

**ACCURACY EVALUATION OF MULTICOMPONENT SPECTROPHOTOMETRY
AND ITS APPLICATION IN REAL-TIME MONITORING OF THE DEGRADATION
OF DYES IN MIXED SOLUTIONS****

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With methyl orange, Congo red, rhodamine B, methyl violet and methylene blue as the research objects, the accuracy of spectrophotometry in determining the dye concentration of two-component and three-component solutions with different ratios was evaluated. The experimental results showed that when the interference among dyes was small, the measurement errors of two-component and three-component solutions were less than 5 and 10%, respectively. Meanwhile, multicomponent spectrophotometry was applied to a degradation experiment of β -FeOOH to test its catalytic degradation performance in the mixed solution of methyl orange and Congo red. The results showed that in the case of single components, the degradation rate of methyl orange and Congo red with β -FeOOH was 44.64 and 71.95% (4 h), respectively, while in the mixed solution, it was 29.54 and 80.17% (4 h), respectively. The significance of this work is to evaluate the accuracy of multicomponent spectrophotometry and provide a low-cost as well as a rapid method for evaluating the multicomponent catalytic ability of photocatalysts.

Keywords: spectrophotometry, photocatalyst, two-component and three-component solutions.

**ОЦЕНКА ТОЧНОСТИ МНОГОКОМПОНЕНТНОЙ СПЕКТРОФОТОМЕТРИИ
И ЕЕ ПРИМЕНЕНИЕ ДЛЯ МОНИТОРИНГА ДЕГРАДАЦИИ КРАСИТЕЛЕЙ
В СМЕШАННОМ РАСТВОРЕ В РЕЖИМЕ РЕАЛЬНОГО ВРЕМЕНИ**

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Для красителей метилового оранжевого, красного конго, родамина B, метилового фиолетового и метиленового синего оценена точность спектрофотометрии при определении концентрации красителя в двух- и трехкомпонентных растворах с различными соотношениями компонентов. При небольшой интерференции между красителями погрешности измерения двух- и трехкомпонентных растворов <5 и <10 %. Многокомпонентная спектрофотометрия применена в эксперименте по разложению β -FeOOH для проверки эффективности его катализитического разложения в смешанном растворе метилового оранжевого и красного конго. В случае отдельных компонентов скорость разложения метилового оранжевого и конго красного с β -FeOOH составляет 44.64 и 71.95 % (4 ч), в то время как в смешанном растворе — 29.54 и 80.17 % (4 ч). Оценена точность многокомпонентной спектрофотометрии и предложен недорогой и быстрый метод определения многокомпонентной катализитической способности фотокатализаторов.

Ключевые слова: спектрофотометрия, фотокатализатор, двухкомпонентные и трехкомпонентные растворы.

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Introduction. In recent years, due to the rapid development of industries and agriculture, organic wastewater has become one of the main sources of environmental pollution [1]. The direct discharge of organic wastewater will lead to the eutrophication of water, and most organic pollutants have a strong carcinogenicity [2] – for example, in the production and application of dyes, a large amount of dye wastewater with a high alkalinity, a high chroma and a peculiar smell will be produced [3, 4]. Even worse, the composition of such dyestuff wastewater is complex, and usually contains carcinogens such as benzene rings, amino groups and azo groups, which have great biological toxicity and are difficult to degrade [3, 5, 6]. The wastewater discharged without treatment will cause not only serious harm to human health, but also serious environmental pollution. Although people have thought of many ways to control sewage discharge, it is still very large; therefore, how to treat wastewater efficiently and reasonably has aroused widespread concern in society. At present, the main treatment methods are membrane separation [7], adsorption [6, 8], and other physical methods, as well as ozone oxidation [9], Fenton catalytic method [10], photocatalytic oxidation [11], and other chemical methods.

Compared with other organic wastewater treatment methods, photocatalysis is a more environmentally friendly method [2]. In general, under the action of ultraviolet light, the photocatalysts produce photogenerated electron pairs (e^- and h^+), which induce H_2O_2 to generate OH radicals, thus realizing the degradation of organic compounds [12]. Titanium dioxide (TiO_2) [13], β -FeOOH [14, 15], zinc oxide (ZnO) [16], cadmium sulfide (CdS) [17], and so on are well-studied photocatalysts, among which TiO_2 has already been widely used [17]. The degradation rate and efficiency of photocatalysts are often used as important indicators to evaluate their quality. However, in most studies, researchers only consider the degradation performance of photocatalysts for a single organic matter, which is not consistent with the actual situation. Organic wastewater contains a lot of carbohydrates, phenols, plasticizers, proteins, oils, dyes, surfactants and so on [18]. In wastewater treatment, the situation will be more complex than the treatment of a single pollutant; therefore, it is necessary to evaluate the photocatalytic performance of photocatalysts with multicomponent pollutants.

In a multicomponent solution, due to the serious interference and overlapping of the absorption peaks of each component, how to accurately determine the content of each component and the repeatability of test methods has become the main problem faced by researchers [19]. At present, the main methods used to determine the concentration of multicomponent solutions include derivative spectrophotometry [19], high-performance liquid chromatography [20], cloud point extraction and partial least squares regression method, etc. [21]. Among these methods, derivative spectrophotometry is an effective method for measuring multicomponent systems, through which the influence of baseline offset and tilt can be eliminated, thereby acquiring more accurate concentration information [22–24]. However, derivative spectrophotometry requires continuous measurement of samples at continuous wavelengths, including complex mathematical calculations [25]. In contrast, it is a simple method to establish the equations of absorbance at different wavelengths directly using the additivity of absorbance, which is easy to operate and can be used to determine the concentration of two or more dyes at the same time; however, its accuracy needs further verification. Based on this, the feasibility and accuracy of determining the concentration of various dyes in mixed solutions through the preceding multicomponent spectrophotometry were discussed and applied to studies on the photocatalytic performance of β -FeOOH for multicomponent dyes.

Fundamental. According to Lambert-Beer's Law

$$A = \varepsilon bc,$$

where A is the absorbance, ε is the molar absorption coefficient, b is the thickness of the solution layer, and c is the dye concentration. In a mixed solution, there is the following relationship between the absorbance of each component and the sum of absorbance at a specific wavelength:

$$A_w = \sum A_{iw} = \sum \varepsilon_{iw} b c_i = \sum K_{iw} c_i,$$

where A_w and A_{iw} are the absorbance of the mixed solution and dye i at the wavelength w , c_i is the concentration of dye i , ε_{iw} is the molar absorption coefficient of dye i at the wavelength w , K_{iw} is equal to the product of ε_{iw} , and b is the constant of dye i at wavelength w in the experiment. In this work, a two-component mixed solution and a three-component mixed solution have been studied.

For the two-component mixed solution:

$$\begin{aligned} A_1 &= K_{11}c_1 + K_{21}c_2, \\ A_2 &= K_{12}c_1 + K_{22}c_2. \end{aligned}$$

For the three-component mixed solution:

$$\begin{aligned} A_1 &= K_{11}c_1 + K_{21}c_2 + K_{31}c_3, \\ A_2 &= K_{12}c_1 + K_{22}c_2 + K_{32}c_3, \end{aligned}$$

$$A_3 = K_{13}c_1 + K_{23}c_2 + K_{33}c_3.$$

The concentration of each component in the mixed solution can be calculated through the following formula. For the two-component mixed solution:

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} \cdot \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \Rightarrow \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix}^{-1} \cdot \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} \quad (1)$$

For the three-component mixed solution:

$$\begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \begin{bmatrix} K_{11} & K_{21} & K_{13} \\ K_{12} & K_{22} & K_{23} \\ K_{13} & K_{23} & K_{33} \end{bmatrix} \cdot \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \Rightarrow \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} K_{11} & K_{21} & K_{13} \\ K_{12} & K_{22} & K_{23} \\ K_{13} & K_{23} & K_{33} \end{bmatrix}^{-1} \cdot \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \quad (2)$$

A spectrophotometer can be used to quickly measure the value of A_w in real time, and the value of K_{fw} is a constant in the experiments. According to the matrix calculation, the concentration of each component in the solution is obtained.

Experimental. Methyl orange (AR) was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd., Congo red (AR) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., methylene blue (AR) was purchased from Wuxi Asia Pacific United Chemical Co., Ltd., Rhodamine B (AR) and methyl violet (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., PBS phosphate powder (pH 7.2–7.4) was purchased from Phygene Life Sciences Co., Ltd., and anhydrous ethanol was purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. All the reagents were stored in a drying oven and used directly without purification; deionized water was produced via reverse osmosis using pure water equipment (Aquapro, AHL-2001-P).

