RESIDUES AND TRACE ELEMENTS

Cloud-Point Extraction of Rhodamine 6G by Using Triton X-100 as the Non-Ionic Surfactant

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Cloud-point extraction (CPE) using the non-ionic surfactant Triton X-100 was used successfully to remove a highly toxic dye, rhodamine 6G (R6G), from water and wastewater. The effects of different analytical parameters such as pH, concentration of Triton X-100 (TX-100) and salts, equilibrium temperature, and incubation time on the efficiency of the extraction of R6G were studied in detail, and optimum conditions for dye extraction were obtained. Thermodynamic parameters including changes in Gibbs free energy, enthalpy, and entropy were also calculated, and these parameters indicated that the CPE of R6G was feasible, spontaneous, and endothermic in the temperature range of 75–95°C. The equilibrium solubilization capacity of TX-100 was found to be 1.10 mmol/mol by using Langmuir isotherm models. No significant interference effects were observed in the presence of phenol and its derivatives, some acidic and basic dyes and most of the anions and cations. It was concluded that the CPE process described in this paper can be an alternative technique for removal of dyes and other pollutants from waters and wastewaters.

Among the different pollutants released with effluents from various industries, such as textiles, pulp mills, leathers, plastics, cosmetics, foods, and pharmaceuticals, and dyes and pigments, some of the most dangerous and considerable water pollutants. Some dyes cause toxic, and mutagenic, teratogenic, and carcinogenic effects in aquatic life and humans when they were present in water, even at low concentrations (1, 2). As a result of direct contact, inhalation, or ingestion, dyes can cause eye burns,

rapid or difficult breathing, nausea and vomiting, etc., in humans (3). Various methods—including ultrafiltration, coagulation, flocculation, biological oxidation, chemical precipitation, reverse osmosis, filtration, and adsorption—have been used by many researchers to remove dyes from contaminated wastewater (4). The adsorption technique is usually considered an appropriate treatment process. However, the adsorbents used in the adsorption process are impractical for the treatment of effluents in the modern textile industry (5). Although activated carbon has a large surface area and high adsorption capacity, its high cost and the difficulties in recovering activated carbon particles from treated water limit its use as an adsorbent (6). On the other hand, cloud-point extraction (CPE) has become an effective and versatile techniques for the separation, purification, and preconcentration of organic compounds, (such as phenol and its derivatives), dyes, and pigments, and of inorganic compounds such as toxic heavy-metal ions (7). The CPE technique is based on the assumption that non-ionic surfactants generate micelles in aqueous solutions and become turbid when heated above the temperature known as the cloud-point temperature (CPT). Above the CPT, the micellar solution separates into two phases: (*1*) a surfactant-rich phase in a small volume that mainly contains more surfactant, and is called the coacervate phase (CP) and (*2*) a bulk-diluted aqueous phase containing a small amount of surfactant with a critical micellar concentration (CMC). During formation of the two phases, the hydrophobic species can be entrapped in the CP. This process is called CPE (7–9). The use of the CPE technique has several advantages, such as low cost, higher safety, simplicity, and a low volume of organic solvent, which is generally highly toxic (10–13). Although different non-ionic surfactants are available, in the present study we used Triton X-100 (TX-100) because the derivatives of Triton X surfactants are low-cost and commercially available, with high purity and low toxicity (14).

Rhodamine 6G (R6G), used in the present study, is a basic dye and used widely in acrylic, nylon, silk, and wool
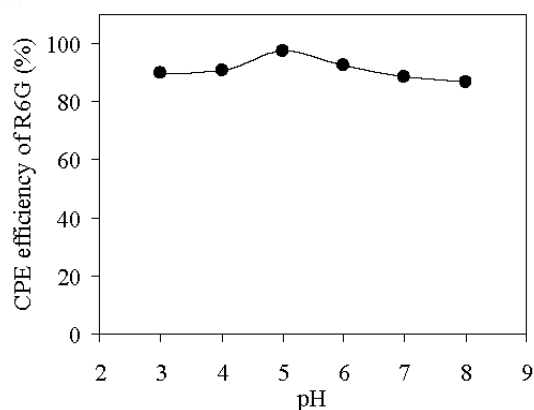
Figure 1. Effect of pH on the CPE of R6G (initial R6G concentration, 2.09×10^{-4} M, TX-100 concentration, 0.2 M).

