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Analysis of Three Reactive Dyes and Their Six Derivatives by Capillary Electrophoresis

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Abstract: Reactive dyes with different reactive groups exhibit different hydrolysis and dyeing behaviors. This is particularly evident in the combination dyeing process, where the competion between hydrolysis and dyeing reactions increases the complexity. Therefore, developing an effective method to monitor the changes in reactive dyes during the dyeing process is important. This study aims to develop a capillary electrophoresis (CE) technique combined with an ultraviolet (UV) detector (CE-UV) for detecting three reactive dyes and their six derivatives (a total of nine analytes). The optimized CE conditions are 20.0 mmol/L sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), acetonitrile (ACN) with a volume fraction of 15.0%, 20.0 mmol/L α-cyclodextrin (α-CD), and at a pH value of 9.0 (adjusted with 0.5 mol/L H_3BO_3). The limit of detection (LOD) (a signal-to-noise ratio of 3) for the nine analytes ranges from 1.38 to 5.06 mg/L. The relative standard deviations (RSDs) for peak areas and migration time are 2.19%–4.96% and 0.29%–2.75%, respectively. The method is capable of accurately identifying three reactive dyes and their six derivatives and monitoring alterations in composition and dyeing behavior during single and combination dyeing processes.

Keywords: reactive dye; capillary electrophoresis (CE); hydrolyzed product; combination dyeing
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0 Introduction

Reactive dyes are widely used in the textile industry because of their bright color and excellent color fastness[1]. Various dye-fiber and dye-dye interactions occur during the dyeing process. In particular, uncontrollable factors occurring during the dyeing process may lead to the production of unsatisfactory results[2]. Reactive dyes are developed based on acid dyes, and the structural difference between reactive dyes and acid dyes is that reactive dyes contain reactive groups[3]. The reactive groups react with fiber molecules through nucleophilic substitution or nucleophilic addition, forming covalent bonds[4]. When the reactive groups interact with —OH groups in water, they undergo a hydrolysis reaction[5-6]. In particular, under alkaline conditions, the combination dyeing of fabrics using different reactive dyes results in the production of a great number of hydrolysis products[7]. These may affect the reproducibility of the dyeing process. This practice not only increases the cost but also pollutes the aquatic ecosystem and soils, which may subsequently impact human health through the food chain[8-9]. To accurately and rapidly detect the content of reactive dyes and their hydrolysis products in dye solutions, it is necessary to develop an effective detection method.

Haque et al.[10] analyzed three reactive dyes and measured the absorbance of the post-dye and post-wash liquors by ultraviolet-visible (UV-Vis) spectroscopy, and the solution concentrations were calculated by the Beer-Lambert law. Nevertheless, this method is only capable of determining the total absorbance, and it is not possible to analyze the different structures of the reactive dyes in the mixed solution. The application of the UV-Vis spectroscopy for the determination of multi-component samples necessitates the use of dual-wavelength spectrophotometry, with the maximum absorption wavelength λ_{max} being determined by solving a set of simultaneous equations based on the Beer-Lambert law[11-13]. The ensuing calculation process is inherently cumbersome, resulting in poor quantitative accuracy or even inaccurate results. Raman spectroscopy was employed to detect the concentration of reactive dyes with different structures under various dyeing conditions[14-15]. Javoršek et al.[16] analyzed the hydrolysis and formation of dye-fiber bonds during the dyeing process by using high-performance liquid chromatography (HPLC). However, HPLC is challenging for analyzing dyes in complex matrices, and inadequate pretreatment or sample preparation may affect the accuracy of the analytical results[17-19].

Capillary electrophoresis (CE) is driven by a high-voltage direct current electric field, utilizing a capillary

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tube as its separation channel, and realizes the separation of the target substances based on the differences in the mobility and partitioning behaviors of the components in the specimen. It has been proven to be capable of quantitatively determining drugs[20-21], inorganic ions[22], biogenic amines[23] and other substances[24].

Ojstrsek et al.[25] examined the hydrolysis process of some reactive dyes and analyzed the behavior of color index (C. I.) reactive black 5 in single dyeing. Most of the studies focused on monitoring the hydrolysis reaction of reactive dyes in wastewater by CE, but there were no simultaneous analyses of different reactive dyes or studies on the detection of combination dyeing processes[26-28].

A previous study from our group has successfully analyzed three heterobifunctional dyes (C. I. reactive red 195, C. I. reactive yellow 145 and C. I. reactive blue 194), as well as single dyeing and combination dyeing processes[29]. However, combination dyeing uses different dye mixtures, which requires different CE conditions to analyze various processes.

This study aims to analyze three different types of reactive dyes, namely C. I. reactive blue 19 (monofunctional), C. I. reactive black 5 (bifunctional), C. I. reactive red 195 (heterobifunctional), and their activation and hydrolysis forms. When analyzed under the background electrolyte (BGE) conditions used in Ref. [29], the activation form and the hydrolysis form of C. I. reactive blue 19 were found to be poorly separated, and the migration time of the nine analytes was too long. Therefore, there is a need to explore optimized CE conditions. The developed method can be used to evaluate single dyeing and combination dyeing processes, which can help to improve dyeing quality.

