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ORIGINAL ARTICLE

# Simultaneous determination of five commercial cationic dyes in stream waters using diatomite solid-phase extractant and multivariate calibration

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## KEYWORDS

Commercial cationic dyes;  
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**Abstract** A simple spectrophotometric method was developed for the simultaneous determination of five commercial cationic dyes at  $2.0\text{--}8.5\ \mu\text{g L}^{-1}$  level after using diatomite as solid-phase extractant. The method is based on preconcentration of the five dyes on natural diatomite solid-phase extractant and on multivariate calibration using partial least squares method (PLS-1). Compared with commonly used chromatographic or electrophoretic methods the developed method is simple and sensitive. With enrichment factors between 89 and 96, diatomite outperformed zeolite and activated carbon for dyes preconcentration. Before preconcentration and using PLS-1 method, the cationic dyes were simultaneously analyzed with linear ranges of 0.18–4.5, 0.32–5.0, 0.23–4.5, 0.45–8.0 and 0.82–12.0  $\text{mg L}^{-1}$  for crystal violet, malachite green, methylene blue, safranin O, and thioflavin T, respectively. The detection limits of dyes were estimated using Lorber's method and found to be within the range 43–245  $\mu\text{g L}^{-1}$ . The proposed SPE/PLS-1 method was applied to spiked stream water samples with good accuracy (79–91%) and precision (RSD 1.8–7.3%) but with slightly lower enrichment factors (80–92).

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## 1. Introduction

Natural and synthetic dyes are heavily used in many industries including food, cosmetics, textiles, pharmaceuticals, and leather tanning (Crini, 2006). Unlike natural dyes synthetic dyes are toxic at high concentrations (Crini, 2006). It has been shown that some synthetic dyes and their degraded products are hazardous on human health (Pérez-Urquiza et al., 2000). According to their chemical structures, dyes can be classified as acidic and basic dyes. Basic dyes (cationic dyes) are water-soluble with positive charge that are widely applied to acrylic fibers and paper but rarely applied to wool and silk. Cationic dyes are toxic even at trace levels (Crini, 2006), for example,

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the concentration of malachite green (cationic dye) should not exceed  $1.0 \mu\text{g L}^{-1}$  in drinking water and  $100 \mu\text{g L}^{-1}$  in potable waters (Šafařík and Šafaříková, 2002).

Recently, several papers have outlined the separation and determination of dyes (cationic and anionic) using liquid chromatography/mass spectrometry, capillary electrophoresis/mass spectrometry, and ion-pair HPLC/UV-vis (Farry et al., 1997; Schönsee et al., 1997; Riu et al., 1998; Vaněková et al., 2007). Analytical methods based on sensitive instruments like HPLC/MS or CE/MS were often slow and associated with high running and maintenance costs and the need for expert analysts. Therefore, simpler analytical methods were developed to replace the current analytical methods. The chemometric methods (also known as multivariate calibration methods) were successfully applied to analyze mixtures containing many solutes without the need for prior separation or sample clean up procedures (Beebe and Kowalski, 1987; Haaland and Thomas, 1988; Dinç et al., 2002). Among the reported multivariate calibration methods, principle component regression (PCR) and partial least squares (PLS, type 1&2) calibration methods were the most effective for mixtures resolution with a high degree of accuracy (Goicoechea and Olivieri, 2000; Hemmateenejad et al., 2007). However, a very limited number of publications appeared on using multivariate calibration for analyzing dye mixtures (Dinç et al., 2002; Şahin et al., 2006; Peralta-Zamora et al., 1998). To the best of our knowledge, the application of multivariate calibration for analyzing complex mixture of crystal violet, malachite green, methylene blue, safranin O, and thioflavin T has not been reported in the literature.

Usually, cationic dyes are present in natural and treated wastewater and even in potable waters at  $\mu\text{g}$  or  $\text{ng}$  per liter (Šafařík and Šafaříková, 2002), therefore, a preliminary preconcentration step is essential before analysis using instruments of moderate sensitivity. A good option for cationic dyes preconcentration is the application of solid-phase extraction SPE technique because this technique has many advantages such as low running cost, speed, low solvent consumption, and ensures high enrichment factors (Korn et al., 2006). The important point in any SPE study is the proper selection of the extractant that yields high enrichment factors for all solutes of interest using minimum sample volume (Korn et al., 2006). Many solid extractants such as C18, inorganic cation exchangers, and many functionalized polystyrene-divinylbenzene polymers were used for anionic dyes preconcentration (Riu et al., 1998), however, few extractants were used for the preconcentration of cationic dyes from wastewater (Šafařík and Šafaříková, 2002). Commercially activated carbon, natural zeolite and natural diatomite are also effective adsorbents for cationic dyes (Crini, 2006), therefore, these materials are expected to work as effective extractants for dyes at trace levels.