Accurately weigh standard samples of methyl orange, Congo red, Rhodamine B, methyl violet and methylene blue, dissolve them in PBS buffer solution and fix the volume at 250 mL to obtain a standard solution. With PBS as the blank control, the diluted standard solution was scanned via a UV-Vis spectrophotometer (INESA, L5, China) within a wavelength range of 380–780 nm to obtain the absorption curve of the dye. The absorbance of the solution was measured via a spectrophotometer (Yoke Instrument-721, China). A standard curve was drawn with absorbance as the ordinate and concentration as the abscissa.

4 g of anhydrous FeCl_3 was dissolved in 250 mL of deionized water, into which 10 mL of 0.01 mol/L HCl was added, the pH was adjusted to 2, and reacted at 60°C for 24 h. Then, the reaction solution was centrifuged and the precipitate was washed three times with deionized water. After freeze-drying, the $\beta\text{-FeOOH}$ catalyst was obtained and put into a drying oven for standby purposes.

0.005 g of $\beta\text{-FeOOH}$ was accurately weighed into the reactor, dye solution was added to the mixture, which was stirred and kept in dark for 30 min to achieve an adsorption-desorption equilibrium. After measuring the absorbance, 3 mL of 30% H_2O_2 was added. The reactor was placed under UV for photocatalytic degradation and the timer was started. 3 mL of supernatant was taken at a certain interval of time, the residual $\beta\text{-FeOOH}$ was removed with a filter membrane, and the absorbance was measured, which lasted for 4 h continuously, then the time and corresponding absorbance were recorded.

Results and discussion. Spectrophotometry is a cheap and rapid method for the analysis of dye concentration. Different dyes have different absorptions at different wavelengths. According to Lambert Beer's Law, the concentration of different dyes in a solution can be determined through spectrophotometry; thus, it is a common method to test the photocatalytic performance of catalysts. In most studies, researchers usually consider the degradation effect of single-component solutions, while its catalytic performance in multicomponent solutions is ignored. In the application, it is difficult to have a situation where single-component pollutants need to be degraded, most of which are complex. Therefore, it is necessary to establish a method to monitor the concentration change of each component in mixed-dye solutions in real time. Spectrophotometry is accurate in measuring the concentration of single-component dyes, but whether it can maintain accuracy in the case of multicomponent dyes is a problem worthy of study. Using the additivity of absorbance, the concentration of dyes in mixed solutions can be quickly determined through multicomponent spectrophotometry [26, 27]. Compared with derivative spectrophotometry, this method is simple and direct, but attention is paid to its accuracy in few studies. In this work, the accuracy of multicomponent spectrophotometry has been systematically studied, and the catalyst $\beta\text{-FeOOH}$ has been taken as an example to evaluate its degradation ability in the case of two-component solutions.

Dye structure and the maximum absorption wavelength (λ_{max}). Congo red, methyl orange, methylene blue, Rhodamine B, and methyl violet are commonly-used dyes in degradation experiments, whose structures are shown in the Fig. 1. Congo red and methyl orange are negatively charged, while methylene blue, Rhodamine B and methyl violet are positively charged. When dyes with different charges are mixed, the interaction among them may affect the absorbance. On the other hand, with different pH values, the structure of chromogenic groups will change, resulting in the change in the light absorption coefficient; therefore, a stable proton concentration is very important for the accuracy of spectrophotometry. PBS buffer solution (pH 7.4) was used to maintain the proton concentration in this work. With pH 7.4, the structure of Congo red is similar to that of methyl orange, with azobenzene as the chromogenic group and $\lambda_{max} = 490$ and 460 nm, respectively. Rhodamine B, methyl violet, and methylene blue have different chromogenic groups, whose $\lambda_{max} = 550$, 590, and 660 nm, respectively.

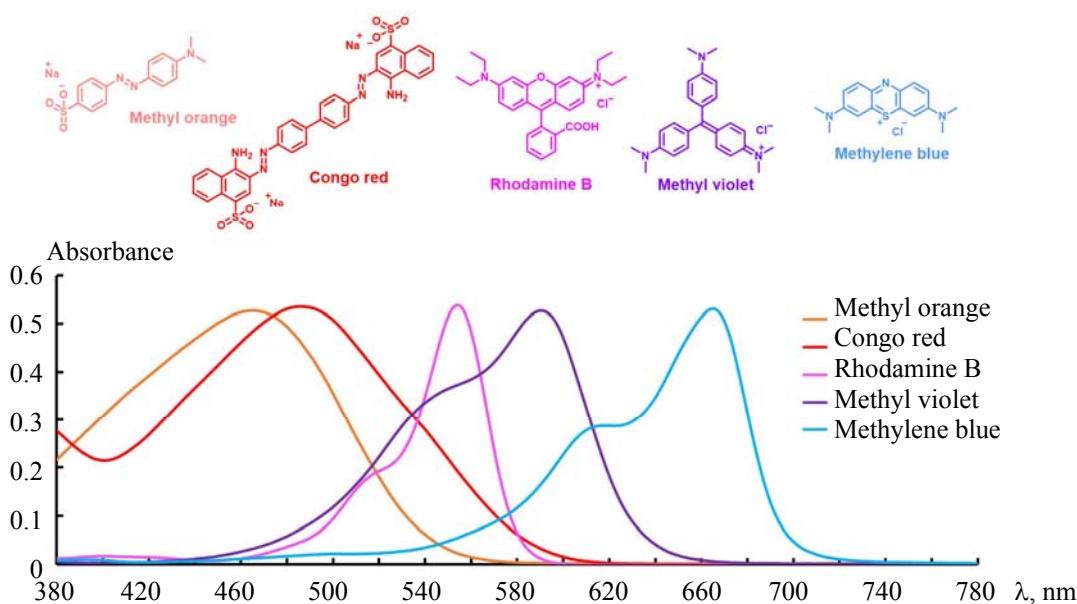


Fig. 1. Molecular structure of dyes and absorption curves in a visible range.

Standard curve of absorbance and determining the K_{iw} . For single-component solutions, only the standard curve of absorbance at λ_{max} is needed to track the dye concentration. However, for multicomponent solutions, the standard curve of all dyes at all λ_{max} needs to be established. In a mixed solution, the absorbance at each λ_{max} is measured, equations are established through the standard curves and are solved to obtain the concentration of all dyes—for example, in the mixed solution of methyl orange ($\lambda_{max} = 460$ nm) and Congo red ($\lambda_{max} = 490$ nm), the absorbance of the mixed solution at 460 nm includes that of methyl orange and Congo red (Fig. 2a, points A and D). Therefore, to calculate the concentration of each dye in this mixed solution, it is necessary to measure the absorbance at 460 nm (Fig. 2a, points A and D) and 490 nm (Fig. 2a, points B and E). In this work, a total of five dyes were used to verify multicomponent spectrophotometry, the standard curve of each at λ_{max} for these five dyes is shown in Fig. 2b–f. The K values of dyes at different wavelengths are listed in Table 1.

TABLE 1. The K (mg^{-1}/L) Value of Dyes at Different Wavelengths (by Standard Curve)

| Dye | 460 nm | 490 nm | 550 nm | 590 nm | 660 nm |
|----------------|--------|--------|--------|--------|--------|
| Methyl orange | 0.0433 | 0.0345 | 0.0023 | 0.0002 | 0.0001 |
| Congo red | 0.0137 | 0.0151 | 0.0058 | 0.0010 | 0.0000 |
| Rhodamine B | 0.0073 | 0.0267 | 0.2233 | 0.0078 | 0.0018 |
| Methyl violet | 0.0081 | 0.0264 | 0.1066 | 0.1520 | 0.0025 |
| Methylene blue | 0.0009 | 0.0019 | 0.0055 | 0.0190 | 0.0616 |

