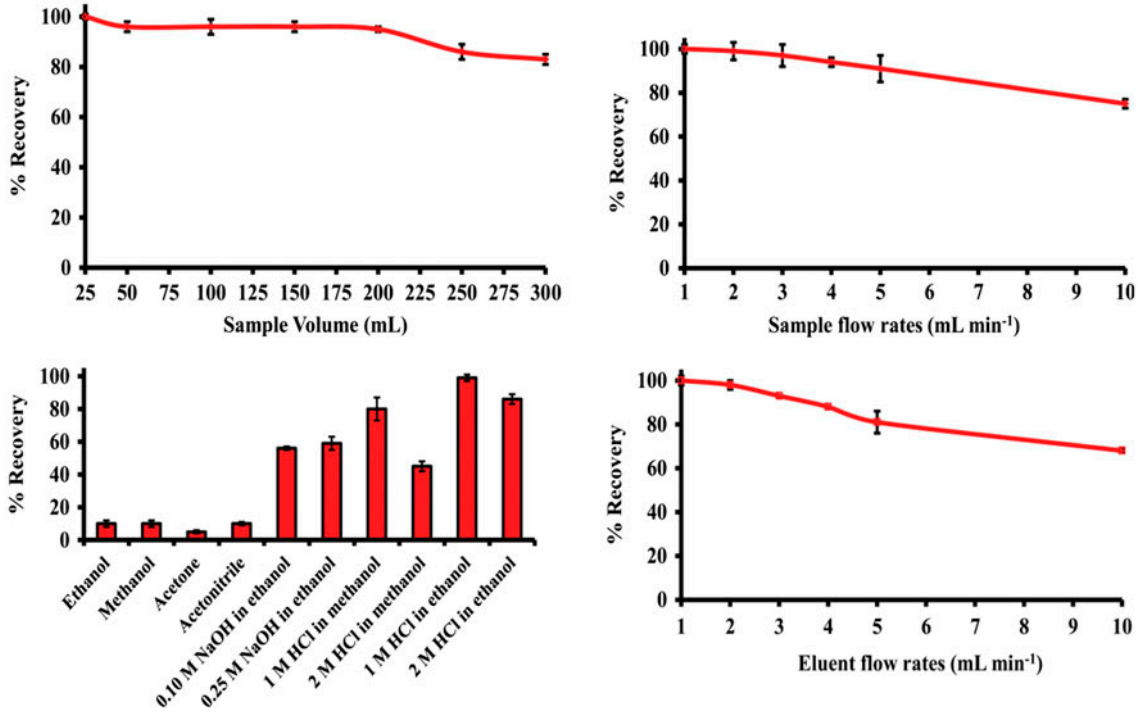


Fig. 5. Effect of sample volume, sample, and eluent flow rate and eluent type on the recovery of LB2R dye. (dye: 5 μg, N = 4).

Table 2
Influences of some dye matrixes (including λ_{max}) on the recovery of LB2R, ($N = 4$)*

Dye matrix I			Dye matrix II			Dye matrix III		
[a]Dye	Ratio	% Recovery CPE/SPE	Dye	Ratio	% Recovery CPE/SPE	Dye	Ratio	% Recovery CPE/SPE
L.Y.	1:1	99 ± 2/100 ± 3	L.Y.	$\frac{1}{1:1:1}$	99 ± 3/98 ± 3	L.Y.	$\frac{1}{1:1:1:1:1:1}$	106 ± 3/105 ± 2
L.G.	1:1	101 ± 2/100 ± 2	L.O.			L.O.		
B.B.	1:1	104 ± 4/105 ± 4	L.R.			L.R.		
L.O.	1:1	98 ± 3/100 ± 2	B.B.	$\frac{1}{1:1:1}$	105 ± 2/104 ± 5	B.B.		
L.R.	1:1	98 ± 2/97 ± 3	L.G.			L.G.		
M.B.	1:1	103 ± 3/105 ± 5	M.B			M.B.		

[a]λ_{max} L.Y.: 438 nm, L.G.: 590 nm, B.B.: 601 nm, L.O.: 416 nm, L.R.: 501 nm and M.B.: 665 nm.
*($x_{avr} \pm sd$).

3.6. Dye matrix and real sample analysis

The effects of some other dyes on the extraction processes should also be evaluated when the analyte is a dye molecule. In order to determine the effect of different dye molecules on the extraction of LB2R, a three set of dye matrix was prepared. The first set was only one dye containing matrix and the LB2R was mixed in the same concentration, the second set was including three different dye matrixes and the LB2R, the third set was a combination of all matrix dyes and LB2R analyte. The CPE and SPE procedures were applied to these dye mixtures under optimal conditions and the results are given in Table 2.