This work describes the development of SPE-multivariate calibration procedure for simultaneous spectrophotometric determination of crystal violet, malachite green, methylene blue, safranin O, and thioflavin T at  $\mu\text{g L}^{-1}$  level. To achieve the highest enrichment factor for dyes, three solid-phase extractants are evaluated, namely, activated carbon, zeolite and natural diatomite. Finally, the proposed analytical method was applied for analysis of the five cationic dyes in stream water samples.

## 2. Experimental

### 2.1. Instrumentation and software

The absorbance measurements were obtained using a double-beam spectrophotometer (Cary 50 UV-vis spectrophotometer, USA). The spectra of dyes were recorded over the wavelength range of 200–800 nm and the absorbance values were transferred to a Pentium (IV) personal computer for further analysis. Data treatment and mathematical calculations were carried out using MATLAB (version 6.1). pH measurements were carried out using digital pH meter (WTW-Inolab, Germany).

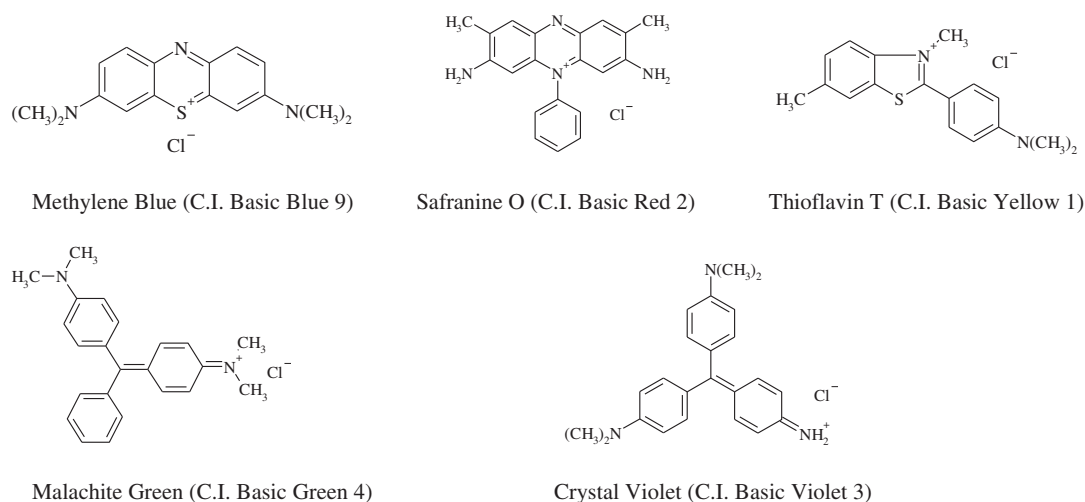
### 2.2. SPE materials and dyes

Zeolite and diatomite were kindly donated from the Natural Resources Authority (Amman, Jordan). The samples were crushed and sieved into different particle size ranges using standard sieving apparatus (Endecotts Ltd., London, England). The sieved samples were washed several times with deionised water, dried at  $100^\circ\text{C}$  for 24 h, and allowed to cool in a desiccator. Extraction tests were conducted using 63–125  $\mu\text{m}$  particle size range. Chemical composition, electron micrograph, infrared spectra, and mineral constitution of zeolite and diatomite were provided by the Natural Resources Authority. The scanning micrographs of diatomite samples indicate the presence of both centric and pennate types of diatom. The centric diatoms have a radius of approximately 10  $\mu\text{m}$ , while the length of the pinnate shape is greater than 20  $\mu\text{m}$ . The chemical composition of zeolite (wt%) was:  $\text{SiO}_2$  74.3,  $\text{Al}_2\text{O}_3$  13.6,  $\text{Fe}_2\text{O}_3$  5.3, and  $\text{Na}_2\text{O}$  4.2. For zeolite, the analysis confirmed the presence of philipsite as a major mineral and fassaite as a minor mineral. The chemical composition of zeolite was (wt%):  $\text{SiO}_2$  56.47%,  $\text{Al}_2\text{O}_3$  19.13%,  $\text{Fe}_2\text{O}_3$  7.13%,  $\text{CaO}$  1.10%,  $\text{MgO}$  1.53%,  $\text{K}_2\text{O}$  3.22%,  $\text{Na}_2\text{O}$  0.53%, and LOI (loss on ignition) 11.41%. Activated carbon was purchased from the Calgon Company (Pittsburgh, Pennsylvania, USA). The bulk density and the porosity of the adsorbent were  $0.64 \text{ g cm}^{-3}$  and 0.4, respectively. The chemical composition of activated carbon was (wt%): C 86.5, H 6.2, and O 7.3. The carbon was also sieved to particle range of 63–125  $\mu\text{m}$ .