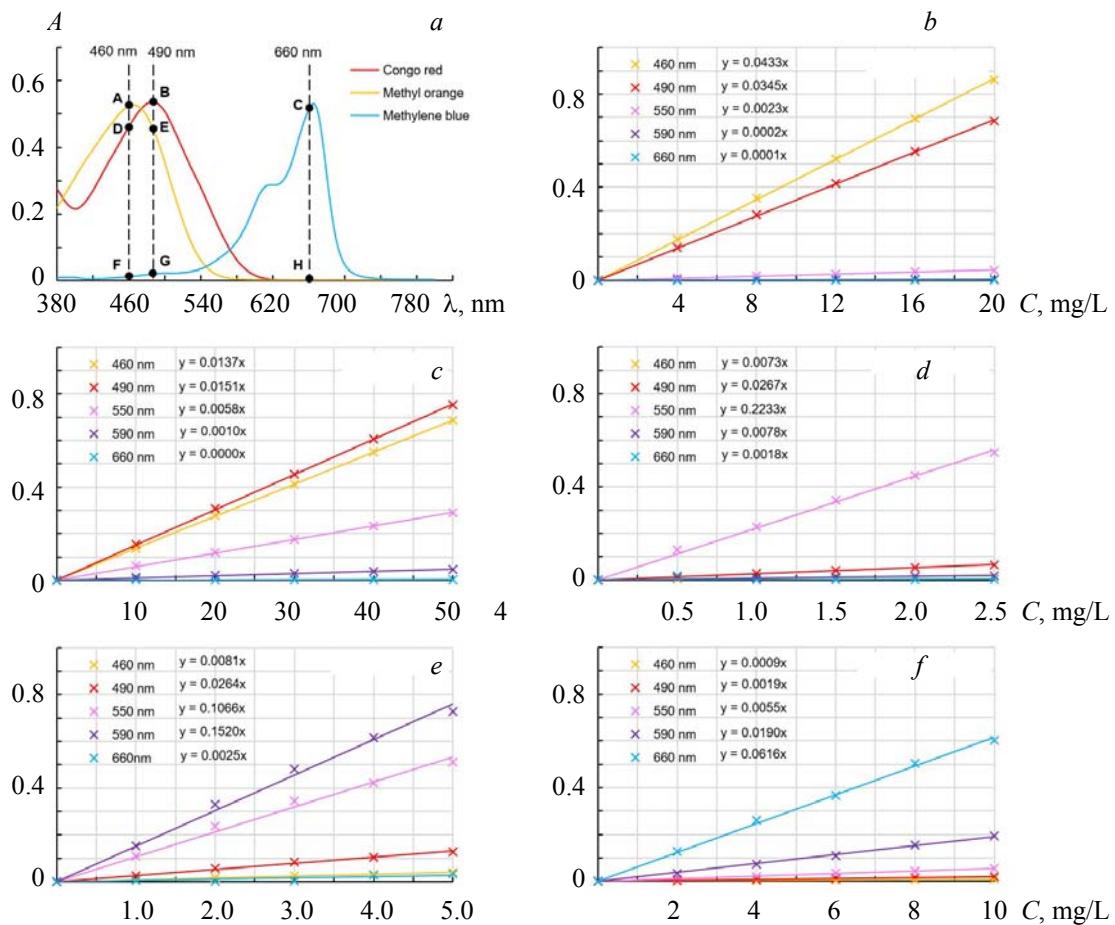


Fig. 2. Standard curve of dyes at wavelengths 460, 490, 550, 590, and 660 nm (a) illustration of the mixed solution, (b) Methyl orange, (c) Congo red, (d) Rhodamine B, (e) Methyl violet, (f) Methylene blue.

The linearity of all dyes at λ_{\max} is good, which shows that spectrophotometry can be used to accurately measure the concentration of single-component solutions. However, in multicomponent solutions, the absorption of one dye at λ_{\max} of other dyes may be low, resulting in measurement errors. For example, the standard curves of methyl orange and Congo red at their λ_{\max} (Fig. 2a, points A, B, D, and E) have a good linearity, so the measurement errors of the spectrophotometer are small; however, the mixing of methylene blue with methyl orange or Congo red will lead to greater errors. Because the absorption of methylene blue at 460 and 490 nm is very low (Fig. 2a, points F and G), the measurement errors of absorbance will become larger. In this work, in order to evaluate the influence of these errors on the accuracy of multicomponent spectrophotometry, two-component and three-component dyes with different concentrations were prepared and measured.

Two-component solution. A total of ten combinations of five dyes were used to evaluate multicomponent spectrophotometry. In order to fully consider the influence of concentration on measurement results, different concentration ratios were tested in each combination. For example, in the combination of Congo red and methyl orange, two-component solutions with different concentrations were obtained by mixing the original solutions in different proportions, with mixing ratios 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, and 10:1.

The multicomponent spectrophotometric test results of the mixed solution of Congo red and methyl orange are shown in Table 2. The maximum absorption wavelength of methyl orange is similar to that of Congo red (460 and 490 nm), so their absorption is good, which ensures the linearity of their standard curve. From the experimental results (Table 2), the concentration determined through multicomponent spectrophotometry is very close to the theoretical concentration, and the errors are within an acceptable range. In addition, it should be noted that most of the errors are negative, which indicates that the concentration measured through multicomponent spectrophotometry is smaller than the theoretical value. In mixed solutions, there is

interference among each component dye, which cannot be eliminated in the standard curve equation. Besides, in order to ensure that the absorbance value of a mixed solution is between 0.1 and 0.9, it needs to be diluted proportionally. Dilution contributes to reducing the interference between dyes and measurement errors of the spectrophotometer, but the errors caused by experimental operation increase at the same time.

TABLE 2. Determine the Concentration of Congo Red and Methyl Orange in a Mixed Solution through Multicomponent Spectrophotometry

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Methyl orange and Congo red $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0433 & 0.0137 \\ 0.0345 & 0.0151 \end{bmatrix}$ | 10:1 | Methyl orange | 8.96 | $\begin{bmatrix} 0.397 \\ 0.320 \end{bmatrix}$ | 8.86 | -1.04 |
| | | Congo red | 0.95 | $\begin{bmatrix} 0.376 \\ 0.307 \end{bmatrix}$ | 0.96 | 0.71 |
| | 5:1 | Methyl orange | 8.21 | $\begin{bmatrix} 0.376 \\ 0.307 \end{bmatrix}$ | 8.15 | -0.77 |
| | | Congo red | 1.75 | $\begin{bmatrix} 0.376 \\ 0.307 \end{bmatrix}$ | 1.69 | -3.15 |
| | 2:1 | Methyl orange | 6.57 | $\begin{bmatrix} 0.326 \\ 0.274 \end{bmatrix}$ | 6.48 | -1.38 |
| | | Congo red | 3.50 | $\begin{bmatrix} 0.326 \\ 0.274 \end{bmatrix}$ | 3.34 | -4.35 |
| | 1:1 | Methyl orange | 4.93 | $\begin{bmatrix} 0.280 \\ 0.244 \end{bmatrix}$ | 4.86 | -1.35 |
| | | Congo red | 5.24 | $\begin{bmatrix} 0.280 \\ 0.244 \end{bmatrix}$ | 5.08 | -3.19 |
| | 1:2 | Methyl orange | 3.28 | $\begin{bmatrix} 0.231 \\ 0.213 \end{bmatrix}$ | 3.12 | -4.99 |
| | | Congo red | 6.99 | $\begin{bmatrix} 0.231 \\ 0.213 \end{bmatrix}$ | 7.00 | 0.10 |
| | 1:5 | Methyl orange | 1.64 | $\begin{bmatrix} 0.184 \\ 0.181 \end{bmatrix}$ | 1.62 | -1.15 |
| | | Congo red | 8.74 | $\begin{bmatrix} 0.184 \\ 0.181 \end{bmatrix}$ | 8.30 | -5.02 |
| | 1:10 | Methyl orange | 0.90 | $\begin{bmatrix} 0.160 \\ 0.165 \end{bmatrix}$ | 0.86 | -4.19 |
| | | Congo red | 9.53 | $\begin{bmatrix} 0.160 \\ 0.165 \end{bmatrix}$ | 8.97 | -5.94 |

Note. The concentration of each component dye is about 10 mg/L, which is calibrated before mixing. Take the average value of A_1 , A_2 in three tests. Take the corresponding value from Table 1 for K_{iw} . The test value is calculated through Eq. (1).