1 Materials and Methods

1.1 Materials

Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., China. Boric acid (H_3BO_3) and sodium hydroxide (NaOH) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. C. I. reactive black 5 and α-cyclodextrin (α-CD) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., China. Acetonitrile (ACN) was purchased from Shanghai Adamas Reagent Co., Ltd., China. C. I. reactive blue 19 was purchased from Shanghai Xianding Biotechnology Co., Ltd., China. C. I. reactive red 195 was purchased from Shanghai Yuanye Biotechnology Co., Ltd., China. The area density of the fabric was 115 g/m^2; the warp density and weft density of the fabric were 526 ends per 10 cm and 288 picks per 10 cm, respectively.

1.2 CE conditions

All experiments were conducted on the CE instrument (G1600AX, Agilent Technologies Inc., USA). Bare fused silica capillary was purchased from Yongnian Ruifeng Chromatography Device Ltd., China. The dimension of the capillary was 58.5 cm (50.0 cm to the UV detector) × 75.0 μm (the inner diameter). The temperature of the capillary cassette was 25 ℃. The BGE was a mixture of 20.0 mmol/L $Na_2B_4O_7 \cdot 10H_2O$, 20.0 mmol/L α-CD, 15.0% (volume fraction) ACN, at a pH of 9.0 (adjusted with 0.5 mol/L H_3BO_3). New capillary activation was performed by rinsing the capillary with 1.0 mol/L NaOH solution (30 min), water (10 min) and BGE (10 min) at 1.0×10^5 Pa. Before each injection, the capillary was conditioned sequentially with 0.1 mol/L NaOH solution (3 min), water (3 min) and BGE (3 min) at 1.0×10^5 Pa. This procedure eliminated the effect of dye adsorption on the results, thereby ensuring the reproducibility of the experiment. The experimental conditions were set as follows: hydrodynamic injection was performed at a pressure of 3.5×10^3 Pa for a duration of 4.0 s, a separation voltage of 20.0 kV was applied, and a UV detection was carried out at a wavelength of 200.0 nm.

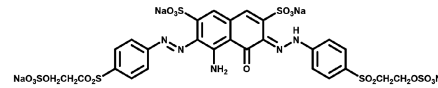
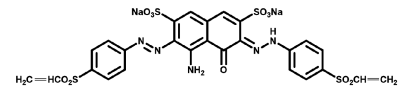
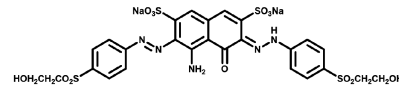
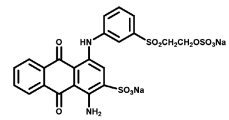
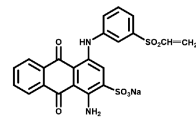
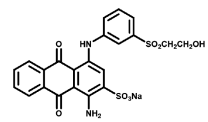
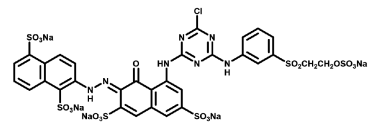
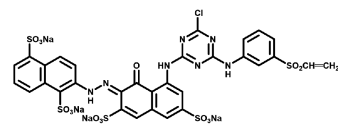
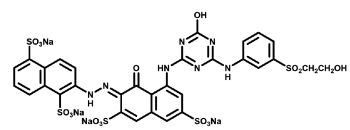
1.3 Preparation of stock solution

Three reactive dye stock solutions were prepared with C. I. reactive blue 19, C. I. reactive black 5 and C. I. reactive red 195 at a mass concentration of 2.0 g/L, respectively. The concentrations of other stock solutions were 50.0 mmol/L for $Na_2B_4O_7 \cdot 10H_2O$, 0.5 mol/L for H_3BO_3, 50.0 mmol/L for α-CD, and 1.0 mol/L for NaOH.

Vinyl sulfone (VS) reactive dyes (activation forms of dyes) and completely hydrolyzed reactive dyes (hydrolysis forms of dyes) were prepared from their respective precursors β-sulfatoethyl sulfone (SES) reactive dyes.

SES can hydrolyze in one or two steps to VS and hydroxyethyl sulfone (HES). The monochlorotriazinyl group (Cl) hydrolyzes to a hydroxytriazinyl group. The procedure for preparing VS reactive dyes was dissolving 10.0 mg dyes in 0.01 mol/L NaOH solution. After the reaction proceeded for a period, the reaction solutions were neutralized with 1.0 mol/L HCl to produce 1.0 g/L stock solutions. The procedure for preparing completely hydrolyzed reactive dyes involved dissolving 0.25 g dyes in 0.1 mol/L NaOH solution and reacting in a water bath at 60 ℃. Then, the solutions were cooled to room temperature and neutralized with 1.0 mol/L HCl solution to produce 1.0 g/L stock solutions. The structural formulas of three reactive dyes and their six derivatives are shown in Table 1.