Five cationic dyes that have a wide industrial application were selected, namely, crystal violet, malachite green, methylene blue, safranin O, and thioflavin T. The dyes in their pure form (>99% purity) were purchased from Aldrich. The chemical structures of dyes were illustrated in Fig. 1.

### 2.3. Reagents and samples

Standard stock solutions ( $150 \text{ mg L}^{-1}$ ) of dyes were prepared individually by dissolving  $0.150 (\pm 0.001) \text{ g}$  in double-distilled water in a 1000 mL volumetric flask. Dilute solutions were prepared by the serial dilution of the above stock solution using double-distilled water. Acetate buffer (1.0 M, pH 5.0) was prepared by mixing solutions of acetic acid and sodium acetate, the volume of the mixture was diluted to one liter. The stream water was obtained by mixing many portions collected from three different locations on different days. The streams were located within Al-Zarqa area. The samples were stored in polyethylene bottles at  $10^\circ\text{C}$ . Before use, the samples were filtered



**Figure 1** Chemical structures of basic (cationic) dyes.

through a cellulose membrane filter (Millipore) of 0.45 mm pore size to remove any suspended matter.

#### 2.4. Calibration and prediction sets for multivariate calibration

Calibration set is used to build the model, while the effectiveness of the proposed model for prediction is testified in the validation set. Due to the high spectral overlap between dyes (51–98%) a large number of calibration samples are necessary. Typical one-compound calibration experiments (univariate calibration) were carried out to establish the concentration ranges for dyes determination in the mixture. Twenty-five standard mixtures of dyes were prepared at pH 5. To reduce the collinearity in the absorption data, the design for calibration set was based on four-level fractional factorial design according to Brereton's procedure (Brereton, 1997). The prediction set was made of 10 mixtures and its design was selected randomly. The concentration ranges of dyes were: 0.18–4.5, 0.32–5.0, 0.23–4.5, 0.45–8.0, and 0.82–12.0 mg L<sup>-1</sup> for crystal violet, malachite green, methylene blue, safranin O, and thioflavin T, respectively. For better calibration results, the spectral range 280–800 nm was selected. Each spectrum contains 261 spectral points and the spectral data below 280 nm were excluded to avoid any light absorption by the solvent or other components present in the stream water. Within the 280–800 nm region, all dyes absorb effectively. Therefore, the dimension of calibration matrix (*A*) is 25 × 261. It is advisable that the concentration ranges of dyes in the prediction set within the range were used in the calibration set.

#### 2.5. Extraction studies

In a typical solid-phase extraction procedure, a polyethylene tube (1 cm diameter and 10 cm height) is packed with few hundred mg of the extractant of interest and washed three times with double-distilled water. Next, a portion of dyes solution (200–1000 mL, buffered at 5.0 using 0.5 M acetic acetate/sodium acetate) containing 5 µg L<sup>-1</sup> of dyes is passed through SPE column under an appropriate flow rate. After that, the trapped dyes are eluted with a portion of 0.02 M HNO<sub>3</sub>. The

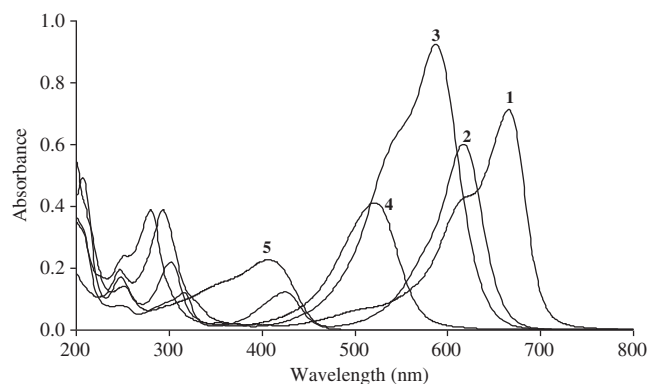
concentrations of dyes in the eluate were simultaneously determined spectrophotometrically using multivariate calibration. The extraction tests were carried out under controlled flow rates using Visiprep vacuum manifold (Supelco, USA).