TABLE 3. Average Error (%) of Multicomponent Spectrophotometry in a Two-Component Dye Mixed Solution

| Dye | Methyl orange (460 nm) | Congo red (490 nm) | Rhodamine B (550 nm) | Methyl violet (590 nm) | Methylene blue (660 nm) |
|-------------------------|------------------------|--------------------|----------------------|------------------------|-------------------------|
| Methyl orange (460 nm) | — | 2.67±1.95 | 2.87±2.33 | 3.52±2.87 | 3.75±3.13 |
| Congo red (490 nm) | 2.67±1.95 | — | 4.87±3.18 | 36.31±17.50 | 33.47±27.03 |
| Rhodamine B (550 nm) | 2.87±2.33 | 4.87±3.18 | — | 2.32±1.61 | 3.87±2.68 |
| Methyl violet (590 nm) | 3.52±2.87 | 36.31±17.50 | 2.32±1.61 | — | 4.54±3.25 |
| Methylene blue (660 nm) | 3.75±3.13 | 33.47±27.03 | 3.87±2.68 | 4.54±3.25 | — |

In addition to the combination of Congo red and methyl orange, the experimental results of two-component spectrophotometry of other dye combinations are shown in the supporting information (Tables S1–S9). Here, the errors of each test on the 10 combinations are counted to evaluate the accuracy of multicomponent spectrophotometry in the measurement of two-component solutions. The detailed results are

shown in Table 3. Among the 10 two-component combinations, the average error of eight of them is small (average error $<5\%$), and that of the other two combinations is large, which are Congo red mixed with methyl violet ($36.31\pm17.50\%$) and Congo red mixed with methylene blue ($33.47\pm27.03\%$). The measurement errors of Congo red mixed with methyl violet and methyl blue may be caused by the chemical reaction among them, and the structure of chromogenic groups are changed. In general, multicomponent spectrophotometry can be used to quickly measure the concentration of each component dye in a mixed solution (two-component dyes) in most cases.

Three-component solution. In a three-component solution, there are three dyes with different structures, which have a strong mutual interference and a larger interference to the test results. Therefore, in the test on three-component solutions, a closer component ratio is selected, which is 1:1:1, 2:1:1, 1:2:1, 1:1:2, 3:2:1, 3:1:2, 1:3:2, 2:3:1, 1:2:3, and 2:1:3, respectively. Table 4 shows the test results of the mixed solution of methyl orange, Rhodamine B and methyl violet. In a two-component solution, the average error of methyl orange and Rhodamine B is $2.87\pm2.33\%$, that of methyl orange and methyl violet is $3.52\pm2.87\%$, and that of Rhodamine B and methyl violet is $2.32\pm1.61\%$. In a three-component solution of these three dyes, the average error between the test concentration and the theoretical concentration is $2.31\pm2.05\%$ (Table 4). Comparing the test results of each component, it can be found that the average error of methyl orange is the largest ($3.89\pm2.16\%$), that of methyl violet is the next ($2.43\pm1.61\%$), and that of Rhodamine B is the smallest ($0.60\pm0.50\%$). In general, multicomponent spectrophotometry can be used to measure the mixed solution of methyl orange, Rhodamine B and methyl violet, the concentration error of each of which is small.

The test results of the other three-component solutions are shown in the supporting information. Table S10 shows the concentration calculation and experimental errors of a mixed solution of Rhodamine B, methylene blue and methyl violet. The average error of all dyes is $3.73\pm3.72\%$, and for each component of Rhodamine B, methylene blue and methyl violet, the average error is 0.95 ± 1.07 , 8.35 ± 1.15 , and $1.89\pm2.48\%$, respectively. This shows that multicomponent spectrophotometry is applicable here; however, similar to two-component solutions, this method fails when chemical reactions occur among components. For example, in a mixed solution of methyl orange, Congo red and methyl violet, the experimental errors of spectrophotometry are much higher than those of other groups. A possible reason for that is that Congo red reacts with methyl violet, resulting in the change of the absorption wavelength of the chromogenic groups. Nevertheless, in most cases, it is feasible to determine the concentration of dyes in three-component solutions through spectrophotometry, and the errors are controlled within 10%.

TABLE 4. Determine the Concentration of Methyl Orange, Methyl Violet, and Rhodamine B in Mixed Solutions Through Multicomponent Spectrophotometry

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$ | Test value, mg/L | Error, % |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|---------------------------------------------------------|------------------|----------|
| Methyl orange and Rhodamine B and Methyl violet $\begin{bmatrix} K_{11} & K_{21} & K_{31} \\ K_{12} & K_{22} & K_{32} \\ K_{13} & K_{23} & K_{33} \end{bmatrix} =$ $\begin{bmatrix} 0.0433 & 0.0073 & 0.0081 \\ 0.0023 & 0.2233 & 0.1066 \\ 0.0002 & 0.0078 & 0.1520 \end{bmatrix}$ | 1:1:1 | Methyl orange | 3.29 | $\begin{bmatrix} 0.091 \\ 0.513 \\ 0.239 \end{bmatrix}$ | 3.13 | -4.9 |
| | | Rhodamine B | 3.15 | $\begin{bmatrix} 0.513 \\ 0.239 \end{bmatrix}$ | 3.15 | 0.0 |
| | | Methyl violet | 3.05 | $\begin{bmatrix} 0.239 \end{bmatrix}$ | 2.97 | -2.5 |
| | 2:1:1 | Methyl orange | 4.94 | $\begin{bmatrix} 0.121 \\ 0.387 \\ 0.176 \end{bmatrix}$ | 4.78 | -3.2 |
| | | Rhodamine B | 2.36 | $\begin{bmatrix} 0.387 \\ 0.176 \end{bmatrix}$ | 2.37 | 0.4 |
| | | Methyl violet | 2.29 | $\begin{bmatrix} 0.176 \end{bmatrix}$ | 2.19 | -4.2 |
| | 1:2:1 | Methyl orange | 2.47 | $\begin{bmatrix} 0.077 \\ 0.649 \\ 0.187 \end{bmatrix}$ | 2.33 | -5.7 |
| | | Rhodamine B | 4.72 | $\begin{bmatrix} 0.649 \\ 0.187 \end{bmatrix}$ | 4.73 | 0.3 |
| | | Methyl violet | 2.29 | $\begin{bmatrix} 0.187 \end{bmatrix}$ | 2.22 | -3.1 |
| | 1:1:2 | Methyl orange | 2.47 | $\begin{bmatrix} 0.080 \\ 0.514 \\ 0.360 \end{bmatrix}$ | 2.43 | -1.5 |
| | | Rhodamine B | 2.36 | $\begin{bmatrix} 0.514 \\ 0.360 \end{bmatrix}$ | 2.37 | 0.5 |
| | | Methyl violet | 4.58 | $\begin{bmatrix} 0.360 \end{bmatrix}$ | 4.62 | 0.8 |
| | 3:2:1 | Methyl orange | 4.94 | $\begin{bmatrix} 0.121 \\ 0.434 \\ 0.126 \end{bmatrix}$ | 4.78 | -3.2 |
| | | Rhodamine B | 3.15 | $\begin{bmatrix} 0.434 \\ 0.126 \end{bmatrix}$ | 3.13 | -0.5 |
| | | Methyl violet | 1.53 | $\begin{bmatrix} 0.126 \end{bmatrix}$ | 1.49 | -2.3 |
| | 3:1:2 | Methyl orange | 4.94 | $\begin{bmatrix} 0.122 \end{bmatrix}$ | 4.80 | -2.7 |

Continue Table 4

| | | | | | | |
|-------|---------------|---------------|------|---------------------------|------|------|
| | | Rhodamine B | 1.57 | | 1.55 | -1.2 |
| | | Methyl violet | 3.05 | | 3.05 | -0.2 |
| 1:3:2 | Methyl orange | Methyl orange | 1.65 | [0.064 0.680 0.238] | 1.64 | -0.4 |
| | | Rhodamine B | 4.72 | | 4.70 | -0.4 |
| | Methyl violet | Methyl violet | 3.05 | | 2.89 | -5.4 |
| | | Methyl orange | 3.29 | | 3.04 | -7.7 |
| 2:3:1 | Rhodamine B | Rhodamine B | 4.72 | [0.089 0.608 0.131] | 4.71 | -0.1 |
| | | Methyl violet | 1.53 | | 1.48 | -3.2 |
| | Methyl orange | Methyl orange | 1.65 | | 1.74 | 5.6 |
| | | Rhodamine B | 3.15 | | 3.11 | -1.1 |
| 1:2:3 | Methyl violet | Methyl violet | 4.58 | [0.067 0.591 0.357] | 4.53 | -1.0 |
| | | Methyl orange | 3.29 | | 3.16 | -4.0 |
| | Rhodamine B | Rhodamine B | 1.57 | | 1.55 | -1.5 |
| | | Methyl violet | 4.58 | | 4.50 | -1.6 |

Note. The concentration of each component dye is about 10 mg/L, which is calibrated before mixing. Take the average value of A_1 , A_2 , A_3 in three tests. Take the corresponding value from Table 1 for K_{iw} . The test value is calculated through Eq. (2).

