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Characterization of the Binding Interaction between Poly(Epicholorohydrin-Diamine) and Reactive Dyes using a Multiple Linear Regression and Quartz Crystal Microbalance Methods

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Characterization of the Binding Interaction between Poly(Epicholorohydrin-Diamine) and Reactive Dyes using a Multiple Linear Regression and Quartz Crystal Microbalance Methods

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Abstract: The binding processes of Reactive Red K-2BP (K-2BP) and Reactive Violet K-3R (K-3R) onto poly(epicholorohydrin-diamine)(PEPIDA) in solution and film were investigated by spectrophotometric and quartz crystal microbalance (QCM) methods, respectively. By using a multiple linear regression technique, the concentrations of the colored components in the mixtures of dye + PEPIDA were measured simultaneously from the absorbance spectra. The binding equilibrium constants for K-3R and K-2BP onto PEPIDA in solution were estimated to be 9.31×10^6 and 1.86×10^6 $\mathrm{L \cdot mol^{-1}}$, respectively. The difference in the color removal between K-3R and K-2BP by PEPIDA was discussed. The binding processes of K-3R and K-2BP onto PEPIDA film were followed by the QCM. The binding equilibrium constants were evaluated to be 1.27×10^6 and 3.28×10^5 $\mathrm{L \cdot mol^{-1}}$ for K-3R and K-2BP onto PEPIDA film, respectively. They are less than those determined in PEPIDA solutions. The binding rate constants for K-3R and K-2BP onto PEPIDA film were estimated to be 1.43×10^5 and 1.72×10^5 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$, respectively.

Keywords: Color removal, polyelectrolyte, binding constant, reactive dye

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INTRODUCTION

The electrostatic field around polyelectrolyte chains results in attracting many kinds of inorganic and organic molecules. Polyelectrolytes exhibit strong tendencies to interact with suitable counterion species. Polyelectrolyte behavior at the solid–liquid interface plays an important role in many industrial processes, such as water treatment, papermaking, mineral extraction, and oil field exploitation, as well as in several key biological areas (1–4). Polyelectrolyte flocculants have the advantages of effectiveness in widely different pH ranges, easy to handle, and immediately soluble in aqueous systems (5, 6). The binding interaction of polyelectrolytes with water-soluble ionic dyes is a scientific problem and exerts a key role in the color removal of dye wastewaters in coagulation and flocculation processes (7–12). To obtain a good removal efficiency, fundamental research about the binding process under chemical coagulation conditions is still needed. As one polyelectrolyte molecule possesses many sites for dyes binding in its chain, the stoichiometric ratio of dyes to polyelectrolyte depends on the feed ratio. The concentration-dependent stoichiometric ratio makes it difficult to measure the binding equilibrium constant according to the mass law in chemical equilibrium theory. Hence, few binding equilibrium constants between dyes and polyelectrolyte were reported in literature.

In this contribution, we wish to report here the ways for the measurements of the binding equilibrium constants of dyes to polymer flocculants. Commercially available poly(epicholorohydrin-diamine) (PEPIDA) was chosen as the model flocculant. PEPIDA is mainly employed as a new kind stabilizer for clays in the petroleum industry. It is also applied to remove oil, and turbidity from wastewaters (13). The applicability PEPIDA in combination with alum in dye wastewater treatment was reported (14, 15). Reactive Red K-2BP (K-2BP) and Reactive Violet K-3R (K-3R) were employed as the model dyes because of the widespread use of reactive dyes in the textile dyeing industry (16). A multiple linear regression (MLR) method (17) was applied to analyze the spectrophotometric data of the mixture of dye+ PEPIDA in the flocculation processes. The residual color profiles in the samples of mixed dyes+ PEPIDA were determined simultaneously. The binding equilibrium constants were estimated according to the binding model proposed. The influence from free dyes, the complexes of dyes and PEPIDA and light scattering by the flocs dispersed in solution on the color remove efficiency was distinguished. The difference in removal efficiency between the two dyes in the binary mixture was discussed.

In processes such as flocculation and coagulation, particles are brought together by various means to form aggregates (3) can more easily settle out. We are interested in how fast a dye binds to flocculant. Hence, the binding processes of K-2BP and K-3R onto PEPIDA film were monitored in real time by a quartz crystal microbalance (QCM). The bound mass was followed from the frequency shifts of the QCM, which is in a linear correction to the mass change with a detection of nanogram (18). The rate constants and equilibrium constants for the binding processes were measured. The difference for the binding equilibrium constants of dyes to PEPIDA in solution and in film was discussed.

MATERIALS AND METHODS

Chemicals and Materials

The commercially available PEPIDA (cationic ratio 5.6 mmol/kg) was purchased from the Shandong Binzhou Chemical Plant and used as received. Reactive dyes, K-2BP and K-3R were obtained from the Tianjing Tianshun Chemical Dye Manufactory. The structural formulae of the reactive dyes and PEPIDA are illustrated in Fig. 1. Silica particle with specific area of $220 \pm 20\,\mathrm{m}^2 \cdot \mathrm{g}^{-1}$ was purchased from Cabot Co. Deionized water was used everywhere in the study. The stock solutions of dyes and PEPIDA were prepared by phosphate buffer (pH = 7, 0.01 mol/L Na^+). 3-Mercaptopropionic acid (MPA, 99%) was obtained from Aldrich Chemical Co. AT-cut 10 MHz quartz crystals (with diameter of 12 mm) were supplied by the International Crystal Manufacturing Co., Oklahoma City, OK. Two “key-hole” shaped gold electrodes with a diameter of 6.5 mm were evaporated on a chromium adhesion layer in center of both sides of the quartz disc.