Table 1 Structural formulas of three reactive dyes and their six derivatives

Analyte	Abbreviation	Structure
C. I. reactive black 5	SES-SES-black-5	
Activation form of C. I. reactive black 5	VS-VS-black-5	
Hydrolysis form of C. I. reactive black 5	HES-HES-black-5	
C. I. reactive blue 19	SES-blue-19	
Activation form of C. I. reactive blue 19	VS-blue-19	
Hydrolysis form of C. I. reactive blue 19	HES-blue-19	
C. I. reactive red 195	SES-Cl-red-195	
Activation form of C. I. reactive red 195	VS-Cl-red-195	
Hydrolysis form of C. I. reactive red 195	HES-OH-red-195	

The preparation of the derivatives of C. I. reactive black 5 is shown in Fig. 1. Samples were collected at different time during the preparation process and analyzed by the CE technique combined with an ultraviolet (UV) detector (CE-UV). The electropherograms show that the SES-SES-black-5 peak decreases, while the VS-VS-black-5 peak gradually increases (Fig. 2 (a)). The preparation of the hydrolysis form results in a reaction type Ⅱ situation, whereby either of the two reactive groups may be preferentially hydrolyzed, resulting in the production of a partially hydrolyzed product, named HES-VS-black-5 (Fig. 1). The final conversion to the fully hydrolyzed product, named HES-HES-black-5, is shown in Fig. 2 (b). Electropherograms of the preparation of the activation and hydrolysis forms of C. I. reactive blue 19 and C. I. reactive red 195 are shown in Figs. 2 (c)–2(f).

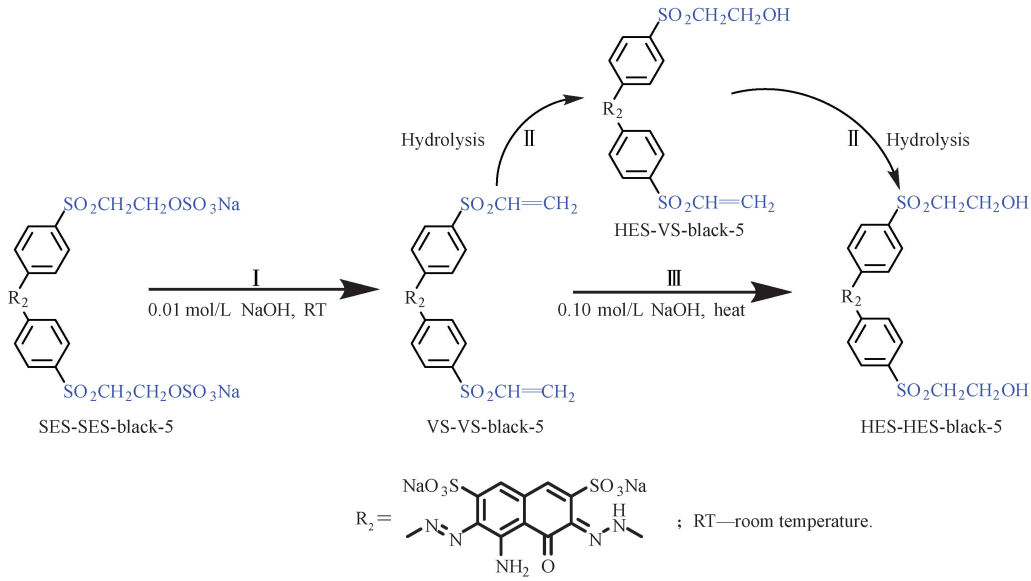


Fig. 1 Preparation routes for activation form and hydrolysis form of C. I. reactive black 5 under different conditions