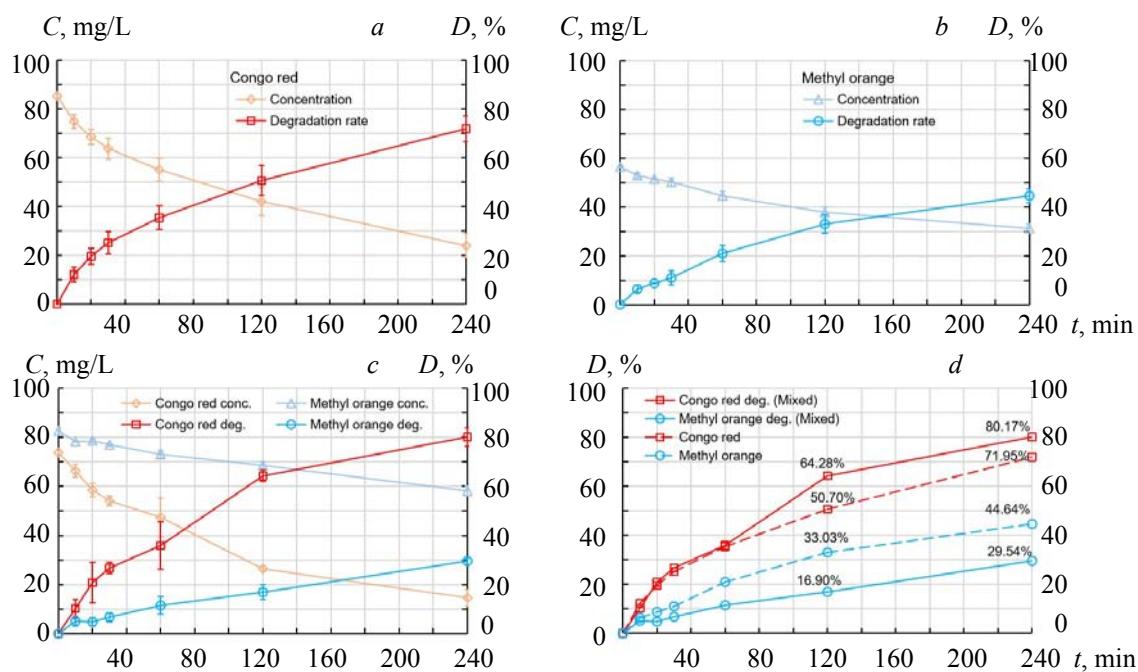


Fig. 3. Photodegradation of methyl orange and Congo red catalyzed by β -FeOOH, (a) Degradation of Congo red, (b) Degradation of methyl orange, (c) Degradation of Congo red and methyl orange in the mixed solution, (d) Comparison of degradation rate of single-component and two-component solutions.

Monitor the degradation of dyes in the mixed solution. Multicomponent spectrophotometry can be used to quickly measure the concentration of dyes in mixed solutions, which can be used to monitor the degradation rate of dyes in mixed solutions in real time and evaluate the catalytic performance of catalysts. Figure 3 shows that the degradation of methyl orange and Congo red is catalyzed with β -FeOOH alone, together with the degradation of their mixed solution. In the case of single-component solutions, after 4 h of degradation,

the concentration of Congo red decreased from 85.34 to 23.97 mg/L with a degradation rate of 71.95% (Fig. 3a). Under the same conditions, the concentration of methyl orange decreased from 56.51 to 31.29 mg/L, and the degradation rate was 44.64% (Fig. 3b). However, in the case of two-component solutions, the degradation rate of Congo red and methyl orange changed. After 4 h of degradation, the concentration of Congo red decreased from 73.80 to 14.61 mg/L with degradation rate of 80.17%; while the concentration of methyl orange decreased from 82.58 to 58.19 mg/L with a degradation rate of 29.54% (Fig. 3c). The experimental results show that the catalytic performance of β -FeOOH is different in the face of single-component and multi-component dyes. After 4 h of degradation, the concentration of Congo red (single-component) and methyl orange (single-component) decreased by 61.37 and 25.22 mg/L, respectively, while in the mixed solution, the concentration of Congo red and methyl orange decreased by 59.19 and 24.39 mg/L, respectively (83.58 mg/L in total). This shows that mixed dyes degrade faster with β -FeOOH. A possible reason is that the total concentration of the mixed solution is high, which improves the reaction rate. Although β -FeOOH accelerates the degradation rate of mixed dyes, the degradation rate of different dyes is different. It can also be found that the degradation rate of Congo red increased by 8.22% and that of methyl orange decreased by 15.10% in the mixed solution (Fig. 3d). A possible reason is that Congo red is easier to degrade than methyl orange, which reduces the degradation rate of methyl orange and accelerates its own degradation rate.

Conclusions. The accuracy of spectrophotometry for multicomponent solutions was evaluated, and the degradation process of a two-component solution was monitored. With methyl orange, Congo red, Rhodamine B, methyl violet and methylene blue as the research objects, the accuracy of spectrophotometry was systematically studied in the case of two-component and three-component solutions. The experimental results show that dyes will interfere with each other during spectrophotometry, which greatly affects its accuracy. When the dyes interfere with each other weakly, the dye concentration errors of two-component and three-component solutions are less than 5 and 10%, respectively. Multicomponent spectrophotometry provides a simple and effective means for the real-time monitoring of the degradation of mixed dyes, which is of great significance for evaluating the catalytic ability of catalysts under the condition of multicomponent dyes. Here, β -FeOOH was used as a catalyst for dye degradation. The results showed that the mixed solution was catalyzed faster with β -FeOOH, which might be due to the high total dye concentration in the mixed solution. In addition, when two dyes are mixed, the degradation rate of more degradable dyes will accelerate, while that of less degradable dyes will slow down. In general, the accuracy of multicomponent spectrophotometry and its application in the evaluation of catalyst catalytic performance were discussed in this work, proving that it is a simple, cheap, fast and accurate analytical method with an important potential in the field of environment and catalysis.

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Supplement

TABLE S1. Concentration Calculation and Experimental Error of Mixed Solution of Methyl Orange and Rhodamine B

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Methyl orange and Rhodamine B $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix}$ $= \begin{bmatrix} 0.0433 & 0.0073 \\ 0.0023 & 0.2233 \end{bmatrix}$ | 10:1 | Methyl orange | 9.05 | $\begin{bmatrix} 0.396 \\ 0.210 \end{bmatrix}$ | 9.00 | -0.59 |
| | | Rhodamine B | 0.90 | $\begin{bmatrix} 0.370 \\ 0.366 \end{bmatrix}$ | 0.85 | -5.77 |
| | 5:1 | Methyl orange | 8.29 | $\begin{bmatrix} 0.309 \\ 0.719 \end{bmatrix}$ | 8.28 | -0.14 |
| | | Rhodamine B | 1.65 | $\begin{bmatrix} 0.125 \\ 0.542 \end{bmatrix}$ | 1.56 | -5.54 |
| | 2:1 | Methyl orange | 6.64 | $\begin{bmatrix} 0.309 \\ 0.719 \end{bmatrix}$ | 6.60 | -0.59 |
| | | Rhodamine B | 3.29 | $\begin{bmatrix} 0.125 \\ 0.542 \end{bmatrix}$ | 3.15 | -4.24 |
| | 1:1 | Methyl orange | 4.98 | $\begin{bmatrix} 0.125 \\ 0.542 \end{bmatrix}$ | 4.96 | -50.13 |
| | | Rhodamine B | 4.94 | $\begin{bmatrix} 0.125 \\ 0.542 \end{bmatrix}$ | 4.80 | -51.41 |
| | 1:2 | Methyl orange | 3.32 | $\begin{bmatrix} 0.094 \\ 0.719 \end{bmatrix}$ | 3.28 | -50.61 |
| | | Rhodamine B | 6.59 | $\begin{bmatrix} 0.094 \\ 0.719 \end{bmatrix}$ | 6.40 | -51.39 |
| | 1:5 | Methyl orange | 1.66 | $\begin{bmatrix} 0.063 \\ 0.892 \end{bmatrix}$ | 1.55 | -53.29 |
| | | Rhodamine B | 8.23 | $\begin{bmatrix} 0.063 \\ 0.892 \end{bmatrix}$ | 7.98 | -51.56 |
| | 1:10 | Methyl orange | 0.90 | $\begin{bmatrix} 0.050 \\ 0.955 \end{bmatrix}$ | 0.85 | -52.84 |
| | | Rhodamine B | 8.47 | $\begin{bmatrix} 0.050 \\ 0.955 \end{bmatrix}$ | 8.54 | -49.56 |

TABLE S2. Concentration Calculation and Experimental Error of Mixed Solution of Congo Red and Rhodamine B