Measurement of Color Removal Efficiency

Decolorization tests were carried out with the PEPIDA at room temperature (ca. 20°C). In the flocculating experiments, 500 ml dye solution was added to each of the one-liter beakers and a Janke and Kunkel five-paddle stirrer (IKA-Labortechnik, Reihenruhrwerk RER, Germany) was used for mixing. The solutions were stirred rapidly at 120 rpm. The requisite amounts of PEPIDA solutions were added. The mixtures of dye and PEPIDAC were stirred for 3 min at 120 rpm, then the paddle speed was reduced to 40 rpm and continued for 25 min. After a quiescent settling for 30 min, samples were taken for analysis from a layer 2 cm below the surface. The residual absorbance was measured in UV-Vis spectrophotometer (HP8453E). The spectra in the wavelength region of 400–760 nm were recorded with an interval of 1 nm. The averaged values of three measurements were used for concentration determinations.

Because the absorption spectra of the samples are usually variable in the coagulation processes, the color removal efficiency (CRE) was calculated as

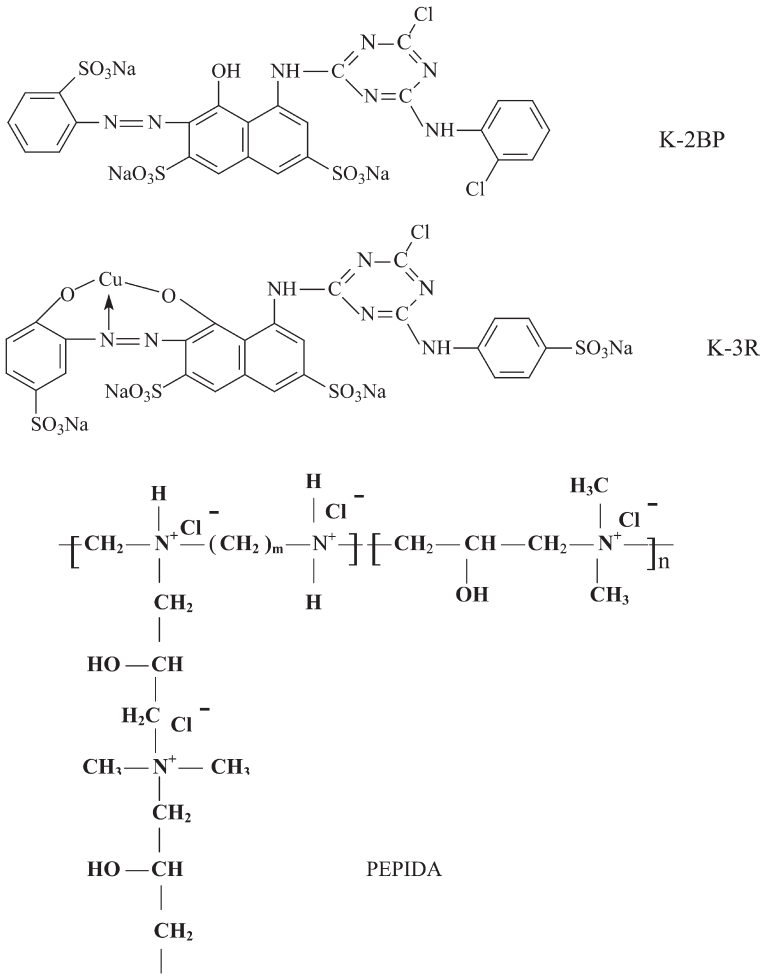

Figure 1. Structural formulas of K-2BP, K-3R and PEPIDA.

follows:

$$\mathrm{CRE} = (1 - \bar{A}_1/\bar{A}_0) \times 100\% \tag{1}$$

where $\bar{A}_0$ and $\bar{A}_1$ are the averaged absorbance of the samples before and after flocculation treatments, respectively. The averaged absorbance of a sample was calculated by

$$\bar{A} = \frac{1}{361}\sum_{\lambda i=400}^{760} A_{\lambda i} \tag{2}$$

Measurement of the Residual Color Profiles by MLR Method

Based on Beer's law, the absorbance of the sample that has *m* colored components under *n* wavelengths was expressed by:

$$\begin{bmatrix} A_1 \\ A_2 \\ \cdots \\ A_n \end{bmatrix} = \begin{bmatrix} 1 & k_{11} & k_{12} \cdots k_{1m} \\ 1 & k_{21} & k_{22} \cdots k_{2m} \\ \cdots & \cdots & \cdots \\ 1 & k_{n1} & k_{n2} \cdots k_{nm} \end{bmatrix} \bullet \begin{bmatrix} A_0 \\ C_1 \\ C_2 \\ \cdots \\ C_1 \end{bmatrix} + \begin{bmatrix} e_1 \\ e_2 \\ \cdots \\ e_n \end{bmatrix} \tag{3}$$

where A_i is the absorbance at λ_i wavelength, k_{ij} the absorption coefficients of *jth* component at a wavelength of λ_i, A_0 the absorbance due to the scattering of large flocs particles, C_j the concentrations of *jth* component, and e_i the measurement error, respectively.