Matrix dyes used in the experiments were Lanaset Yellow (L.Y.), Lanaset Grey (L.G.), Basic Blue 41 (B.B.), Lanaset Orange RN (L.O.), Lanaset Red (L.R.), and Methylene Blue (M.B.) and their amounts were same with the analyte LB2R dye which was 5 μg. According to results, Lanaset dyes did not affected the recovery values for CPE and SPE. On the other hand, B.B and M.B dyes slightly raised the recovery values. It was obvious that some matrix dyes extracted with analyte LB2R. But the maximum absorbance wavelengths of Lanaset series were not relatively close to our target dye molecule. While the wavelengths of M.B and B.B were close to LB2R molecule which may cause a slight raise on the recovery values in the presence of M.B and B.B. On the conclusion, different dye matrixes did not significantly affect the CPE and SPE procedures.

The real sample analyses were conducted with and without adding analytes on the two different water samples. First sample was a wastewater collected from a textile factory and the second one was water used in a textile dye process. In the first step, CPE and SPE methods directly applied to 50 mL of each samples under optimal conditions. In the second step, 10 μg and 20-μg LB2R added to the samples and CPE and SPE was performed. Obtained results are given in Table 3. Results of real samples were calculated for 50-mL sample volume and given as μg.

The LB2R analyte was successfully extracted from wastewater and dye process water samples. It couldn't be observed any LB2R in the wastewater samples even after CPE and SPE without adding analyte. But 11.6 and 11.5-μg LB2R found in process water sample by CPE and SPE, respectively. Satisfactory recovery values were also gained after adding 10 and 20-μg analyte to the water samples.

Table 3
Real water sample analysis and recovery studies with CPE and SPE methods, ($N = 4$)*

Sample	Added (μg)	Found (μg)		Recovery (%)	
		SPE	CPE	SPE	CPE
Waste water from textile factory	–	BDL	BDL	–	–
	10.0	10.1 ± 0.5	9.9 ± 0.4	101 ± 5	99 ± 4
	20.0	20.0 ± 0.5	20.2 ± 0.6	100 ± 2	101 ± 3
Dying process water	–	11.6 ± 0.2	11.5 ± 0.4	–	–
	10.0	21.2 ± 0.4	21.6 ± 0.4	98 ± 2	100 ± 2
	20.0	30.0 ± 0.6	30.1 ± 0.5	95 ± 2	96 ± 2

*($x_{avr} \pm sd$), BDL: below detection limit.

Table 4
Comparison of the optimization characteristics of two methods

Parameters	CPE	SPE
pH	6.0	6.0
Eluent	Methanol	1 M HCl in ethanol
Sample volume	50 mL	200 mL
Preconcentration factor	10	40
Detection limit	21 μg L^{-1}	9 μg L^{-1}
Limit of quantification	58 μg L^{-1}	21 μg L^{-1}
Linear dynamic range	1.25–25 μg mL^{-1}	1–10 μg mL^{-1}
RSD (%)	<7	<5

Table 5
Some recent dye extraction and determination studies by UV–vis

Detection system	Method	Determined dye	LOD (μg L^{-1})	% RSD	PF	Reference
HPLC-UV	CPE	Sudan (I–IV)	4	3	20	[28]
UV–vis	CPE	Orange II	0.67	1.49	10	[29]
UV–vis	CPE	Sunset yellow	5	1.49	33.3	[30]
UV–vis	SPE	Sunset yellow	2	7	60	[31]
UV–vis	SPE	Tartrazine	3.4	–	5	[32]
UV–vis	SPE	Sunset yellow	5.2	3.9	150	[33]
UV–vis	CPE/SPE	Lanaset Blue 2R	21/9	7/5	10/40	Present study

3.7. Comparison of proposed methods

An overall comparison for optimization procedures were given in Table 4.

As it can be seen from Table 4, linear dynamic range of CPE was higher than SPE while the limit of quantification was smaller for SPE. The optimum sample volume of SPE was 200 mL which allowed a higher preconcentration factor than CPE for determination of LB2R.

The obtained analytical parameters of studied methods were compared with other studies in the literature and are shown in Table 5.

According to Table 5, the obtained results in the present study both with SPE and CPE methods are compatible with the results of some dye extraction and determination results of the literature.

4. Conclusion

This work introduces a comparison of two simple, fast, and reliable methods for the determination and removal of LB2R dye in real water samples.

Based on the good recovery and precision of the method, CPE technique using Tergitol NP-7 surfactant has high analytical potential for the preconcentration and removal of organic dye LB2R from wastewater samples. To the best of our literature survey, this is the first attempt to use Tergitol NP-7 as micelle source for CPE of LB2R dye molecules.

Both methods successfully determined and removed the LB2R analyte from test solutions and real water samples. SPE was a time-consuming process while the CPE was much faster but three times higher sample volumes could be examined by SPE.

On the conclusion, LB2R dye was determined and removed by CPE and SPE and the proposed methods may be useful for preconcentration and determination of LB2R from aqueous samples.

Acknowledgments

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