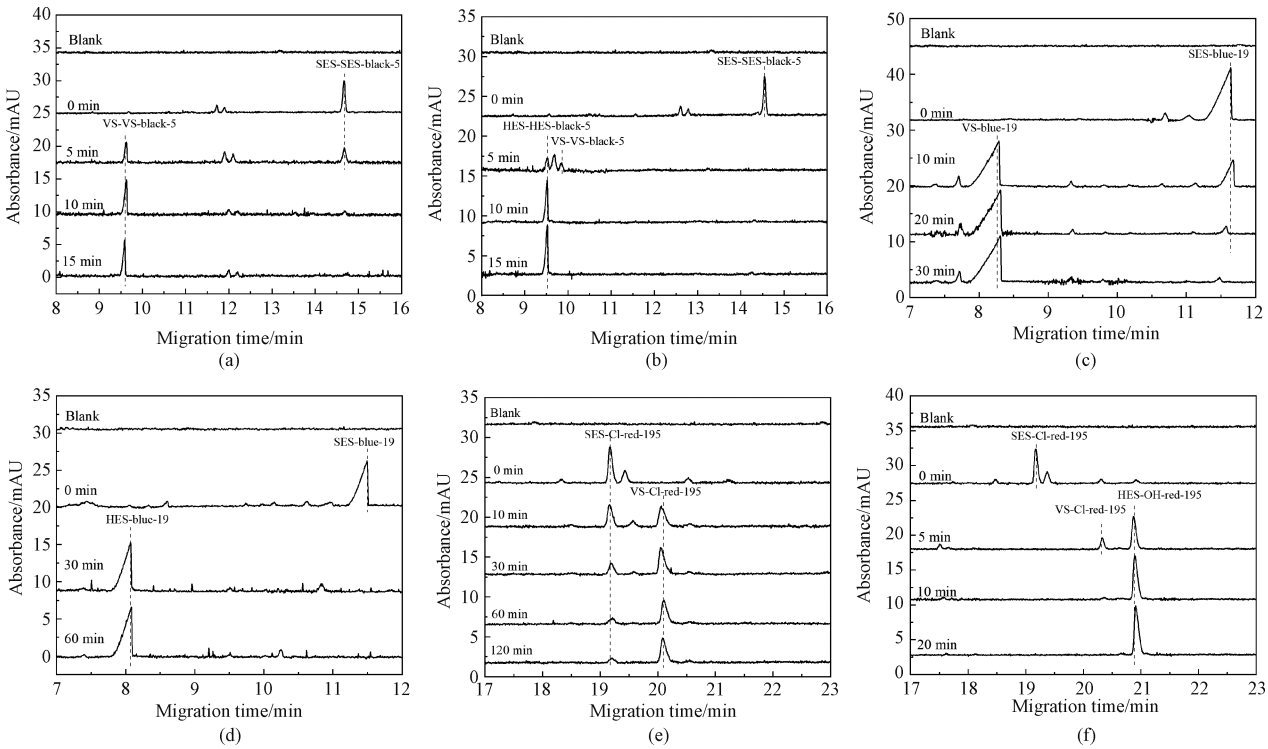


Fig. 2 Electropherograms of analytes in the preparation process at different time: (a) VS-VS-black-5; (b) HES-HES-black-5; (c) VS-blue-19; (d) HES-blue-19; (e) VS-Cl-red-195; (f) HES-OH-red-195

1.4 Dyeing procedure

The formulation for the single dyeing was a dye dosage of 2.0% on-mass of fabric (omf), 5.0 g cotton fabric, and a liquor-to-good ratio of 20∶1. The dye was dissolved in 100 mL water, 4.0 g/L Na_2SO_4 was added, and after a certain period of dyeing, Na_2CO_3 was added. The dyeing procedure is shown in Fig. 3. The formula for the combination dyeing was a dye dosage of 6.0% omf, with a mass ratio of 1∶1∶1 for the three reactive dyes. The rest of the conditions were the same as those for the single dyeing.

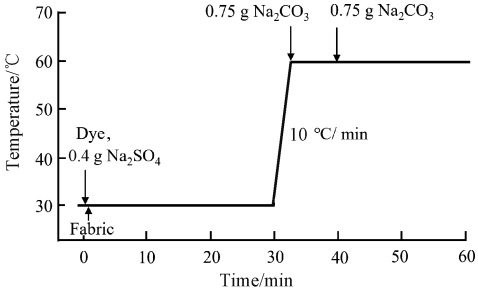


Fig. 3 Dyeing procedure curve

2 Results and Discussion

2.1 Selection and optimization of CE conditions

Adjusting the content of $Na_2B_4O_7 \cdot 10H_2O$, α-CD and ACN and the pH of the BGE can enhance the disparity in the flow rates of the neighboring components, thus optimizing the separation. The absorption spectra of three reactive dyes and their six derivatives were measured by UV-Vis spectroscopy. Though λ_{max} of the nine analytes were different in the UV wavelength range, they had high absorption intensity at 200.0 nm. Therefore, the detection wavelength of 200.0 nm was finally selected.

2.1.1 Effect of $Na_2B_4O_7 \cdot 10H_2O$ concentration on separation efficiency

The effect of $Na_2B_4O_7 \cdot 10H_2O$ concentration on the separation efficiency of nine analytes was investigated. The result is shown in Fig. 4. Increasing the $Na_2B_4O_7 \cdot 10H_2O$ concentration within a certain range enhances sample separation. However, beyond this range, further increases reduce the electroosmotic flow (EOF) and slow sample migration without improving the separation efficiency. Excessive $Na_2B_4O_7 \cdot 10H_2O$ concentration causes excessive Joule heating, resulting in peak broadening and reducing sensitivity and separation efficiency. Therefore, a $Na_2B_4O_7 \cdot 10H_2O$ concentration of 20.0 mmol/L was selected. The corresponding sample peaks are as follows. 1: HES-blue-19, 2: VS-blue-19, 3: SES-blue-19, 4: HES-HES-black-5, 5: VS-VS-black-5, 6: SES-SES-black-5, 7: HES-OH-red-195, 8: VS-Cl-red-195, 9: SES-Cl-red-195.