Ignoring the term of measurement error, Eq. (3) was simplified as

$$\boldsymbol{A} = \boldsymbol{KC} \tag{4}$$

where $\boldsymbol{A}$, $\boldsymbol{K}$, and $\boldsymbol{C}$ are the matrices of absorbance, absorption coefficient and concentration, respectively. According to the MLR method (17), the concentrations for each of the colored components were given by:

$$\boldsymbol{C} = (\boldsymbol{K}^T\boldsymbol{K})^{-1}\boldsymbol{K}^T\boldsymbol{A} \tag{5}$$

when $\boldsymbol{A}$ and $\boldsymbol{K}$ are known, the concentration matrix $\boldsymbol{C}$ can be readily obtained from Eq. (5). The calculation of Eq. (5) was done with a software named Matlab 6.0. The absorbance data at 40 wavelengths (see Fig. 2) were used in solving of the $\boldsymbol{C}$ matrix. The absorption coefficients of dyes were obtained from the absorbance of a set of single dye solutions. The adsorption coefficients of the complex of dye-PEPIDA were obtained from the mixture of dye and much over-dosed PEPIDA. The scattering spectrum used was from the particles of SiO_2-PEPIDA because the scattering spectra of the residual colored flocs of dye-PEPIDA were difficult to measure. The validity of the Eq. (5) was repeatedly tested in a set of solutions made of K-2BP, K-3R, and silica particles. Silica particles are used to simulate the influence of scatter of the flocs. Good agreement was obtained between the experimental and calculated concentrations from Eq. (5).

Measurement of the Dyes Bound Processes by a QCM Sensor

The gold surface of the QCM was functionalized by immersion for 2 h in an ethanol solution of MPA (1 mmol/L) (followed by rinsing), creating a uniformly charged (negative) substrate surface by a self-assembled monolayer (SAM) process. The SAM modified QCM was immersed in a solution of 100 mg/L PEPIDA solution for 1 h to assemble a PEPIDA film. The PEPIDA film was rinsed by distilled water and dried by a stream of

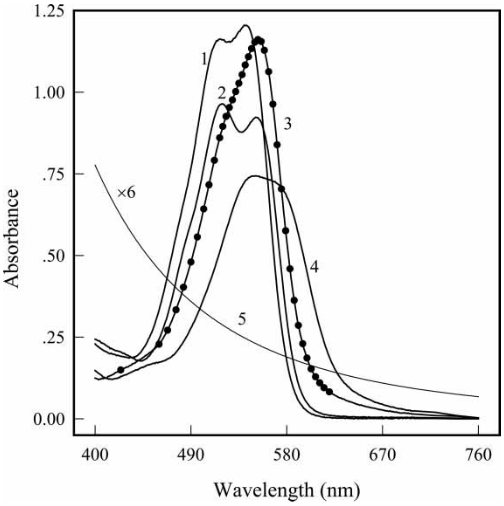

Figure 2. Absorption spectra of colored components related to color removal by PEPIDA flocculation method. (1): 50 mg/L K-2BP; (2): 50 mg/L K-2BP + 100 mg/L PEPIDA; (3): 50 mg/L K-3R; (4): 50 mg/L K-3R + 100 mg/L PEPIDA; (5): 20 mg/L SiO_2 + 100 mg/L PEPIDA.

nitrogen. This prepared QCM was mounted in the detection cell with one side facing the liquid and the other side exposed to air (19). 50 ml phosphate buffer ($pH = 7, 0.1\ mmol \cdot L^{-1}\ Na^+$) was added into the detection cell. The resonant frequency of the QCM was measured by a precision impedance analyzer (Agilent 4294A). After the stability of the baseline, the resonant frequency (F_0) was recorded as the reference. A requisite amount of the dye solution was added and the frequency shifts of the QCM, $\Delta F = F_1 - F_0$, were recorded. The bound mass of dye onto the PEPIDA film, Γ, was calculated according to Sauerbrey Equation (20) as follows:

$$\Gamma = -4.42 \times 10^5 f_0^{-2} \Delta F \tag{6}$$

where f_0 is the fundamental frequency of the QCM. In this work, $f_0 = 10^7$ Hz, a frequency decrease of 1 Hz was corresponded to a bound mass of 4.42 ng/cm^2 according to Eq. (6).

RESULTS AND DISCUSSION

Binding Isotherm Model for Dye onto PEPIDA

The equilibrium binding isotherm is a fundamental in describing the interactive behavior between a dye and a flocculant, and it is important in the design of a coagulation system. Because the molecular weight of PEPIDA is much greater than that of K-2BP or K-3R, one PEPIDA molecule can bind many dye molecules. As a result, the stoichiometric ratio of dye onto PEPIDA depends on the feed ratio, which makes it difficult to measure the binding equilibrium constant according to the mass law in chemical equilibrium theory. To obtain a quantitative description of the binding isotherms, a simplified binding model was used.