### 3. Result and discussion

#### 3.1. Spectral overlap and importance of multivariate calibration

Separation of cationic or anionic dyes from wastewater can be carried out using high performance liquid chromatography (HPLC), liquid chromatography/mass spectrometry (LC-MS), capillary electrophoresis (CE), and gas chromatography/mass spectrometry (GC-MS) (Pérez-Urquiza et al., 2000; Šafařík and Šafaříková, 2002; Farry et al., 1997; Schönsee et al., 1997; Riu et al., 1998; Vaněková et al., 2007). However, chromatographic determination of dyes does take much longer analysis and require prior separation and clean-up steps because of the large spectral or chromatographic peak overlap. Multivariate calibration methods such as principal component regression (PCR) and partial least squares (PLS) have been applied to resolve complex spectra and chromatograms successfully (Hemmateenejad et al., 2007; Şahin et al., 2006). The advantages of applying multivariate calibration methods are to minimize or even eliminate sample preparation and solutes separation steps (Brereton, 1997). The zero-order absorption spectra of cationic dyes are presented in Fig. 2. As can be seen in Fig. 2, a high degree of spectral overlap occurs between dyes. The method used by Goicoechea and Olivieri was used to estimate the degree of spectral overlap between dyes (Goicoechea and Olivieri, 1998).

The extent of absorption spectral overlap between pairs of dyes was: 95%, 89%, 78%, 71%, 59%, 83%, 61%, 89%, 52%, and 51% for methylene blue–malachite green, methylene blue–crystal violet, methylene blue–safranin O, methylene blue–thioflavin T, malachite green–crystal violet, malachite green–safranin O, malachite green–thioflavin T, crystal violet–safranin O, crystal violet–thioflavin T, and safranin O–thioflavin T, respectively. The above values indicate a significant spectral overlap between the absorption spectra of dyes. For

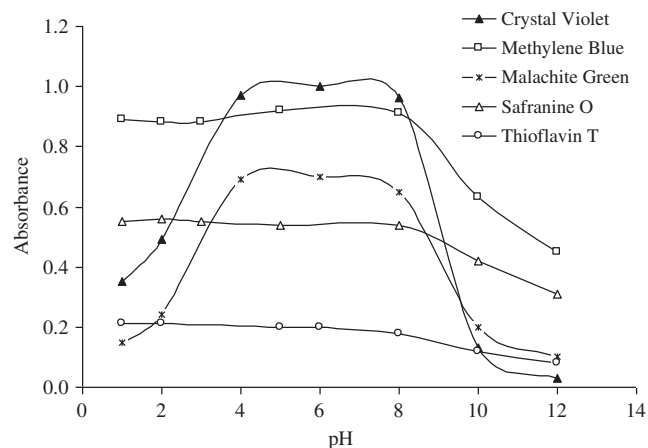


**Figure 2** Absorption spectra of basic dyes at pH 5. (1) Methylene Blue ( $4 \text{ mg L}^{-1}$ ); (2) Malachite Green ( $4 \text{ mg L}^{-1}$ ); (3) Crystal Violet ( $4 \text{ mg L}^{-1}$ ); (4) Safranin O ( $4 \text{ mg L}^{-1}$ ); (5) Thioflavin T ( $6 \text{ mg L}^{-1}$ ).

all systems, the overlap was more than 50%. Methylene blue showed a large overlap with other dyes and the highest overlap (95%) was obtained with malachite green. On the other hand, Safranin O–thioflavin T system exhibited the least overlap of 51%. Due to the significant spectral overlapping, conventional calibration procedures would have a limited application for quantitative determination of this complex system. Therefore, the simultaneous determination of these dyes requires: (a) the use of a separation technique such as HPLC and CE, or (b) the application of multivariate calibration for resolution of this complex system. The second option was chosen, owing to its simplicity, rapidity and low cost.