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Congo red and Rhodamine B $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0151 & 0.0267 \\ 0.0058 & 0.2233 \end{bmatrix}$ | 10:1 | Congo red | 9.53 | $\begin{bmatrix} 0.154 \\ 0.224 \end{bmatrix}$ | 8.81 | -7.58 |
| | | Rhodamine B | 0.85 | $\begin{bmatrix} 0.168 \\ 0.362 \end{bmatrix}$ | 0.77 | -8.90 |
| | 5:1 | Congo red | 8.74 | $\begin{bmatrix} 0.186 \\ 0.710 \end{bmatrix}$ | 8.65 | -0.98 |
| | | Rhodamine B | 1.55 | $\begin{bmatrix} 0.186 \\ 0.710 \end{bmatrix}$ | 1.40 | -9.82 |
| | 2:1 | Congo red | 6.96 | $\begin{bmatrix} 0.100 \\ 0.533 \end{bmatrix}$ | 7.04 | 1.15 |
| | | Rhodamine B | 3.29 | $\begin{bmatrix} 0.100 \\ 0.533 \end{bmatrix}$ | 3.00 | -9.00 |
| | 1:1 | Congo red | 5.22 | $\begin{bmatrix} 0.114 \\ 0.727 \end{bmatrix}$ | 5.09 | -2.56 |
| | | Rhodamine B | 4.94 | $\begin{bmatrix} 0.114 \\ 0.727 \end{bmatrix}$ | 4.64 | -6.09 |
| | 1:2 | Congo red | 3.48 | $\begin{bmatrix} 0.118 \\ 0.888 \end{bmatrix}$ | 3.71 | 6.50 |
| | | Rhodamine B | 6.59 | $\begin{bmatrix} 0.118 \\ 0.888 \end{bmatrix}$ | 6.42 | -2.55 |
| | 1:5 | Congo red | 1.74 | $\begin{bmatrix} 0.081 \\ 0.638 \end{bmatrix}$ | 1.64 | -5.69 |
| | | Rhodamine B | 8.23 | $\begin{bmatrix} 0.081 \\ 0.638 \end{bmatrix}$ | 7.91 | -3.91 |
| | 1:10 | Congo red | 0.95 | $\begin{bmatrix} 0.081 \\ 0.638 \end{bmatrix}$ | 0.97 | 2.55 |
| | | Rhodamine B | 8.47 | $\begin{bmatrix} 0.081 \\ 0.638 \end{bmatrix}$ | 8.55 | 0.95 |

TABLE S3. Concentration Calculation and Experimental Error of Mixed Solution of Methyl Orange and Methyl Violet

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Methyl orange and Methyl violet $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0433 & 0.0081 \\ 0.0002 & 0.1520 \end{bmatrix}$ | 10:1 | Methyl orange | 8.96 | $\begin{bmatrix} 0.388 \\ 0.122 \end{bmatrix}$ | 8.81 | -1.64 |
| | | Methyl violet | 0.87 | $\begin{bmatrix} 0.363 \\ 0.227 \end{bmatrix}$ | 0.79 | -9.08 |
| | 5:1 | Methyl orange | 8.21 | $\begin{bmatrix} 0.311 \\ 0.437 \end{bmatrix}$ | 8.10 | -2.21 |
| | | Methyl violet | 1.59 | $\begin{bmatrix} 0.311 \\ 0.437 \end{bmatrix}$ | 1.48 | -2.15 |
| | 2:1 | Methyl orange | 6.64 | $\begin{bmatrix} 0.250 \\ 0.653 \end{bmatrix}$ | 6.64 | 0.04 |
| | | Methyl violet | 3.01 | $\begin{bmatrix} 0.250 \\ 0.653 \end{bmatrix}$ | 2.87 | -4.74 |
| | 1:1 | Methyl orange | 4.98 | $\begin{bmatrix} 0.194 \\ 0.888 \end{bmatrix}$ | 4.98 | 0.05 |
| | | Methyl violet | 4.51 | $\begin{bmatrix} 0.194 \\ 0.888 \end{bmatrix}$ | 4.29 | -5.00 |
| | 1:2 | Methyl orange | 3.32 | $\begin{bmatrix} 0.070 \\ 0.581 \end{bmatrix}$ | 3.40 | 2.35 |
| | | Methyl violet | 6.02 | $\begin{bmatrix} 0.070 \\ 0.581 \end{bmatrix}$ | 5.84 | -2.99 |
| | 1:5 | Methyl orange | 1.66 | $\begin{bmatrix} 0.055 \\ 0.637 \end{bmatrix}$ | 1.79 | 7.74 |
| | | Methyl violet | 7.52 | $\begin{bmatrix} 0.055 \\ 0.637 \end{bmatrix}$ | 7.65 | 1.66 |
| | 1:10 | Methyl orange | 0.90 | $\begin{bmatrix} 0.055 \\ 0.637 \end{bmatrix}$ | 0.97 | 7.59 |
| | | Methyl violet | 8.21 | $\begin{bmatrix} 0.055 \\ 0.637 \end{bmatrix}$ | 8.38 | 2.07 |

TABLE S4. Concentration Calculation and Experimental Error of Mixed Solution of Methyl Orange and Methylene Blue

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|----------------|----------------------|------------------------------------------------|------------------|----------|
| Methyl orange and Methylene blue $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0433 & 0.0009 \\ 0.0001 & 0.0616 \end{bmatrix}$ | 10:1 | Methyl orange | 8.96 | $\begin{bmatrix} 0.387 \\ 0.057 \end{bmatrix}$ | 8.93 | |
| | | Methylene blue | 0.86 | | 0.92 | 6.54 |
| | 5:1 | Methyl orange | 8.29 | $\begin{bmatrix} 0.362 \\ 0.102 \end{bmatrix}$ | 8.33 | 0.38 |
| | | Methylene blue | 1.54 | | 1.65 | 6.84 |
| | 2:1 | Methyl orange | 6.64 | $\begin{bmatrix} 0.292 \\ 0.198 \end{bmatrix}$ | 6.68 | 0.62 |
| | | Methylene blue | 3.08 | | 3.20 | 3.68 |
| | 1:1 | Methyl orange | 4.98 | $\begin{bmatrix} 0.225 \\ 0.293 \end{bmatrix}$ | 5.10 | 2.42 |
| | | Methylene blue | 4.63 | | 4.75 | 2.75 |
| | 1:2 | Methyl orange | 3.32 | $\begin{bmatrix} 0.154 \\ 0.367 \end{bmatrix}$ | 3.43 | 3.24 |
| | | Methylene blue | 6.17 | | 5.95 | -3.60 |
| | 1:5 | Methyl orange | 1.66 | $\begin{bmatrix} 0.085 \\ 0.472 \end{bmatrix}$ | 1.81 | 9.20 |
| | | Methylene blue | 7.71 | | 7.65 | -0.74 |
| | 1:10 | Methyl orange | 0.90 | $\begin{bmatrix} 0.055 \\ 0.506 \end{bmatrix}$ | 0.99 | 9.61 |
| | | Methylene blue | 8.41 | | 8.21 | -2.43 |

TABLE S5. Concentration Calculation and Experimental Error of Mixed Solution of Rhodamine B and Methyl Violet

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Rhodamine B and Methyl violet $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.2233 & 0.1066 \\ 0.0078 & 0.1520 \end{bmatrix}$ | 10:1 | Rhodamine B | 8.98 | $\begin{bmatrix} 0.689 \\ 0.066 \end{bmatrix}$ | 8.85 | -1.40 |
| | | Methyl violet | 0.82 | | 0.84 | 2.57 |
| | 5:1 | Rhodamine B | 7.76 | $\begin{bmatrix} 0.650 \\ 0.098 \end{bmatrix}$ | 8.01 | 3.22 |
| | | Methyl violet | 1.51 | | 1.52 | 0.87 |
| | 2:1 | Rhodamine B | 6.59 | $\begin{bmatrix} 0.591 \\ 0.168 \end{bmatrix}$ | 6.52 | -1.07 |
| | | Methyl violet | 3.01 | | 2.97 | -1.13 |
| | 1:1 | Rhodamine B | 4.94 | $\begin{bmatrix} 0.525 \\ 0.244 \end{bmatrix}$ | 4.87 | -1.43 |
| | | Methyl violet | 4.51 | | 4.57 | 1.17 |
| | 1:2 | Rhodamine B | 3.29 | $\begin{bmatrix} 0.451 \\ 0.309 \end{bmatrix}$ | 3.23 | -1.87 |
| | | Methyl violet | 6.02 | | 5.93 | -1.41 |
| | 1:5 | Rhodamine B | 1.55 | $\begin{bmatrix} 0.401 \\ 0.403 \end{bmatrix}$ | 1.63 | 4.88 |
| | | Methyl violet | 7.57 | | 7.87 | 3.97 |
| | 1:10 | Rhodamine B | 0.85 | $\begin{bmatrix} 0.371 \\ 0.427 \end{bmatrix}$ | 0.90 | 6.03 |
| | | Methyl violet | 8.25 | | 8.37 | 1.51 |