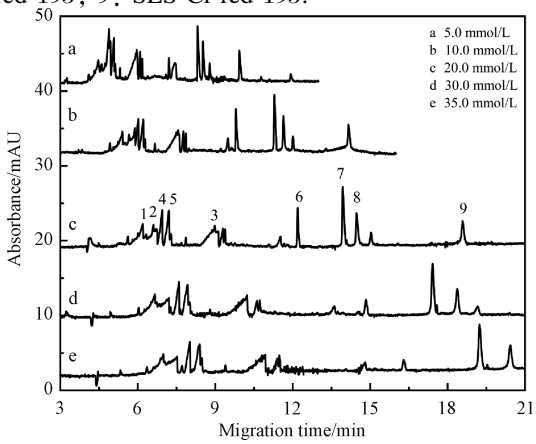


Fig. 4 Effect of $Na_2B_4O_7 \cdot 10H_2O$ concentration on separation efficiency of analytes

2.1.2 Effect of ACN volume fraction on separation efficiency

It is found that organic additives increase the solubility of hydrophobic solutes in the aqueous phase, which affects the retention factor of the analytes and may change the resolution of the analytes[30]. As the volume fraction of ACN increases, the EOF decreases, resulting in longer migration time for each analyte. When the volume fraction of ACN is higher than 20.0%, the migration time increases significantly, as shown in Fig. 5. Furthermore, an excess volume fraction of ACN has been observed to result in a decline in the BGE stability. Consequently, an ACN volume fraction of 15.0% was selected.

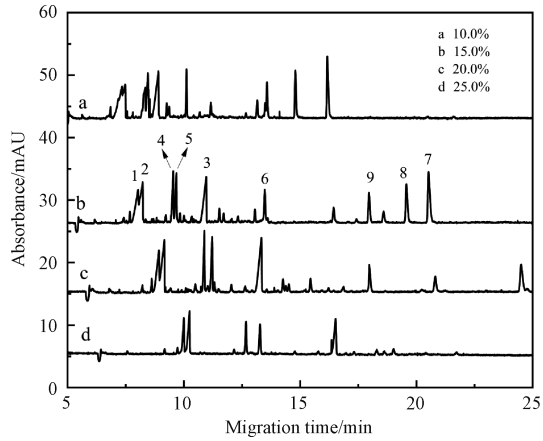


Fig. 5 Effect of ACN volume fraction on separation efficiency of analytes

2.1.3 Effect of α-CD concentration on separation efficiency

The forms of analytes include complexes with α-CD and also have solubilizing effects. The addition of α-CD to the BGE also reduces the interaction between the analytes and the capillary wall, thus increasing the reproducibility of the method and improving the peak shape[30]. In a concentration range of 5.0 mmol/L to 20.0 mmol/L, the separation improves progressively with increasing the α-CD concentration, as shown in Fig. 6. Consequently, a α-CD concentration of 20.0 mmol/L was selected.

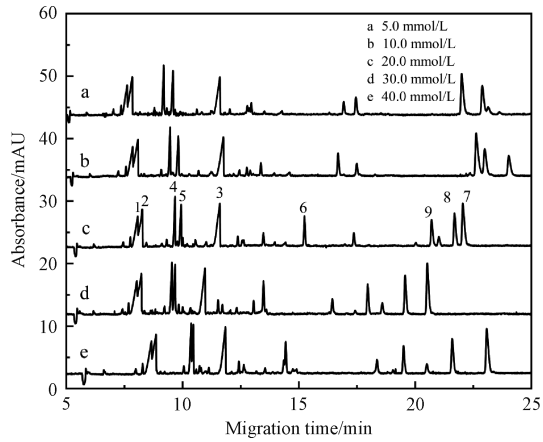


Fig. 6 Effect of α-CD concentration on separation efficiency of analytes

2.1.4 Effect of pH on separation efficiency

For uncoated fused silica capillaries, pH plays an important role in controlling EOF and has a significant impact on the separation process. The pH of the BGE affects the structure and charge of the analytes, increasing the differences between the analytes to be analyzed and thus affecting the separation of the analytes[31]. When comparing the two pH values (8.5 and 9.0), a higher pH results in an increased EOF and a decreased migration time for analytes, as shown in Fig. 7. However, in a pH range of 9.0 – 10.0, increasing pH results in longer migration time, but no improvement in the separation efficiency. Consequently, a pH of 9.0 was selected for the BGE.