dyeing (15). Because it is commonly used in industrial applications, removal of R6G from industrial wastewater is an important application in the protection of public health, the environment, and aquatic life. In the present study, we have proposed a simple, fast, and highly effective CPE procedure using a non-ionic surfactant, TX-100, for removal of a toxic dye, R6G, from water and wastewater. The effects of various experimental parameters such as pH, surfactant concentration, equilibrium temperature, and incubation time, on the CPE of R6G were evaluated. The solubilization isotherm model and the thermodynamic parameters of the CPE process selected were also investigated using the experimental data.

Experimental

Apparatus

The measurements for R6G determination were performed with a double beam UV-Vis spectrophotometer (ATI Unicam UV-Vis Spectrometer UV2, Cambridge, UK). The pH measurements were made with a Hanna pH-211 digital pH meter (HANNA Instruments, Cluj-Napoca, Romania) with a glass electrode. A Sigma 3-16P centrifuge (Osterode am Harz, Germany) was used for the centrifugation of solutions. A Nüve Model BM 402 (Ankara, Turkey) thermostat bath, maintained at the desired temperature, was used for the CPE experiments.

Reagents and Solutions

All chemicals used in this work were analytical grade from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), unless otherwise specified. Deionized water was used for all dilutions. All glassware and plastics were soaked in 10% (w/v) nitric acid solution for 1 day before use, then cleaned repeatedly with deionized water. The R6G (Merck) used in the present study is a cationic dye. The Colour Index No. of R6G is 45.160, the chemical formula is $C_{28}H_{31}ClN_2O_3$, the formula weight is 479.02 g/mol, and the absorbance maximum (λ_{max}) is 547 nm. TX-100 (isooctylphenoxypolyethoxyethanol; molecular weight,

628 g/mol, λ_{max}, 226 nm), procured from Merck, was used as the non-ionic surfactant. The CMC and cloud point of TX-100 are 2.8×10^{-4} M (16) and 65°C (17), respectively.

CPE Procedure for R6G

For the CPE experiments, 15 mL solution containing R6G, 3 mL 0.2 M TX-100 and 2 mL 0.2 M NaCl were combined; the resulting solution was adjusted to pH 5 with 0.1 M NaOH or 0.1 M HCl and kept at 85°C for 60 min in a thermostatic bath. The phase separation can be accelerated by centrifugation for 10 min at 3000 rpm. After cooling for 5 min in an ice bath, the surfactant-rich phase became viscous, and the dilute phase was analyzed for residual R6G concentration by using a double-beam UV-Vis spectrophotometer at 524 nm. All experiments were conducted in triplicate, and the averages of the results were used for data analysis. The efficiency of the CPE of R6G was calculated by using the following equation:

$$Efficiency\ of\ CPE = \frac{C_o - C_d}{C_o} \times 100 \qquad (1)$$

where C_o (mol/L) and C_d (mol/L) are the R6G concentrations of the initial solution and the dilute phase, respectively.

Results and Discussion

Effect of pH

The pH of the solution plays a critical role in the ionization of dye molecules; therefore, the efficiency of the CPE of R6G was investigated in the pH range of 3–8. Figure 1 shows that the extraction efficiency of R6G is not strongly pH-dependent. However, because the maximum extraction was obtained at pH 5.0, when compared with highly acidic and basic media pH 5 was selected for further CPE experiments.

Effect of TX-100 Concentration

The effect of TX-100 concentration on the efficiencies of the extraction of different initial R6G concentrations was studied over the TX-100 concentration range of 0.005–0.3 M. The extraction percentage of R6G increased sharply as the TX-100 concentration was increased from 0.005 to 0.2 M. Figure 2a shows that for an initial dye concentration of 1.04×10^{-4} M, nearly 100% of the dye was extracted, and for initial dye concentrations of 2.09×10^{-4} and 5.22×10^{-4} M, the extraction efficiencies were 94 and 93%, respectively, when the TX-100 concentration was 0.2 M. Beyond 0.2 M, the increase in extraction efficiency was negligible.