### 3.2. Determination of cationic dyes by multivariate calibration

Solution pH and ionic strength are the most significant factors that affect absorption properties of dyes. For better analytical sensitivity, the absorption measurements of dyes should be carried out at a pH where the maximum absorption occurs. The effect of solution pH on dyes absorption was studied over a wide pH range (1–12) and at constant solution ionic strength (0.01 M NaCl). Fig. 3 shows the absorbance–pH plots for



**Figure 3** Absorbance–pH plot. Measurements were recorded at  $\lambda_{\text{max}}$  for each dye and at  $5.0 \text{ mg L}^{-1}$ .

the five dyes in which absorbance was recorded at  $\lambda_{\text{max}}$  for each dye.

It is evident from Fig. 3 that in the pH range of 4–8 all dyes exhibit stable absorption characteristics. The absorption characteristics for crystal violet and malachite green have been significantly affected at extreme pH conditions. The changes in absorption behavior of the dye could be attributed to the hydrolysis or aggregation at these extreme pH conditions (Goicoechea and Olivieri, 1998). The absorption characteristics of all dyes were not affected by the solution ionic strength over the range 0.0–0.1 M NaCl. Accordingly, the spectral measurements were recorded at pH 5.0 and in 0.1 M NaCl solution.

In this work, principal component regression PCR and partial least squares PLS-1 were employed as full-spectrum methods for the determination of dyes in their mixtures. Classical least squares CLS showed limited application for resolving the dyes mixture. The optimum number of factors of PCR and latent variables of PLS-1 was determined using leave-one-out cross validation procedure (Haaland and Thomas, 1988; Brereton, 1997). The optimum number of factors (6 and 7) and 6-latent variables were always higher than the number of solutes (5 dyes) and this indicates the high complexity and high degree of non-linearity in the current system. The optimized PCR and PLS-1 models were used to predict dyes contents in prediction set. Concentration ranges in the 10-mixtures prediction set were: 0.3–4.0, 0.4–4.5, 0.4–4.0, 0.5–7.5, and 0.9–11.5  $\text{mg L}^{-1}$  for crystal violet, malachite green, methylene blue, safranin O, and thioflavin T, respectively. The employed spectral range for both methods was 280–800 nm, 261 spectral point/spectrum. For PCR, numbers of factors were 6 for methylene blue, thioflavin T, and malachite green and 7 for safranin O and crystal violet. For PLS-1 method, 6-latent variables were found optimum for optimum calibration. Outliers were detected using principal component analysis prior to multivariate calibration. The accuracy and precision were estimated to assess the total performance of both methods for cationic dyes determination and the results were summarized in Table 1.

As indicated in Table 1, both methods were able to resolve the high spectral overlap between dyes and quantify them with an acceptable degree of accuracy and precision. However, PLS-1 has outperformed PCR with better accuracies (99.2–104.5%) and lower precisions (1.0–5.1%). In fact, the resolving power of PLS-1 for many complex mixtures is known as reported in the literature, however, PCR has been applied for accurate determination of complex mixture of five reactive (anionic) dyes in wastewater (Alberghina et al., 2000). Accordingly, PLS-1 was adopted for dyes determination due to its outstanding performance. Sensitivity SEN, selectivity SEL, and limit of detection LOD of dyes determination by multivariate calibration were calculated using net-analyte signal methodology (Al-Degs et al., 2008) and the results were compiled in Table 2.

Using multivariate calibration, dyes were simultaneously quantified with reasonable detection limits ( $43\text{--}245 \text{ } \mu\text{g L}^{-1}$ ) and reasonably good dynamic ranges. Multivariate selectivity values often range between zero (complete overlap between analyte and other analytes or interferences) and unity (very small overlap between analyte and other analytes or interferences). The reported SEL values were much smaller than unity ( $< 1.0$ ) and this confirmed the high overlap between dyes as discussed earlier. Higher values of sensitivity are an indication



**Table 1** Recovery of cationic dyes in validation set by PCR and PLS-1 methods.

Model	Average recovery (RSD, $n = 3$ )				
	Crystal violet	Malachite green	Methylene blue	Safranin O	Thioflavin T
PCR	98.1(8.7)	105.3(4.6)	98.5(5.3)	102.7(2.9)	102.0(4.3)
PLS-1	99.2(1.0)	101.4(5.1)	100.3(2.3)	103.3(2.1)	104.5(1.8)

**Table 2** Analytical characteristics for single and multicomponent spectrophotometric determination of basic dyes.<sup>a</sup>