We assume that the binding rate is proportional to the concentration of the free dye and the number of unbound sites in the PEPIDA molecules, and the unbinding rate is proportional to the amount of bound dye, that is

$$d\theta/\mathrm{dt} = k_a C(1 - \theta) - k_d \theta \tag{7}$$

where θ is the ratio of bound sites to the total binding sites, t is the binding time, C is the concentration of free dye at time of t, and k_a and k_d are the rate constants for binding and unbinding processes, respectively.

After sufficient time since the addition of PEPIDA, a stable bound amount for dye was obtained. According to $d\theta/\mathrm{dt} \approx 0$, the bound amount can be expressed as follows.

$$\theta = \mathrm{KC}/(1 + \mathrm{KC}) = \alpha(C_0 - C)/C_E \tag{8}$$

where $K = k_a/k_d$, is the binding equilibrium constant, C_0 and C_E are the initial concentrations of dye and PEPIDA, respectively, and α is a proportional constant.

Estimation of the Concentrations of the Dye in Mixtures of Dye + PEPIDA

According to Eq. (8), the concentrations of free dye are needed to estimate its binding equilibrium constant. As dye has strong absorbance in the visual region, a spectrophotometric method may be a simple and convenient way to determine the concentrations of the free dye. But in the mixture of dye + polymeric flocculant, the situation is somewhat complicated. According to factor analysis (21), the residual color in the mixtures of K-3R+ PEPIDA or K-2BP+ PEPIDA was related to three components, which were the free dye, the bound dye, and the light scattering from the residual flocs in solution. The reason to treat the light scattering as the third component was that an increase in the absorbance is expected in the spectrometric measurement if part of the incident light is scattered by the fine flocs dispersed in solution, Hence, the resultant residual color in the mixtures of dye+ PEPIDA was a combination of the free dye, bound dye and that originated from the scattering flocs dispersed in solution. As shown in Fig. 2, red shifts in the absorption spectra of the bound dyes were observed with respect to their free dyes. The absorbance peaks of the bound dyes were wider than those of the free dyes. The spectral changes in the mixtures of dye + polyelectrolyte were observed in literatures (7, 9). The difference in the absorption spectra makes it possible to distinguish the contributions of different species to the residual color from the total absorbance of the samples by using the MLR method.

To do an MLR analysis, the scattering spectrum of the flocs of dye-PEPIDA was needed. But the complex of dye-PEPIDA in flocs has a strong absorbance, it is difficult to obtain its scattering spectrum directly. In this work, the scattering spectrum from the colorless flocs of SiO_2-PEPIDA was used instead of that of dye-PEPIDA. This treatment is based on the fact that the pure scattering spectra of the particles are related only to their diameters and the measuring wavelength (22). For example, the scattering spectra of the particles of SiO_2, Al_2O_3, $BaSO_4$, $CaCO_3$, and AgCl were measured. They were in the same shape as the scattering spectrum of SiO_2-PEPIDA shown in Fig. 2. Because the difference in the particle sizes between the residual flocs of the dye-PEPIDA and $SiO_2 +$ PEPIDA, only the relative concentrations of the residual flocs of dye-PEPIDA in the samples were determined.

From the concentrations of free dye in single dye sample, the bound amounts of dye onto PEPIDA were calculated. Figure 3 illustrates the binding isotherms of K-3R and K-2BP onto PEPIDA. By using Eq. (8) as the fitting model, the binding equilibrium constants for K-3R and K-2BP onto PEPIDA were estimated to be 9.31×10^6 and 1.86×10^6 L/mol, respectively. It can be seen (3) the binding equilibrium constant for K-3R is greater than that for K-2BP. This difference may be interpreted below.

As a cationic polymer, one PEPIDA molecule possesses many sites for anionic dyes to bind onto its chain. Beside the electrostatic interaction, hydrophobic interaction, hydrogen bond, and other factors are also involved in the flocculation processes (3, 5). As can be seen in Fig. 1, there are three and four

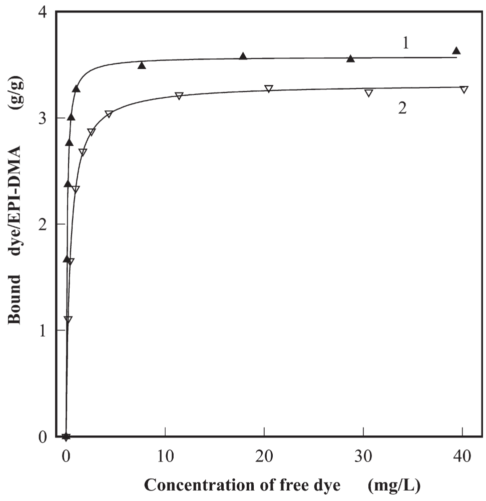

Figure 3. Binding isotherms of single reactive dye onto PEPIDA in solution. (1): K-3R; (2): K-2BP.

negatively charged -SO_3^- groups in K-2BP and K-3R molecules, respectively. The more -SO_3^- groups in K-3R enhance the binding of K-3R onto PEPIDA molecule. Moreover, the fourth -SO_3^- group in the right benzene ring of K-3R has a good freedom due to the linkage by two -NH- groups. Consequently, this -SO_3^- group has the best approachability to the binding sites in the chain of PEPIDA. Thus, the electrostatic interaction between K-3R and PEPIDA is expected to be stronger than that of K-2BP and PEPIDA. On the other hand, the Cu^{2+} in K-3R can bind with the hydroxyls in PEPIDA to form a complex of Cu^{2+}. The larger red shift in the spectra between K-3R+ PEPIDA and K-3R than that between K-2BP+ PEPIDA and K-2BP seems to be the evidence of the complex interaction. Therefore, the binding ability of K-3R onto PEPIDA is greater than that of K-2BP onto PEPIDA.