The fractional CP volume was calculated by using the following equation (18):

$$F_c = \frac{volume\ of\ CP}{total\ volume\ of\ solution} \qquad (2)$$

The fractional CP volume increased with an increase in surfactant concentration (Figure 2b). Because the surfactant
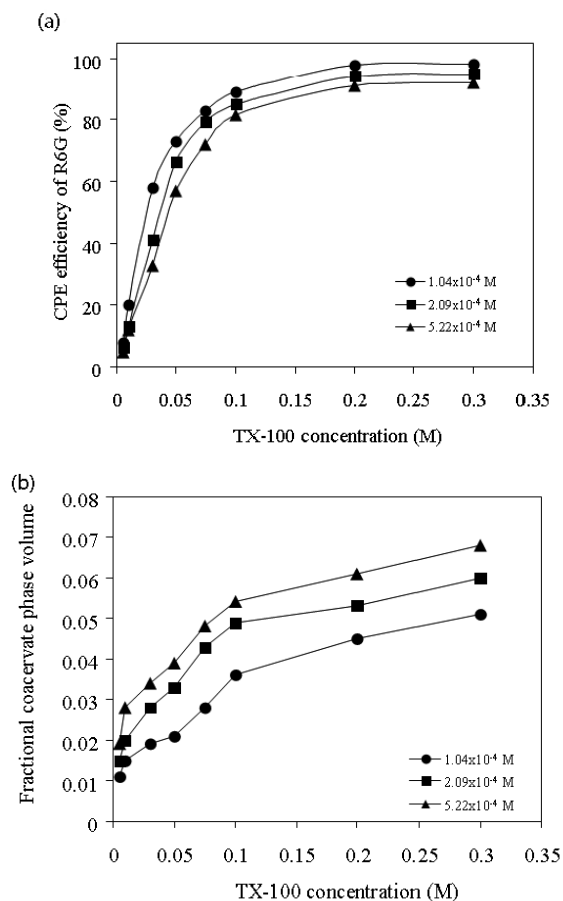
(a)

(b)

Figure 2. (a) Effect of TX-100 concentration on the CPE of R6G; (b) variation in fractional CP volume with TX-100 concentration at three different initial concentrations of R6G.

concentration in the CP remains nearly constant at a fixed temperature, the CP volume increases to maintain material balance. As a result, the presence of more surfactant in the micellar-rich phase induces an increase in the solubilization of R6G and also in the extraction efficiency (19).

Effect of Equilibrium Temperature and Incubation Time

Equilibrium temperature and incubation time are important parameters for complete extraction of R6G and separation of the coacervate and dilute phases. The dependence of extraction efficiency on equilibrium time was studied for a time interval of 2–90 min. The maximum value for extraction efficiency (>90%) for different concentrations of R6G were obtained after 60 min; thus, an incubation time of 60 min was chosen as the optimum value (Figure 3).

As the equilibrium temperature increased from 65 to 95°C, the concentrations of R6G in the CP increased for all initial R6G concentrations studied (Figure 4). The non-ionic surfactants seem to be more hydrophobic at higher temperatures, which lead to an increase in the micellar concentration. Therefore, solubilization of the R6G molecules increased with increasing temperature, causing an increase in
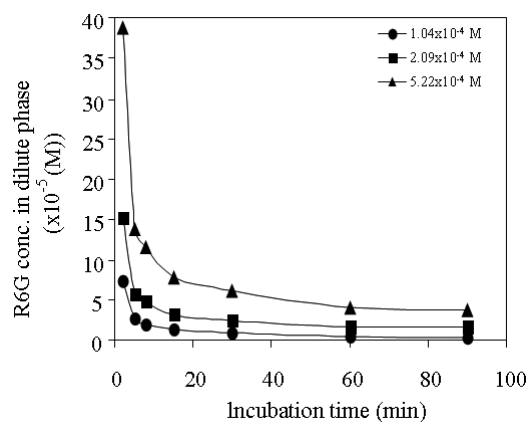

Figure 3. Effect of incubation time on the CPE of R6G (pH 5.0; TX-100 concentration, 0.2 M).