Dye	Single-component measurement				Multicomponent measurement			
	$\lambda_{\max}$ (nm)	$\epsilon$ ( $M^{-1} cm^{-1}$ )	LOD ( $\mu g L^{-1}$ )	Linearity ( $mg L^{-1}$ )	SEN	SEL	LOD ( $\mu g L^{-1}$ )	Linearity ( $mg L^{-1}$ )
Crystal violet	592	$8.0 \times 10^4$	28	0.12–8.0	1.24	0.17	43	0.18–4.5
Malachite green	620	$4.8 \times 10^4$	67	0.21–8.0	0.92	0.31	95	0.32–5.0
Methylene blue	668	$6.0 \times 10^4$	48	0.15–8.0	0.95	0.13	72	0.23–4.5
Safranin O	522	$3.5 \times 10^4$	89	0.29–10.0	0.83	0.16	135	0.45–8.0
Thioflavin T	413	$1.3 \times 10^4$	160	0.56–15.0	0.51	0.22	245	0.82–12.0

<sup>a</sup> Analytical precision was  $< 3.0\%$  in all cases.

of higher accuracy in determination of the solute. As indicated in Table 2, the highest sensitivity (1.24) was reported for crystal violet and accordingly it has the lowest detection limit among dyes ( $43 \mu g L^{-1}$ ). Single-component measurement of dyes was also summarized in Table 2. The high sensitivity and lower detection limit for crystal violet dyes would be attributed to its high molar absorptivity value compared to the other dyes.

### 3.3. SPE of cationic dyes by different extractants

As mentioned earlier, the detection limits of cationic dyes were within the range  $43\text{--}245 \mu g L^{-1}$  and this range, in fact, is much larger than  $5 \mu g L^{-1}$  which is the normal level of cationic dyes in natural or treated water. Therefore, the dyes should be concentrated by suitable extractant before spectrophotometric measurements. Moreover, the factors affecting preconcentration of dyes should be optimized beforehand. The studied factors were mass and type of extractant, volume of sample solution, type and volume of elution solvent, pH, extraction flow rate, and elution flow rate. Initial dyes level and particle diameter of the extractant were maintained at  $5 \mu g L^{-1}$  and  $63\text{--}125 \mu m$ , respectively. The highest enrichment factors for all dyes were achieved under the following conditions; extractant mass: 300 mg, volume of solution:  $1000 cm^3$ , elution solvent:  $0.02 M HNO_3$ , volume of elution solvent:  $10 cm^3$ ,

pH: 5, extraction/elution flow rate:  $1.5 cm^3 min^{-1}$ , and particle diameter:  $63\text{--}125 \mu m$ . Table 3 summarizes the extraction recoveries for different dyes using different solid-phase extractants.

Generally speaking, diatomite was the best extractant for all dyes with extraction recoveries between 89.6% and 96.5%. Zeolite was effective for preconcentration of all dyes except methylene blue and crystal violet with extraction recoveries around 83%. With such high extraction recoveries, the maximum preconcentration factor was  $\sim 97$ , which was reported for Thioflavin T using diatomite. The interesting part in the results is the modest preconcentration power of activated carbon, the extraction recoveries fall within 55.8% and 78.5%. In fact, activated carbon is a porous adsorbent and contains acidic functional groups that are capable of forming strong interactions with dyes which make complete elution of solutes a hard task. In a similar study, Pourreza and Elhami have developed a simple spectrophotometric determination which was limited for malachite green after preconcentration using nonionic surfactant Triton X-100 and reported a working range and a detection limit of  $4\text{--}500$  and  $1.2 \mu g L^{-1}$ , respectively (Pourreza and Elhami, 2007). Šafařík and Šafaříková prepared a magnetic solid-phase extractant which was able to detect malachite green and crystal violet at very low levels:  $0.5\text{--}1.0 \mu g L^{-1}$  (Šafařík and Šafaříková, 2002). In another study, Šafařík and Šafaříková have also prepared a magnetic solid-phase extractant for selective determination of mixtures of safranin O and crystal violet. The proposed analytical method was satisfactory for accurate determination of dye mixtures within the range of  $10\text{--}70 \mu g L^{-1}$  and a high enrichment factor (460) was reported (Šafařík and Šafaříková, 2002). Even though some of the earlier methods (Šafařík and Šafaříková, 2002; Al-Degs et al., 2008) reported much lower detection limit and better sensitivity for cationic dyes, these methods were limited to one or two dyes only. However, the current method can be applied for five cationic dyes with good analytical performance. The inter and intra day precisions for dyes determination by PLS-1 method were evaluated over one week period, the results indicated that both inter and intra day precisions were acceptable with RSD range of 1.6–3.4%.