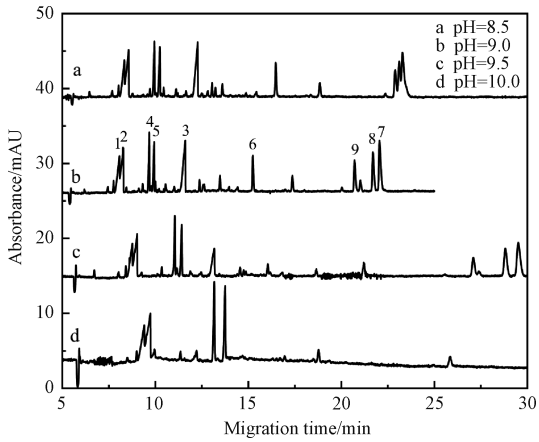


Fig. 7 Effect of pH on separation efficiency of analytes

2.2 Validation of analytical method

The validation parameters for the simultaneous analysis of the three reactive dyes and their activation forms and hydrolysis forms are presented in Table 2. The linear curves obtained for all analytes exhibit a high correlation ($R^2 > 0.995\ 7$, and R^2 is the coefficient of determination). LOD is defined as the minimum concentration that can be detected at a signal-to-noise ratio (S/N) of 3. LQD is the concentration at a S/N of 10. LOD and LQD of nine analytes are found to be in ranges of 1.38 – 5.06 mg/L and 4.61 – 16.87 mg/L, respectively. In the mixed standard solution at a mass concentration of 60.0 mg/L for nine analytes, RSD of peak areas ($n = 5$, where n represents the number of parallel experiments conducted for each analyte) is 2.19% – 4.14% within one day (intraday) and 3.63% – 4.96% within five days (interday), respectively. RSD of migration time ($n = 5$) is 0.29% – 0.84% within one day (intraday) and 0.62% – 2.75% within five days (interday), respectively. The three reactive dyes and their activation and hydrolysis forms have negative charges, which results in a weak adsorption phenomenon on the capillary surface. Conversely, the rinsing procedure was meticulously executed before each analysis, which effectively minimized the adsorption of the dyes on the capillary surface, thereby ensuring the reproducibility of the analytical method. This indicates that the method can accurately and quantitatively analyze reactive dyes.

Table 2 Linearity, reproducibility and limit of detection of analytical method

Analyte	R^2 (5.0–140.0 mg/L)	LOD/(mg/L)	LQD/(mg/L)	RSD/% ($n=5$)	
				Peak area	Migration time
				Intraday/interday	Intraday/interday
SES-blue-19	0.997 9	1.77	5.91	3.71/4.14	0.39/1.50
VS-blue-19	0.995 7	1.38	4.61	2.19/3.68	0.29/0.62
HES-blue-19	0.997 9	1.80	5.99	3.16/4.58	0.30/0.63
SES-SES-black-5	0.997 4	3.58	11.93	3.70/4.45	0.63/2.49
VS-VS-black-5	0.997 9	2.84	9.48	4.14/4.76	0.37/0.98
HES-HES-black-5	0.997 5	2.11	7.03	2.88/3.63	0.36/0.92
SES-Cl-red-195	0.998 8	5.06	16.87	3.41/4.89	0.79/2.75
VS-Cl-red-195	0.999 4	2.66	8.86	3.24/4.96	0.84/2.30
HES-OH-red-195	0.998 1	2.12	7.05	3.53/4.80	0.84/1.98

2.3 Detection of dyeing process

2.3.1 Detection of single dyeing process

Samples were taken every 10 min, after which their pH was adjusted to 7.0 with 0.5 mol/L HCl to stop further hydrolysis, and then the samples were diluted tenfold. Dye-uptake during the single dyeing process was analyzed by CE-UV. For C. I. reactive black 5 (Fig. 8(a)), during the dye adsorption stage (0–30 min), SES-SES-black-5 remains unchanged. During the dye fixation stage (40–60 min), SES-SES-black-5 converts to VS-VS-black-5, with intermediate hydrolysis products (HES-VS-black-5) appearing, followed by HES-HES-black-5. Similar reaction pathways are also observed for C. I. reactive red 195 and C. I. reactive blue 19, as shown

in Figs. 8(b) and 8(c), respectively. The total dye concentration at each time point was determined by summing the concentrations of all forms. The dye-uptake D measured by the CE-UV method is calculated according to

$$D = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

where C_0 is the initial dye concentration in the dye solution; C_t is the concentration of various forms of dyes taken at time t. The UV-Vis method for detecting the dye-uptake during a single dyeing process is based on GB/T 23976.1—2009 standard. The specific determination method is shown in Ref. [29]. Comparative curves of the dye-uptake measured by the CE-UV method and the UV-Vis method are shown in Fig. 8(d).