R6G extraction efficiency (18, 20). The equilibrium temperature selected for further experiments was 85°C.

Thermodynamic Parameters of CPE

The thermodynamic parameters including Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) have a significant role in determining the feasibility, spontaneity, and heat change for the CPE process. These parameters can be calculated by using the following equations (21):

$$\Delta G = -RT \ln K_d \qquad (3)$$

where R is the universal gas constant (8.314 J/mol•K), T is the temperature (°K), and K_d is the distribution coefficient. The K_d value was calculated by using following equation (22, 23):

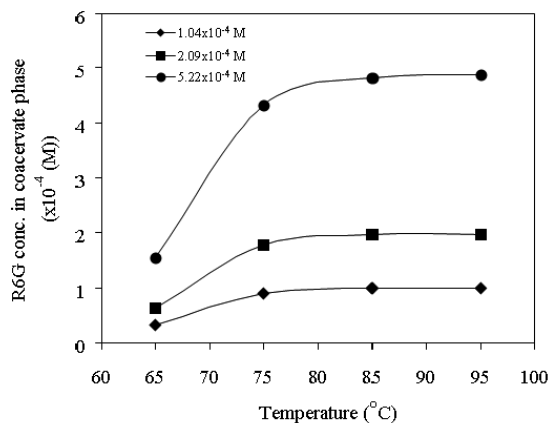$$K_d = \frac{q_e}{C_e} \qquad (4)$$

Figure 4. Effect of equilibrium temperature on the CPE of R6G (pH 5.0; TX-100 concentration, 0.2 M; incubation time, 60 min).

Table 1. Thermodynamic parameters of the CPE of R6G

R6G concn × 10^{-4}, M	T, °C	K_d	ΔG, kJ/mol	ΔS, J/mol•K[a]	ΔH, kJ/mol[a]
1.04	65	0.45	2.22		
	75	6.14	−5.25	370.53	125.82
	85	18.80	−8.73		
	95	19.00	−9.01		
2.09	65	0.43	2.35		
	75	5.85	−5.11	365.82	124.29
	85	15.13	−8.09		
	95	16.54	−8.59		
5.22	65	0.42	2.45		
	75	4.79	−4.53	353.60	120.42
	85	11.82	−7.35		
	95	14.43	−8.17		

[a] Measured between 338 and 368K.

where q_e (mole/L) is the moles of R6G solubilized per liter of TX-100, and C_e (mole/L) is the equilibrium concentration of R6G in the dilute phase. The changes in ΔH and ΔS of the CPE were estimated from the following equation:

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

This equation can be written as follows:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (6)$$

The ΔH and ΔS values were obtained from the slope and intercept, respectively, of the plot of ln K_d versus $1/T$; the values of K_d, ΔH, ΔS, and ΔG are shown in Table 1 for different R6G concentrations. The negative values of ΔG, in the temperature range of 75–95°C, suggested the feasibility of the CPE process and the spontaneous nature of the CPE of R6G, whereas the positive values of ΔH indicated the endothermic nature of CPE, and the positive values of ΔS implied good affinity of the R6G molecules for TX-100 micelles.

Effect of Initial Dye Concentration and Solubilization Isotherms

The effect of the initial R6G concentration on the CPE process was investigated for initial R6G concentrations in the range of 5.0×10^{-5}– 10.4×10^{-4} M. The equilibrium solubilization of R6G increased from 0.08 to 0.92 mmol/mol, whereas the extraction percentage decreased from 99 to 89% when the initial R6G concentration was increased from 5.0×10^{-5} to 10.4×10^{-4} M (Figure 5a). At a constant TX-100 concentration the decrease in extraction efficiency is probably because the solubilization capacity of TX-100 becomes saturated at higher R6G concentrations. Nevertheless, the

extraction efficiency of R6G was nearly 100% for a dye concentration of 5.0×10^{-5} M.

In order to investigate the dye solubilization capacity of TX-100, the experimental data were used to calculate the solubilization isotherms. Although different isotherm models are available to identify the adsorption process, the Langmuir type is the most common model because of its simplicity and reliability. The same model can be also used to explain the solubilization of dyes in surfactant (18, 24). Thus, in the present study, the solubilization of R6G in TX-100 was evaluated in terms of the Langmuir isotherm model.