**Table 3** Solid-phase extraction of dyes in mixture at pH 5.0.<sup>a</sup>

Extractant	Extraction recovery (%) (RSD, $n = 3$ )		
	Activated carbon	Diatomite	Zeolite
Crystal violet	76.4(6.2)	90.6(1.7)	82.4(7.6)
Malachite green	59.4(5.3)	94.3(2.2)	92.3(4.4)
Methylene blue	55.8(2.3)	89.6(2.7)	83.4(1.2)
Safranin O	78.5(3.4)	95.4(6.3)	91.4(6.3)
Thioflavin T	68.4(4.5)	96.5(5.2)	88.6(4.6)

<sup>a</sup> Individual dye concentration was  $5 \mu g L^{-1}$  and particle diameter of extractant  $63\text{--}127 \mu m$ .

**Table 4** Simultaneous determination of cationic dyes spiked at  $5 \mu\text{g L}^{-1}$  in stream water sample using diatomite SPE and PLS-1 calibration (RSD,  $n = 3$ ).

Dye	Extraction recovery (%)
Crystal violet	79.8(2.3)
Malachite green	82.6(7.3)
Methylene blue	83.6(4.2)
Safranin O	89.4(1.8)
Thioflavin T	91.8(2.7)

<sup>a</sup>Conditions: dyes level  $5 \mu\text{g L}^{-1}$ , pH 5.0, mass of diatomite 300 mg, sample volume 1000 mL, elution solvent volume:  $10 \text{ cm}^3$ , extraction/elution flow rate:  $1.5 \text{ cm}^3 \text{ min}^{-1}$ , and particle diameter: 63–125  $\mu\text{m}$ .

<sup>b</sup>The results of stream water analysis were: pH(initial): 7.9, soluble compounds (at  $105^\circ\text{C}$ ):  $110 \text{ mg L}^{-1}$ , insoluble compounds:  $60 \text{ mg L}^{-1}$ ,  $[\text{Cl}^-]$ :  $16.7 \text{ mg L}^{-1}$ ,  $[\text{SO}_4^{2-}]$ :  $45.6 \text{ mg L}^{-1}$ , and total Fe:  $1.3 \text{ mg L}^{-1}$ .

### 3.4. Selective preconcentration of cationic dyes from complex stream water

Evaluation of the extraction efficiency of diatomite for cationic dyes present in real water is necessary. To achieve this,  $1000 \text{ cm}^3$  of stream water was spiked with trace amounts of the five cationic dyes ( $5 \mu\text{g}$ ) and the pH was adjusted to 5. The optimized extraction procedure was applied and then PLS-1 was used for dyes determination. The results of extraction/preconcentration of dyes in stream water were summarized in Table 4.

Using natural diatomite, selective preconcentration of all dyes was established with a preconcentration factor of  $\sim 90$  which is reported for thioflavin T. This preconcentration factor can be further improved by doubling the sample volume; however, this practice would increase the analysis time. In fact, the matrix of stream water has affected the selective-extraction power of diatomite for cationic dyes. The dissolved inorganic and organic matter in natural water systems played a role in reducing the extraction efficiency of diatomite. Sorption of matrix components on diatomite seems to lower the fraction of available active sites for sorption of dye molecules. It should be mentioned that diatomite is a naturally occurring material and less expensive than activated carbon, nanotube-activated carbon, or cationic exchanger resins. Moreover, diatomite was selective for cationic dyes, a property that was not found in many natural adsorbents like zeolite, peat and lignite as experimentally confirmed in our laboratory.

## 4. Conclusions

The proposed method is characterized by high recoveries of all five dyes (89.6–95.6%) which allows determination of  $5 \mu\text{g L}^{-1}$

level in actual water sample. The method does not involve expensive instrumentation and tedious separation of the dyes. The unique combination of SPE preconcentration and multivariate calibration allows accurate and precise determination of five cationic dyes using simple equipment available in every laboratory. Diatomite outperformed activated carbon for cationic dyes preconcentration and high enrichment factors were reported (90–97). The method should find application where sophisticated equipment such as LC/MS is not available. Furthermore the method is executable by average laboratory technicians with minimum time, cost, and waste generation.

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