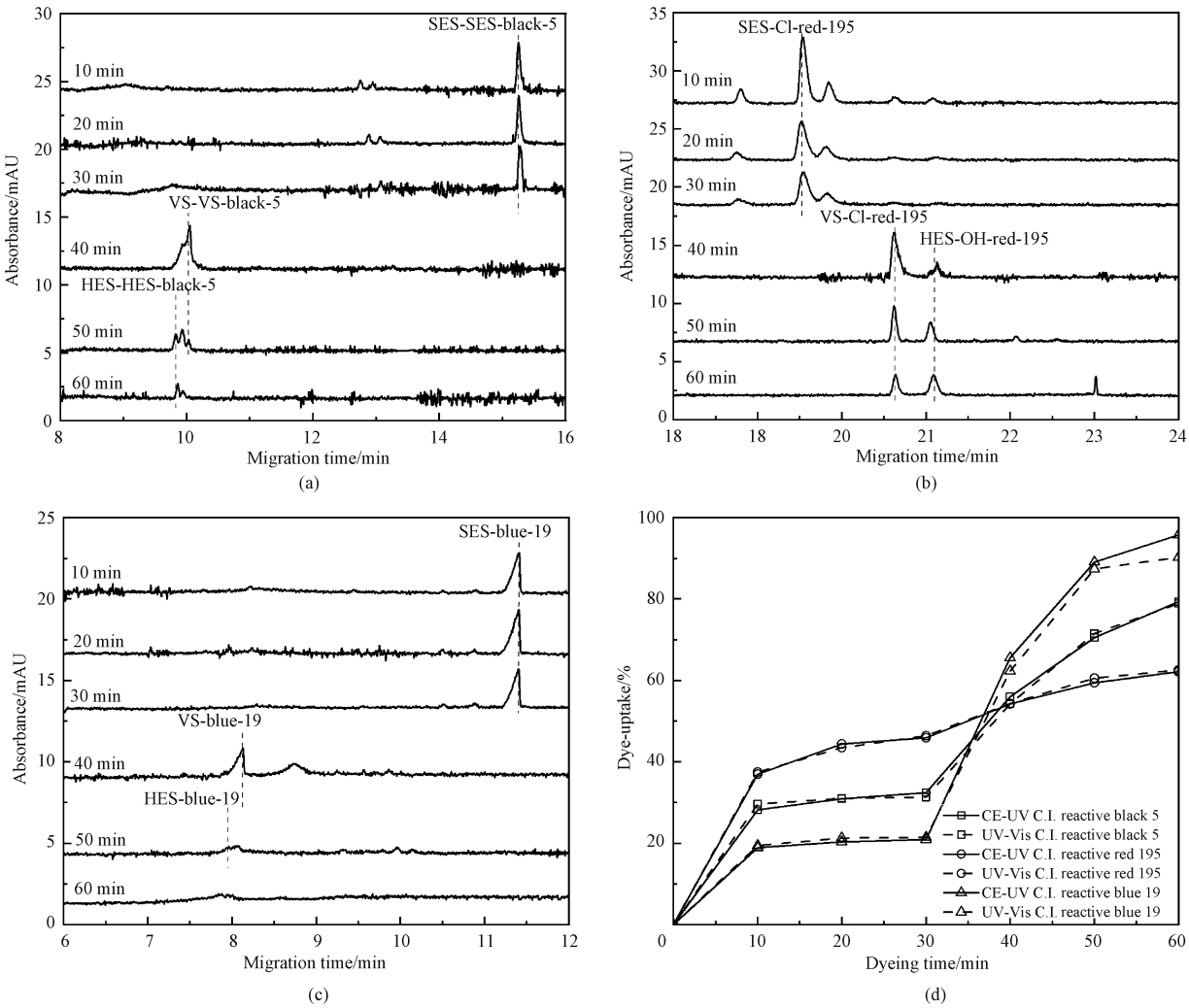


Fig. 8 Electropherograms during single dyeing process and comparative curves of dye-uptake measured by two methods: (a) electropherograms of C. I. reactive black 5; (b) electropherograms of C. I. reactive red 195; (c) electropherograms of C. I. reactive blue 19; (d) comparative curves

2.3.2 Detection of combination dyeing process

Analyses of the combination dyeing process of C. I. reactive blue 19, C. I. reactive black 5 and C. I. reactive red 195 are shown in Fig. 9. During the adsorption stage, only SES-blue-19, SES-SES-black-5 and SES-Cl-red-195 are presented. During the fixation stage, the reactive dyes are converted to VS-type reactive dyes and intermediate hydrolysis products. The final conversion of these intermediates to completely hydrolysis reactive dyes is shown in Fig. 9(a). The dye-uptakes of the three reactive dyes were determined by using two methods. For the CE-UV method, the relevant parameters were measured via CE, and then the dye-uptakes were calculated by using Eq. (1). For the UV-Vis method, the dye-uptakes were calculated as follows. The absorbance coefficients of the three dyes were measured by using the three-wavelength method. Then, they were used to determine the dye concentration and finally calculate the dye-uptake. The dye concentrations during different stages could be approximately determined by applying three linear equations, enabling the calculation of the dye-uptake for

each dye. The comparative curves of dye-uptake measured by the two methods are shown in Fig. 9 (b). Minor differences are observed between the dye-uptake measured by the two methods. When analyzing the dyeing process, the UV-Vis method often requires mathematical approaches to compensate for their limitations. The CE-UV method directly detects all forms of reactive dyes, providing more accurate results.