The Langmuir model is given by the following equation (25):

$$q_e = \frac{bq_{max}C_e}{1+bq_{max}} \qquad (7)$$

where q_e (mmol/mol) is the mmoles of R6G solubilized per mole of TX-100, C_e (mmol/L) is the dilute phase equilibrium concentration of R6G, q_{max} (mmol/mol) is the Langmuir constant related to the maximum solubilization capacity, and b (L/mol) is the constant related to the energy of the solubilization. The Langmuir model in linear form is shown below:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \qquad (8)$$

The values of q_{max} and b obtained from the slope and intercept of the linear plot of C_e/q_e versus C_e (Figure 5b) were found to be 1.10 mmol/mol and 41.32 L/mol, respectively, with a correlation coefficient (R^2) of 0.961. From the results, it can be concluded that the solubilization pattern of R6G in TX-100 is a good fit for the Langmuir isotherm model.
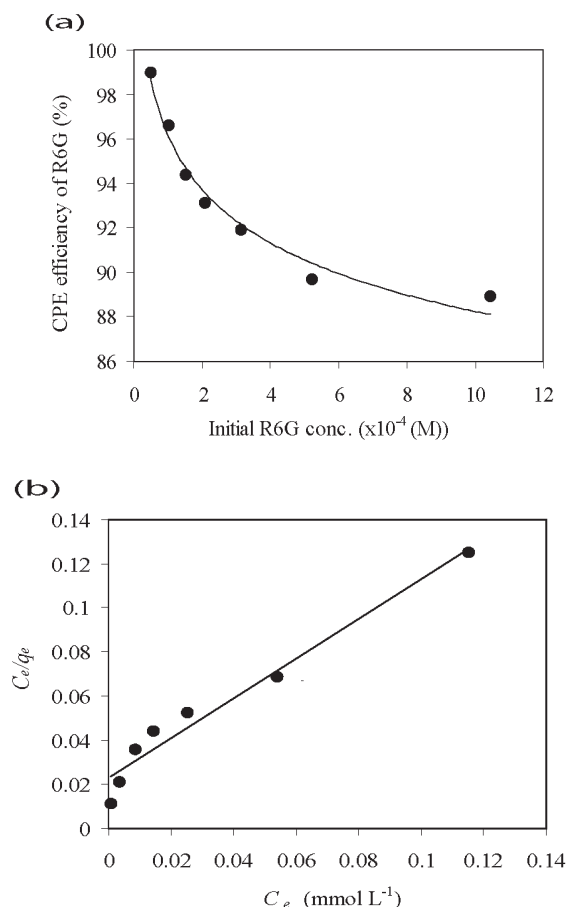
Figure 5. (a) Effect of initial dye concentration on the efficiency of the extraction of R6G (pH, 5.0; TX-100 concentration, 0.2 M; incubation time, 60 min; equilibrium temperature, 85°C); (b) Langmuir solubilization isotherm model for the CPE of R6G.

Figure 6. (a) Effect of salt concentration on the extraction of R6G (initial R6G concentration, 2.09×10^{-4} M; pH 5.0; TX-100 concentration, 0.2 M; incubation time, 60 min; equilibrium temperature, 85°C); (b) variation in fractional CP volume with different concentrations of salts.

Effect of Salt Concentration

The influences of NaCl and BaCl$_2$ as electrolytes were investigated in the concentration range of 0.01–0.3 M, at a fixed initial R6G concentration (2.09×10^{-4} M) and a TX-100 concentration of 0.2 M. As the concentrations of NaCl and BaCl$_2$ were increased from 0.01 to 0.3 M, the efficiencies of the extraction of R6G increased from 84 and 87% to 92 and 93%, respectively (Figure 6a). Because of the salting-out effects of electrolytes, their presence decreases the CPT and stimulates dehydration of the ethoxy groups on the outer surface of the micelles. The result is enhanced micellar concentration, which leads to solubilization of more dye and results in a more efficient extraction (26). The addition of salts also decreases the fractional CP volume (Figure 6b) because more water goes to the dilute phase as a result of the salting-out effects (18).