TABLE S6. Concentration Calculation and Experimental Error of Mixed Solution of Rhodamine B and Methylene Blue

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|----------------|----------------------|------------------------------------------------|------------------|----------|
| Rhodamine B and Methylene blue $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.2233 & 0.0055 \\ 0.0078 & 0.0616 \end{bmatrix}$ | 10:1 | Rhodamine B | 8.98 | $\begin{bmatrix} 0.657 \\ 0.024 \end{bmatrix}$ | 8.80 | -2.02 |
| | | Methylene blue | 0.84 | | 0.91 | 8.38 |
| | 5:1 | Rhodamine B | 8.23 | $\begin{bmatrix} 0.584 \\ 0.036 \end{bmatrix}$ | 7.81 | -5.16 |
| | | Methylene blue | 1.54 | | 1.54 | -0.06 |
| | 2:1 | Rhodamine B | 6.59 | $\begin{bmatrix} 0.470 \\ 0.069 \end{bmatrix}$ | 6.24 | -5.31 |
| | | Methylene blue | 3.08 | | 3.18 | 3.04 |
| | 1:1 | Rhodamine B | 4.94 | $\begin{bmatrix} 0.367 \\ 0.106 \end{bmatrix}$ | 4.81 | -2.59 |
| | | Methylene blue | 4.63 | | 5.01 | 8.19 |
| | 1:2 | Rhodamine B | 3.29 | $\begin{bmatrix} 0.251 \\ 0.139 \end{bmatrix}$ | 3.21 | -2.58 |
| | | Methylene blue | 6.17 | | 6.66 | 7.95 |
| | 1:5 | Rhodamine B | 1.65 | $\begin{bmatrix} 0.398 \\ 0.467 \end{bmatrix}$ | 1.60 | -3.12 |
| | | Methylene blue | 7.71 | | 7.54 | -2.22 |
| | 1:10 | Rhodamine B | 0.90 | $\begin{bmatrix} 0.243 \\ 0.509 \end{bmatrix}$ | 0.89 | -1.42 |
| | | Methylene blue | 8.41 | | 8.24 | -2.08 |

TABLE S7. Concentration Calculation and Experimental Error of Mixed Solution of Congo Red and Methyl Violet

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|---------------|----------------------|------------------------------------------------|------------------|----------|
| Congo red and Methyl violet $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0151 & 0.0264 \\ 0.0010 & 0.1520 \end{bmatrix}$ | 10:1 | Congo red | 9.53 | $\begin{bmatrix} 0.167 \\ 0.089 \end{bmatrix}$ | 10.15 | 6.47 |
| | | Methyl violet | 1.34 | | 0.52 | -61.11 |
| | 5:1 | Congo red | 8.74 | $\begin{bmatrix} 0.190 \\ 0.171 \end{bmatrix}$ | 10.72 | 22.65 |
| | | Methyl violet | 2.46 | | 1.05 | -57.07 |
| | 2:1 | Congo red | 6.99 | $\begin{bmatrix} 0.226 \\ 0.459 \end{bmatrix}$ | 9.80 | 40.19 |
| | | Methyl violet | 4.91 | | 2.96 | -39.84 |
| | 1:1 | Congo red | 5.24 | $\begin{bmatrix} 0.137 \\ 0.455 \end{bmatrix}$ | 3.91 | -25.49 |
| | | Methyl violet | 7.37 | | 2.97 | -59.72 |
| | 1:2 | Congo red | 3.50 | $\begin{bmatrix} 0.156 \\ 0.661 \end{bmatrix}$ | 2.79 | -20.29 |
| | | Methyl violet | 9.82 | | 4.33 | -55.95 |
| | 1:5 | Congo red | 1.75 | $\begin{bmatrix} 0.119 \\ 0.598 \end{bmatrix}$ | 1.98 | 13.50 |
| | | Methyl violet | 12.28 | | 7.86 | -36.03 |
| | 1:10 | Congo red | 0.95 | $\begin{bmatrix} 0.125 \\ 0.664 \end{bmatrix}$ | 1.29 | 35.16 |
| | | Methyl violet | 13.40 | | 8.73 | -34.82 |

TABLE S8. Concentration Calculation and Experimental Error of Mixed Solution of Congo Red and Methylene Blue

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|----------------|----------------------|------------------------------------------------|------------------|----------|
| Congo red and Methylene blue $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.0151 & 0.0019 \\ 0.000 & 0.0616 \end{bmatrix}$ | 10:1 | Congo red | 9.49 | $\begin{bmatrix} 0.116 \\ 0.017 \end{bmatrix}$ | 7.65 | -19.43 |
| | | Methylene blue | 0.84 | | 0.27 | -67.84 |
| | 5:1 | Congo red | 8.70 | $\begin{bmatrix} 0.108 \\ 0.025 \end{bmatrix}$ | 7.08 | -18.65 |
| | | Methylene blue | 1.54 | | 0.41 | -73.33 |
| | 2:1 | Congo red | 6.96 | $\begin{bmatrix} 0.090 \\ 0.040 \end{bmatrix}$ | 5.88 | -15.54 |
| | | Methylene blue | 3.08 | | 0.64 | -79.12 |
| | 1:1 | Congo red | 5.22 | $\begin{bmatrix} 0.077 \\ 0.102 \end{bmatrix}$ | 4.89 | -6.32 |
| | | Methylene blue | 4.63 | | 1.66 | -64.21 |
| | 1:2 | Congo red | 3.48 | $\begin{bmatrix} 0.058 \\ 0.245 \end{bmatrix}$ | 3.34 | -4.04 |
| | | Methylene blue | 6.17 | | 3.98 | -35.44 |
| | 1:5 | Congo red | 1.74 | $\begin{bmatrix} 0.042 \\ 0.402 \end{bmatrix}$ | 1.98 | 13.91 |
| | | Methylene blue | 7.71 | | 6.53 | -15.37 |
| | 1:10 | Congo red | 0.95 | $\begin{bmatrix} 0.035 \\ 0.463 \end{bmatrix}$ | 1.37 | 44.62 |
| | | Methylene blue | 8.41 | | 7.51 | -10.71 |

TABLE S9. Concentration Calculation and Experimental Error of Mixed Solution of Methyl Violet and Methylene Blue

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$ | Test value, mg/L | Error, % |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|----------------|----------------------|------------------------------------------------|------------------|----------|
| Methyl violet and Methylene blue $\begin{bmatrix} K_{11} & K_{21} \\ K_{12} & K_{22} \end{bmatrix} = \begin{bmatrix} 0.1520 & 0.0190 \\ 0.0025 & 0.0616 \end{bmatrix}$ | 10:1 | Methyl violet | 8.21 | $\begin{bmatrix} 0.621 \\ 0.038 \end{bmatrix}$ | 8.05 | -1.86 |
| | | Methylene blue | 0.84 | | 0.91 | 7.81 |
| | 5:1 | Methyl violet | 7.52 | $\begin{bmatrix} 0.549 \\ 0.061 \end{bmatrix}$ | 7.01 | -6.82 |
| | | Methylene blue | 1.54 | | 1.69 | 9.28 |
| | 2:1 | Methyl violet | 6.02 | $\begin{bmatrix} 0.323 \\ 0.073 \end{bmatrix}$ | 5.96 | -0.94 |
| | | Methylene blue | 3.08 | | 3.31 | 7.42 |
| | 1:1 | Methyl violet | 4.51 | $\begin{bmatrix} 0.384 \\ 0.162 \end{bmatrix}$ | 4.41 | -2.19 |
| | | Methylene blue | 4.63 | | 5.07 | 9.58 |
| | 1:2 | Methyl violet | 3.01 | $\begin{bmatrix} 0.569 \\ 0.402 \end{bmatrix}$ | 2.94 | -2.20 |
| | | Methylene blue | 6.17 | | 6.41 | 3.85 |
| | 1:5 | Methyl violet | 1.50 | $\begin{bmatrix} 0.364 \\ 0.479 \end{bmatrix}$ | 1.43 | -4.80 |
| | | Methylene blue | 7.71 | | 7.72 | 0.09 |
| | 1:10 | Methyl violet | 0.82 | $\begin{bmatrix} 0.290 \\ 0.515 \end{bmatrix}$ | 0.87 | 5.69 |
| | | Methylene blue | 8.41 | | 8.33 | -1.0 |