Color Removal Efficiency in Single Dye Mixtures

In the decolorization experiments, the CRE is one of the most important parameters to be measured. Figure 4 depicts the CRE values of K-3R and K-2BP as a function of the dosage of PEPIDA. It can be seen that the CRE values for the two reactive dyes are similar. With increasing dosage of PEPIDA, the CRE increases until to the maximum of 94–96% near 18 mg/L dosage then decreases. But the CRE is only a total indictor for decolorization without detailed information of the colored components. To know the residual color

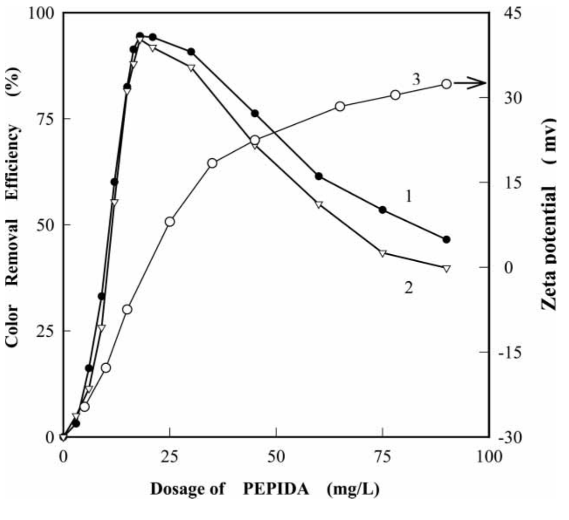

Figure 4. Dependence of the color removal efficiency and zeta potentials of the flocs on the dosage of PEPIDA. (1): removal efficiency for 50 mg/L K-3R; (2): removal efficiency for 50 mg/L K-2BP; (3): zeta potentials of the flocs of K-3R+ PEPIDA.

profile in the mixture of dye + PEPIDA is helpful to understand the decolorization behavior.

Based on the results of MLR analysis, residual color profiles in the flocculation processes for single dye are shown in Figs. 5 and 6. It can be seen that the free dye and the complex of dyes + PEPIDA are the main sources for the residual color in the low and high dosage regions, respectively. The scattering effect from the residual flocs is also a factor in reducing the color removal efficiency.

As the dosage of PEPIDA increases, the residual color from free dyes decreases near linearly then keeps in a very low level. The residual color from the complex increases to a small peak then decreases to the minimum, after then increases with increasing dosage of PEPIDA. The variation in residual color of the complex was related to the concentration and stability of the complex in solution. As can be seen in Fig. 4, the zata potentials of the flocs of K-3R + PEPIDA shift from negative to positive with increasing dosage of PEPIDA. The zata potentials of the flocs of K-2BP + PEPIDA are similar to those of the flocs of K-3R + PEPIDA and were not shown. This result reveals that the zata potentials of the flocs are related mainly to concentration ratio of K-3R to PEPIDA. Reactive dye anion has a stronger binding ability to PEPIDA than Cl^-, $H_2PO_4^-$ and HPO_4^{2-} in solution. One reason is that the electrostatic interaction for K-3R is greater than the inorganic anions, as four negatively charged -SO_3^- groups in a K-3R molecule can be bound onto the chain of PEPIDA. On the other hand, the

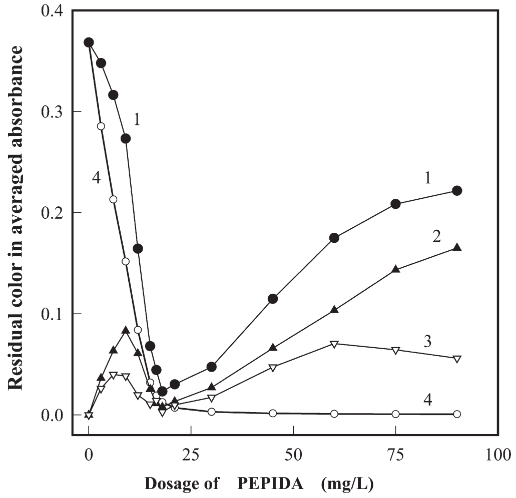

Figure 5. Dependence of the residual color on the dosage of PEPIDA. (1): measured total residual color; (2): calculated residual color from K-2BP+ PEPIDA; (3): calculated residual color from light scattering; (4): calculated residual color from K-2BP.