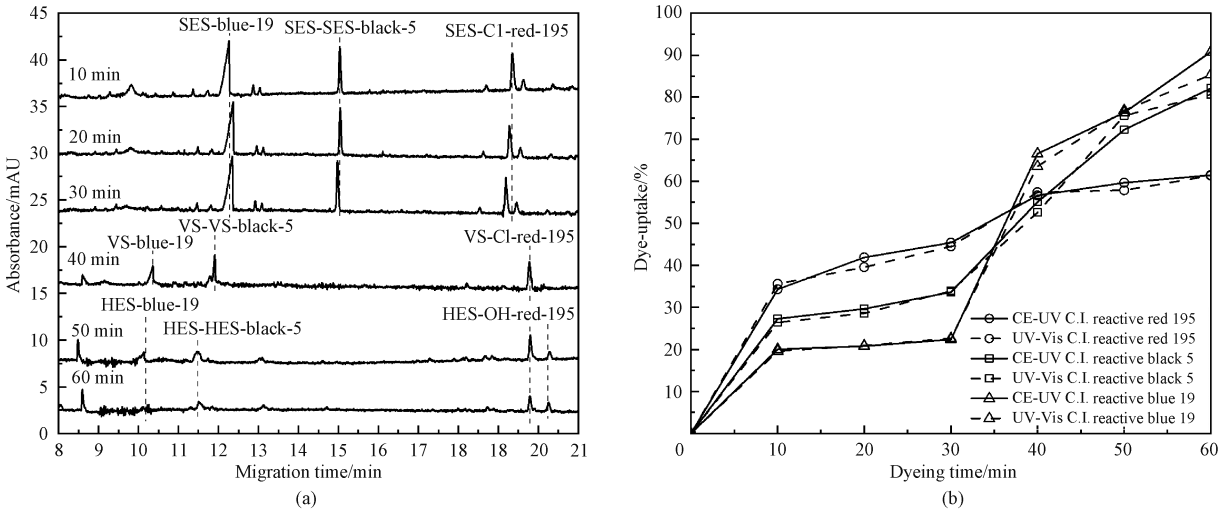


Fig. 9 Electropherograms during combination dyeing process and comparative curves of dye-uptake measured by two methods: (a) electropherograms; (b) comparative curves

3 Conclusions

In this study, a CE-UV method was developed to achieve simultaneous qualitative and quantitative analysis of three reactive dyes and their activation and hydrolyses derivatives. The method showed good sensitivity and reproducibility. The electropherograms showed that the reactive dyes underwent a transformation process during the dyeing process, specifically, the conversion of the reactive dyes to their activation forms and binding to the fibers, and the hydrolysis reaction to generate hydrolysis products. The dye-uptake of C. I. reactive red 195 and C. I. reactive black 5 remained stable during single dyeing and combination dyeing processes, indicating that its stability in binding to fibers was not easily affected by other dyes. In addition, the dye-uptake of C. I. reactive red 195 during the adsorption stage was higher than that of the other dyes, indicating that its monochlorotriazine group helped to enhance the affinity between the dye and the fiber. Comparing the dye-uptake of C. I. reactive blue 19 during single dyeing and combination dyeing processes, it was found that the dye-uptake of combination dyeing was lower than that of single dyeing. This suggested that the dyeing effect of C. I. reactive blue 19 was affected during the combination dyeing process with bifunctional dyes, resulting in lower dye-uptake. The experimental results verified the existence of competition between hydrolysis and up-dyeing reactions of reactive dyes with different structures during the combination dyeing process. In conclusion, this study successfully developed a method to analyze reactive dyes and their derivatives by using the CE-UV method and successfully applied it to monitor and analyze the dyeing process.

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基于毛细管电泳技术的三种活性染料及其六种衍生物分析方法研究

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摘 要: 具有不同活性基团的活性染料表现出不同的水解和染色行为。特别是在拼色染色中, 水解和染色反应的竞争使得染色过程变得更加复杂。因此, 开发一种有效的方法来监测染色过程中活性染料的变化显得尤为重要。本研究旨在开发一种毛细管电泳-紫外检测法以用于检测 3 种活性染料及其 6 种衍生物 (共 9 种分析物)。毛细管电泳条件: 20.0 mmol/L $Na_2B_4O_7 \cdot 10H_2O$, 体积分数为 15.0%的乙腈, 20.0 mmol/L α-环糊精, pH 9.0 (通过添加 0.5 mol/L H_3BO_3 溶液进行调节)。9 种分析物的检出限 (信噪比为 3 时) 为 1.38~5.06 mg/L, 峰面积和迁移时间的相对标准偏差 (relative standard deviation, RSD) 分别为 2.19%~4.96%和 0.29%~2.75%。该方法能够准确识别 3 种活性染料及其 6 种衍生物, 并检测单色染色和拼色染色过程中成分变化及分析上染行为。

关键词: 活性染料; 毛细管电泳; 水解产物; 拼色染色