Interference Studies

The effects of various anions, cations, phenol and its derivatives, and some acidic and basic dyes were investigated as potential interference materials in the CPE of R6G. The
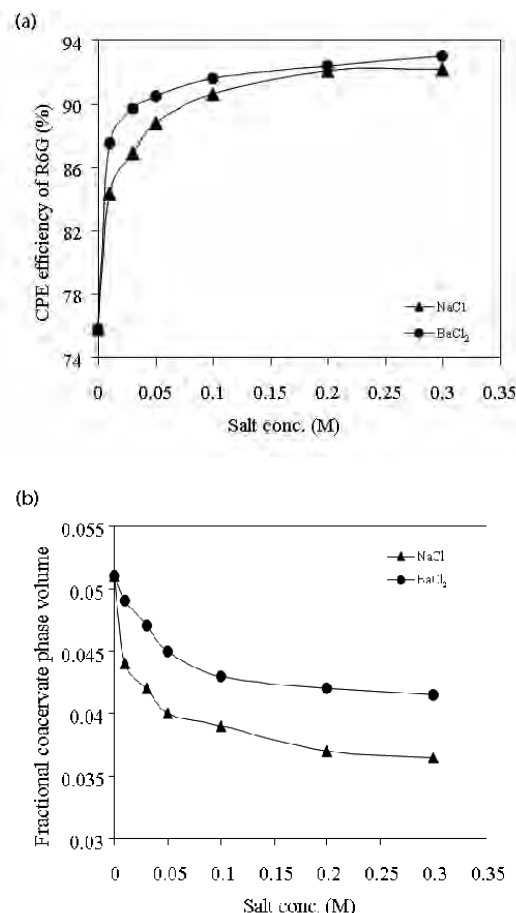
sample solutions containing R6G at 1.46×10^{-4} M and different concentrations of other interference materials and mixtures were prepared, and the developed CPE procedure was applied. Except for CO_3^{2-}, PO_4^{3-}, Al^{3+}, Cr^{3+}, indigocarmin, methylene blue, and toluidine blue O at the concentrations shown (Table 2), the other ions/pollutants in Table 2 allowed extraction efficiencies that were high enough (>90%) for the selectivity of the CPE procedure for R6G.

Application to Real Samples

The developed method was applied to tap water (Kanuni Campus, Karadeniz Technical University, Trabzon, Turkey), sea water (Black Sea, Trabzon, Turkey), and tannery wastewater (Kayseri, Turkey) in order to test the feasibility and reliability of the process. For that purpose, 25 mL of each sample was treated as prescribed under the general CPE procedure. The accuracy of the method was also investigated through spiking tests, and good extraction efficiencies were obtained for the CPE of R6G (Table 3).

Table 2. Effects of various ions and organic pollutants on the efficiency of the CPE of R6G[a]

Ion/pollutant	Added as	Concn, mg/L	Extraction efficiency, %
Mg^{2+}	$Mg(NO_3)_2$	2000	92.2 ± 0.6
K^+	KCl	2000	91.3 ± 0.8
Ca^{2+}	$CaCl_2$	1500	92.6 ± 0.4
CO_3^{2-}	Na_2CO_3	2000	77.8 ± 0.4
NO_3^-	$NaNO_3$	2000	92.0 ± 0.4
PO_4^{3-}	Na_3PO_4	1500	76.8 ± 1.2
SO_4^{2-}	Na_2SO_4	1500	90.5 ± 0.1
Al^{3+}	$Al_2(SO_4)_3$	2000	89.1 ± 1.6
Cr^{6+}	$K_2Cr_2O_7$	2000	94.9 ± 0.5
Cr^{3+}	$CrCl_3$	1000	88.0 ± 0.4
Pb^{2+}	$Pb(NO_3)_2$	2000	91.5 ± 0.4
Cd^{2+}	$Cd(NO_3)_2$	2000	91.6 ± 0.4
Cu^{2+}	$Cu(NO_3)_2$	2000	92.4 ± 0.1
NH_4^+	NH_4NO_3	1500	92.5 ± 0.2
F^-	NaF	1250	92.6 ± 0.6
I^-	KI	1250	92.2 ± 0.6
CH_3COO^-	$NaCH_3COO$	1250	92.3 ± 0.4
Phenol	—	1000	91.0 ± 0.1
2,4-Dichlorophenol	—	1000	91.3 ± 0.4
4-Chlorophenol	—	1000	91.4 ± 0.1
Indigocarmin	—	200	76.2 ± 0.3
Methylene blue	—	200	72.1 ± 0.2
Toluidine blue O	—	200	72.5 ± 1.6
Mixed[b]			73.9 ± 2.6
Mixed[c]			92.0 ± 0.1