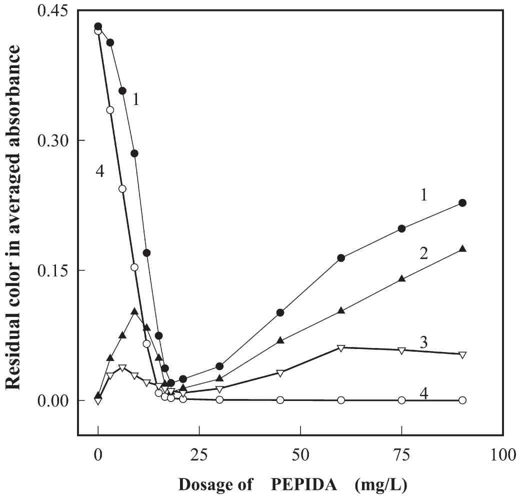

Figure 6. Dependence of the residual color on the dosage of PEPIDA. (1): total residual color; (2): from K-3R+ PEPIDA; (3): from light scattering of residual flocs; (4): from K-3R.

hydrophobic interaction, van der Waals forces and hydrogen bonding can also play roles in the binding of dye to polyelectrolyte (3, 5).

In the region of low dosage of PEPIDA, the flocs are negatively charged because of the excessive dye anions. The fine flocs can be dispersed in solution due to the electrostatic repulsion interaction among the negatively charged flocs. As the dosage of PEPIDA increases, the amount of the bound dye increases, the charge density of the complex decreases, and the stability of the complex in the flocs decreases. As a result, the residual color in the sample is lowered due to the sedimentation of the complex and the CRE is improved. In the region of over dosage of PEPIDA, the amount of the bound dye was close to its initial amount. The positive charge density of the complex increases with an increasing dosage of PEPIDA, which enhances the stability of the complex in the flocs. Hence, the residual color of the complex increases and the CRE decreases.

Dye Removal Efficiency Difference in the Binary Dye Mixture

In the binary dye mixtures, the total residual color was distinguished into five components and shown in Fig. 7. In the region of insufficient dosage of PEPIDA, the free dyes are the main sources for the residual color. With increasing dosage of PEPIDA, the concentration of free K-3R decreases near linearly while the decrease in the concentration of free K-2BP is

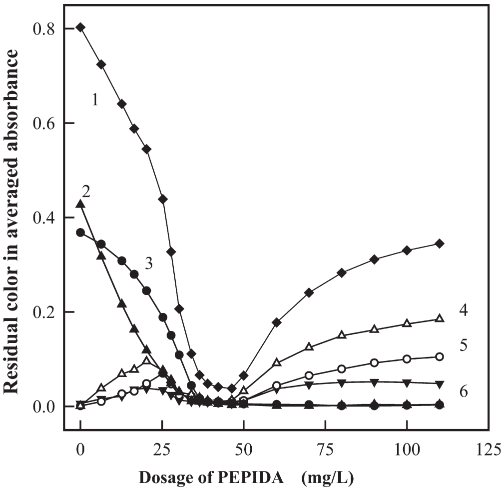

Figure 7. Dependence of the residual color of binary dyes mixture on the dosage of PEPIDA (1): Measured total residual color; (2): calculated residual color from K-3R; (3): calculated residual color from K-2BP; (4): calculated residual color from K-3R+ PEPIDA; (5): calculated residual color from K-2BP+ PEPIDA; (6): calculated residual color from light scattering.

slower. When PEPIDA is over dosed, the re-stabled complexes are the main source for the residual color. The influence of K-3R is a little larger than that of K-2BP. The scattering effect from the residual flocs is also a factor to lower the CRE.

Figure 8 illustrates the dependence of the CRE on the dosage of the PEPIDA. It can be seen that the CRE values for K-3R are higher than those for K-2BP in the region with insufficient dosage of PEPIDA. The optimum dosage in the mixture is close to the sum of that in the single dye systems. Compared with the results for single dye samples, the region of optimum dosage of PEPIDA in the mixture is broader. In the over dosed region, the CRE values in the mixture were greater than those in the single dye systems, especially for K-2BP.

Dependence of the Ratios of the Bound Amount on the dosage of the PEPIDA

Based on the changes in the concentration of free dyes, the ratios of the bound amount of K-2BP and K-3R to PEPIDA, $\theta_{\text{K-2BP}}/\theta_{\text{K-3R}}$, were calculated and illustrated in Fig. 9, It can be seen that the values of $\theta_{\text{K-2BP}}/\theta_{\text{K-3R}}$ increase and approach the unit as the dosage of PEPIDA increases. This result may be analyzed from the binding equilibrium constants between the dyes and PEPIDA.

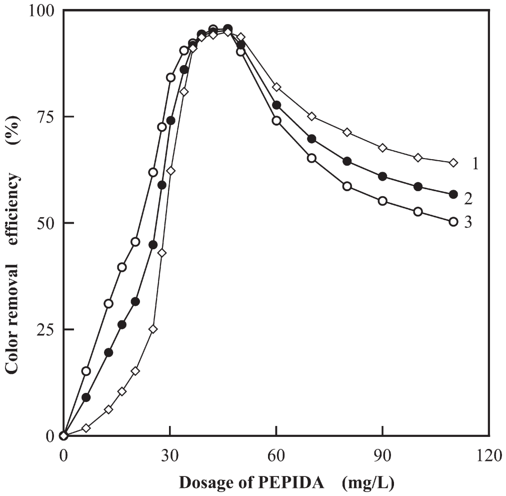

Figure 8. Dependence of the color removal efficiency of binary dye mixture on the dosage of PEPIDA. (1): calculated color removal efficiency for 50 mg/L K-2BP; (2): measured total color removal efficiency (3): calculated color removal efficiency for 50 mg/L K-3R.