TABLE S10. Concentration Calculation and Experimental Error of Mixed Solution of Rhodamine B, Methylene Blue, and Methyl Violet

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$ | Test value, mg/L | Error, % |
|--------------------------------------------------|--------------|----------------|----------------------|---------------------------------------------------------|------------------|----------|
| Rhodamine B and Methylene blue and Methyl violet | 1:1:1 | Rhodamine B | 3.15 | $\begin{bmatrix} 0.522 \\ 0.277 \\ 0.112 \end{bmatrix}$ | 3.13 | -0.5 |
| | | Methylene blue | 3.10 | | 3.39 | 9.4 |
| | | Methyl violet | 3.05 | | 3.06 | 0.1 |
| | 2:1:1 | Rhodamine B | 4.72 | $\begin{bmatrix} 0.646 \\ 0.203 \\ 0.085 \end{bmatrix}$ | 4.71 | -0.1 |
| | | Methylene blue | 2.32 | | 2.53 | 8.7 |
| | | Methyl violet | 2.29 | | 2.11 | -7.7 |
| | 1:2:1 | Rhodamine B | 2.36 | $\begin{bmatrix} 0.403 \\ 0.229 \\ 0.160 \end{bmatrix}$ | 2.40 | 1.8 |
| | | Methylene blue | 4.65 | | 5.03 | 8.3 |
| | | Methyl violet | 2.29 | | 2.27 | -1.1 |
| | 1:1:2 | Rhodamine B | 2.36 | $\begin{bmatrix} 0.509 \\ 0.372 \\ 0.086 \end{bmatrix}$ | 2.37 | 0.4 |
| | | Methylene blue | 2.32 | | 2.54 | 9.4 |
| | | Methyl violet | 4.58 | | 4.46 | -2.6 |
| | 3:2:1 | Rhodamine B | 4.72 | $\begin{bmatrix} 0.613 \\ 0.166 \\ 0.109 \end{bmatrix}$ | 4.68 | -0.8 |
| | | Methylene blue | 3.10 | | 3.34 | 7.9 |
| | | Methyl violet | 1.53 | | 1.53 | 0.0 |
| | 3:1:2 | Rhodamine B | 4.72 | $\begin{bmatrix} 0.697 \\ 0.268 \\ 0.060 \end{bmatrix}$ | 4.73 | 0.3 |
| | | Methylene blue | 1.55 | | 1.69 | 8.8 |
| | | Methyl violet | 3.05 | | 3.07 | 0.7 |
| | 1:3:2 | Rhodamine B | 1.57 | $\begin{bmatrix} 0.351 \\ 0.275 \\ 0.159 \end{bmatrix}$ | 1.63 | 3.6 |
| | | Methylene blue | 4.65 | | 5.01 | 7.8 |
| | | Methyl violet | 3.05 | | 2.91 | -4.6 |
| | 2:3:1 | Rhodamine B | 3.15 | $\begin{bmatrix} 0.445 \\ 0.176 \\ 0.156 \end{bmatrix}$ | 3.13 | -0.6 |
| | | Methylene blue | 4.65 | | 4.91 | 5.7 |
| | | Methyl violet | 1.53 | | 1.55 | 1.3 |
| | 1:2:3 | Rhodamine B | 1.57 | $\begin{bmatrix} 0.425 \\ 0.384 \\ 0.112 \end{bmatrix}$ | 1.55 | -1.3 |
| | | Methylene blue | 3.10 | | 3.40 | 9.6 |
| | | Methyl violet | 4.58 | | 4.55 | -0.7 |
| | 2:1:3 | Rhodamine B | 3.15 | $\begin{bmatrix} 0.600 \\ 0.376 \\ 0.060 \end{bmatrix}$ | 3.14 | -0.1 |
| | | Methylene blue | 1.55 | | 1.67 | 7.9 |
| | | Methyl violet | 4.58 | | 4.58 | 0.1 |

$$\begin{bmatrix} K_{11} & K_{21} & K_{31} \\ K_{12} & K_{22} & K_{32} \\ K_{13} & K_{23} & K_{33} \end{bmatrix} =$$

$$\begin{bmatrix} 0.2233 & 0.0055 & 0.1066 \\ 0.0078 & 0.0190 & 0.1520 \\ 0.0018 & 0.0616 & 0.0025 \end{bmatrix}$$

TABLE S11. Concentration Calculation and Experimental Error of Mixed Solution of Methyl Orange, Congo Red, and Methyl Violet

| Dye | Mixing ratio | Dye component | Standard value, mg/L | $\begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$ | Test value, mg/L | Error, % |
|---------------------------------------------|--------------|---------------|----------------------|---------------------------------------------------------|------------------|----------|
| Methyl orange and Congo red and Rhodamine B | 1:1:1 | Methyl orange | 3.29 | $\begin{bmatrix} 0.212 \\ 0.248 \\ 0.706 \end{bmatrix}$ | 2.87 | -12.9 |
| | | Congo red | 3.46 | | 4.30 | 24.2 |
| | | Rhodamine B | 3.15 | | 3.02 | -4.0 |
| | 2:1:1 | Methyl orange | 4.94 | $\begin{bmatrix} 0.267 \\ 0.271 \\ 0.535 \end{bmatrix}$ | 4.76 | -3.7 |
| | | Congo red | 2.59 | | 2.88 | 11.1 |
| | | Rhodamine B | 2.36 | | 2.27 | -3.6 |
| | 1:2:1 | Methyl orange | 2.47 | $\begin{bmatrix} 0.193 \\ 0.224 \\ 0.539 \end{bmatrix}$ | 2.12 | -14.0 |
| | | Congo red | 5.19 | | 5.83 | 12.4 |
| | | Rhodamine B | 2.36 | | 2.24 | -5.1 |
| | 1:1:2 | Methyl orange | 2.47 | $\begin{bmatrix} 0.084 \\ 0.122 \\ 0.523 \end{bmatrix}$ | 0.75 | -39.0 |
| | | Congo red | 2.59 | | 2.15 | 65.9 |
| | | Rhodamine B | 4.72 | | 2.28 | -3.3 |
| | 3:2:1 | Methyl orange | 4.94 | $\begin{bmatrix} 0.270 \\ 0.262 \\ 0.367 \end{bmatrix}$ | 4.69 | -5.0 |
| | | Congo red | 3.46 | | 3.86 | 11.6 |
| | | Rhodamine B | 1.57 | | 1.50 | -4.8 |
| | 3:1:2 | Methyl orange | 4.94 | $\begin{bmatrix} 0.259 \\ 0.280 \\ 0.707 \end{bmatrix}$ | 4.45 | -9.8 |
| | | Congo red | 1.73 | | 2.69 | 55.6 |
| | | Rhodamine B | 3.15 | | 3.05 | -3.1 |
| | 1:3:2 | Methyl orange | 1.65 | $\begin{bmatrix} 0.161 \\ 0.216 \\ 0.696 \end{bmatrix}$ | 0.95 | -42.2 |
| | | Congo red | 5.19 | | 6.69 | 29.0 |
| | | Rhodamine B | 3.15 | | 2.93 | -6.7 |
| | 2:3:1 | Methyl orange | 3.29 | $\begin{bmatrix} 0.217 \\ 0.226 \\ 0.362 \end{bmatrix}$ | 2.95 | -10.3 |
| | | Congo red | 5.19 | | 5.51 | 6.3 |
| | | Rhodamine B | 1.57 | | 1.45 | -8.1 |
| | 1:2:3 | Methyl orange | 1.65 | $\begin{bmatrix} 0.073 \\ 0.115 \\ 0.517 \end{bmatrix}$ | 0.35 | -58.0 |
| | | Congo red | 3.46 | | 2.69 | 55.5 |
| | | Rhodamine B | 4.72 | | 2.24 | -4.9 |
| | 2:1:3 | Methyl orange | 3.29 | $\begin{bmatrix} 0.096 \\ 0.130 \\ 0.518 \end{bmatrix}$ | 1.18 | -28.2 |
| | | Congo red | 1.73 | | 1.71 | 97.8 |
| | | Rhodamine B | 4.72 | | 2.26 | -4.0 |

$$\begin{bmatrix} K_{11} & K_{21} & K_{31} \\ K_{12} & K_{22} & K_{32} \\ K_{13} & K_{23} & K_{33} \end{bmatrix} = \begin{bmatrix} 0.0433 & 0.0137 & 0.0096 \\ 0.0345 & 0.0151 & 0.0280 \\ 0.0023 & 0.0058 & 0.2233 \end{bmatrix}$$