[a] $n = 3$; initial R6G concentration, 1.46×10^{-4} M; TX-100 concn, 0.20 M.

[b] Mixed solution containing Mg^{2+}, Ca^{2+}, NH_4^+, CO_3^{2-}, PO_4^{3-}, I^-, CH_3COO^-, indigocarmin, methylene blue, and toluidine blue O, each at 200 mg/L; Al^{3+}, Cr^{6+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, F^-, phenol, 2,4-dichlorophenol, and 4-chlorophenol, each at 100 mg/L; NO_3^- at 2300 mg/L; SO_4^{2-} at 1270 mg/L; and K^+ at 260 mg/L.

[c] Mixed solution containing Mg^{2+}, Ca^{2+}, NH_4^+, CO_3^{2-}, PO_4^{3-}, I^-, CH_3COO^-, each at 200 mg/L; Al^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, F^-, phenol, 2,4-dichlorophenol, and 4-chlorophenol, each at 100 mg/L; NO_3^- at 2300 mg/L; SO_4^{2-} at 1270 mg/L; and K^+ at 260 mg/L.

Conclusions

The results of the present study clearly show that the CPE method can successfully remove a highly toxic dye, R6G, from water and wastewater by using a non-ionic surfactant, TX-100. The proposed CPE methodology offers a simple, rapid, inexpensive, and nonpolluting alternative to other removal techniques, and does not require sophisticated

Table 3. Application of the CPE procedure to various real water samples[a]

Sample	R6G added	Extraction efficiency, %
Tap water	0	0
	4.52×10^{-5} M	89.0 ± 2.1
	8.35×10^{-5} M	90.0 ± 0.4
	1.89×10^{-4} M	91.4 ± 0.1
Sea water	0	0
	4.52×10^{-5} M	87.5 ± 1.3
	8.35×10^{-5} M	90.3 ± 0.4
	1.89×10^{-4} M	93.1 ± 0.2
Tannery wastewater	0	0
	4.52×10^{-5} M	88.0 ± 1.8
	8.35×10^{-5} M	90.0 ± 0.2
	1.89×10^{-4} M	92.3 ± 0.2

[a] $n = 3$; TX-100 concentration, 0.2 M; sample volume, 25 mL.

instruments. The non-ionic surfactant TX-100 was chosen because of its commercial availability, high purity, low cost, and low toxicity. The effects of various analytical parameters, such as pH, TX-100 concentration, equilibrium temperature, incubation time, and salt concentrations, on the efficiency of R6G extraction were evaluated. The interference effects of various anions, cations, phenol and its derivatives, and some acidic and basic dyes were also investigated. The solubilization of R6G in TX-100 was evaluated in terms of the Langmuir isotherm model; the solubilization capacity of TX-100 was found to be 1.10 mmol/mol using that model. Thermodynamic parameters of the CPE process were also investigated, and the negative values of ΔG showed that the CPE of R6G was feasible and spontaneous in the temperature range of 75–95°C for all of the initial concentrations of R6G studied. The positive values of ΔH confirmed the endothermic nature of the process, and the positive values of ΔS implied good affinity of R6G molecules for TX-100 micelles. The validation of the CPE process was carried out by spiking tests with various real samples, and good results were obtained. For an initial R6G concentration of 5.0×10^{-5} M, a TX-100 concentration of 0.2 M, an equilibrium temperature of 85°C, an incubation time of 60 min, and a NaCl concentration of 0.2 M, 99% of the dye was extracted. Thus, it can be concluded from these results that the proposed CPE procedure can be applied to the removal of R6G from water and wastewater.

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