Similar to the assumptions used in the samples of signal dye, the bound amounts for each dye in the binary dye mixtures were given by

$$\theta_1 = \mathrm{K_1C_1}/(1 + \mathrm{K_1C_1} + \mathrm{K_2C_2}) \tag{9}$$

$$\theta_2 = \mathrm{K_2C_2}/(1 + \mathrm{K_1C_1} + \mathrm{K_2C_2}) \tag{10}$$

where θ_1 and θ_2 are the ratios of sites bound by dye 1 and dye 2 to the total one, respectively, $\mathrm{K_1}$, $\mathrm{K_2}$, and $\mathrm{C_1}$ and $\mathrm{C_2}$ are the binding equilibrium constants and concentrations of free dye 1 and dye 2, respectively.

Combining Eq.(9) and (10), we have

$$\frac{\theta_1}{\theta_2} = \frac{C_{01} - C_1}{C_{02} - C_2} = \frac{K_1 C_1}{K_2 C_2} \tag{11}$$

where C_{01} and C_{02} are the initial concentrations of dye 1 and dye 2, respectively.

When the dosage of PEPIDA is low, the bound amounts for the dyes are small, there are $C_1 \approx C_{01,}$ $C_2 \approx C_{02,}$ As $C_{01} = C_{02}$ in this work, we have $\theta_1/\theta_2 \approx K_1/K_2$. Hence, K-3R is preferentially removed in the binary mixture due to its larger binding equilibrium constant. As the dosage of PEPIDA increases, the bound amount increases, the value of C_1 is less than C_2 if $K_1 > K_2$. The value of θ_1/θ_2 decreases due to the decrease in the value of C_1/C_2 with increasing dosage of PEPIDA. When PEPIDA is over dosed, most of the dyes were in bound forms, the concentration of free dyes is very low, $C_{01}-$

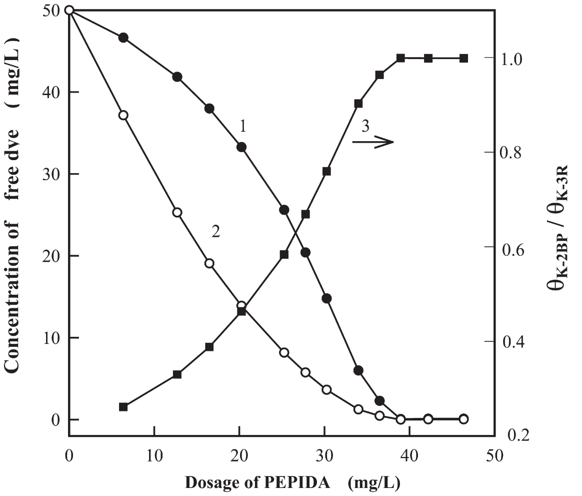

Figure 9. Dependence of the calculated concentration of free dye in binary dye mixture and the ratio of the bound amounts of K-3R to K-2BP on the dosage of PEPIDA. (1): free K-2BP in solution; (2): free K-3R in solution; (3): bound amount ratio of K-2BP to K-3R.

$C_1 \approx C_{01}$, $C_{02}-C_2 \approx C_{02}$, there is $\theta_1/\theta_2 \approx C_{01}/C_{02}$. Under our experimental conditions, we have $\theta_1/\theta_2 \approx 1$ because $C_{01} = C_{02}$. Based on the results of θ_1/θ_2 with the concentration of free dyes larger than 2 mg/L, the value of $K_{\text{K-3R}}/K_{\text{K-2BP}}$ was estimated to be 4.9 ± 0.6 according to Eq. 11, which is close to that calculated from the binding isotherms of a single dye.

Monitor the Bonding of Dye onto PEPIDA Film by QCM

In the decolorization of dyes in a flocculation and coagulation process, the binding of dyes onto flocculants is the most important initial step. It is interesting to know the kinetics parameters about the binding process. In this work, the binding process of K-3R or K-2BP onto a PEPIDA film was monitored in real time by a QCM. The principle of the method is that the bound amount of dye onto PEPIDA film assembled on the QCM corresponds to a linear decrease in the frequency of the QCM. To enhance the adsorption of PEPIDA on the QCM, the surface of gold electrode was first functionalized by a SAM with carboxyl groups. As shown in Fig. 10, the frequency of the QCM decreased after the addition of dye. As the concentration of the dye increases, the frequency shifts approach to the stable value in a shorter time. The frequency shifts during binding can be regressed by the following fitting model.

$$\Delta F = \Delta F_0 + \Delta F_1 \exp(-k_1 t) + \Delta F_2 \exp(-k_2 t) \qquad (12)$$

Where $k_1 \gg k_2$, $|\Delta F_1| \gg |\Delta F_2|$. It was revealed that a fast mass increase step was flowed by a slow one in the binding process. The former corresponds to the initial binding process while the latter is attributed to the configuration adjustment of the dye layer. There are good linear correlations between k_1 and C for the binding of K-2BP or K-3R onto the PEPIDA film in the early binding processes ($t < 20$ min). According to the slopes of the plottings of k_1 versus C, the binding rate constants were estimated to be 143 and 172 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ for K-3R and K-2BP respectively.

By using the frequency-mass coefficient in Sauerbrey Eq. (20), the binding isotherms for K-2BP and K-3R onto the PEPIDA film were calculated and shown in Fig. 11. By using Eq. (8) as the fitting model, the binding equilibrium constants were estimated to be 1.27×10^6 and 3.28×10^5 L/mol for K-3R and K-2BP respectively. The unbinding rate constants were calculated by $k_d = k_a/K$ to be $1.13 \times 10^{-4}\ \mathrm{s^{-1}}$ and $5.24 \times 10^{-4}\ \mathrm{s^{-1}}$ for K-3R and K-2BP respectively.

It can be seen that the binding equilibrium constants of the dyes onto the assembled PEPIDA film are less than measured in solution. One reason is that the assembly of the PEPIDA layer onto the MPA SAM is mainly by electrostatic interaction. Consequently, the charge density of the PEPIDA film was decreased as part of the binding sites in the PEPIDA was used up in the film assembly step. Another reason is that the freedom of the PEPIDA film is much less than PEPIDA in solution. As a result, the special configuration for dye binding in the PEPIDA film is less favorable than that in PEPIDA

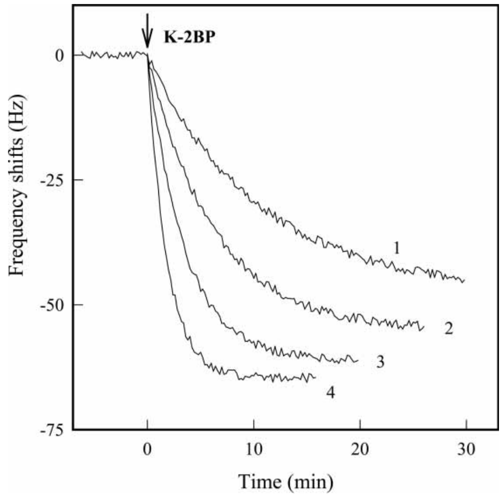

Figure 10. Frequency shifts of the QCM during the binding process of K-2BP onto assembled PEPIDA film. Concentration of K-2BP: (1): 5 mg/L; (2): 10 mg/L; (3): 20 mg/L; (4): 40 mg/L.

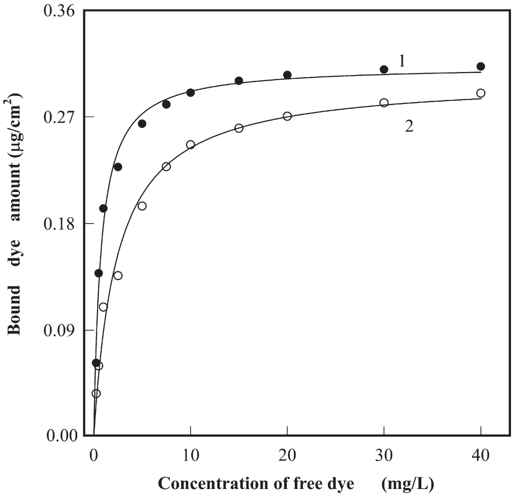

Figure 11. Binding isotherms of single reactive dye onto assembled PEPIDA film. (1): K-3R; (2): K-2BP.

solution. Hence, the binding equilibrium constants of the dyes onto the PEPIDA film are less than those onto PEPIDA in solution.

CONCLUSIONS

The experimental results presented demonstrated clearly that chemometrics and QCM methods were useful tools for investigating the interaction between dyes and polyelectrolyte. It was shown that there are three and five components which respond to the resultant residual color in the single and binary dye samples, respectively. The distribution from each component can be distinguished from the total residual color of the samples. According to changes in the concentrations of the free dyes, the binding equilibrium constants for K-3R and K-2BP onto PEPIDA were estimated to be 9.31×10^6 and 1.86×10^6 $\mathrm{L \cdot mol^{-1}}$, respectively. QCM is a useful tool to study the interaction between dyes and polymer film. The binding equilibrium constants were estimated to be 1.27×10^6 and 3.28×10^5 $\mathrm{L \cdot mol^{-1}}$ for K-3R and K-2BP onto PEPIDA film respectively. The binding and unbinding rate constants were 143 and 172 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$, 1.13×10^{-4} $\mathrm{s^{-1}}$, and 5.24×10^{-4} $\mathrm{s^{-1}}$ for K-3R and K-2BP respectively.

In the region of insufficient dosage of PEPIDA, free dye is the main factor that influences the CRE. In the mixture of K-3R and K-2BP, the influence from K-2BP is greater than that from K-3R. Because the binding equilibrium constant of K-3R is greater than that of K-2BP, K-3R is preferentially removed by the PEPIDA in the binary dye mixtures. When PEPIDA was over dosed, the residual color was mainly due to the re-stabled dye-PEPIDA complexes. In the binary dye mixtures, the influence from the complex of K-3R is larger than that from the complex K-2BP. The light scattering from residual flocs results in a decrease in CRE value.

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