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Mixed Micellar Cloud Point Extraction and Spectrophotometric Determination of Basic Fuchsin Dye

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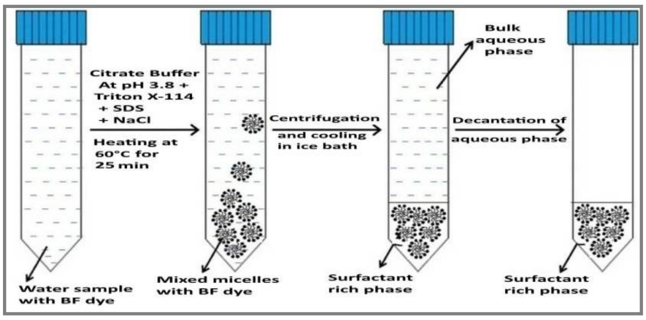
ABSTRACT

A rapid cloud point extraction(CPE) process using a mixed micelle of anionic surfactant sodium dodecyl sulfate (SDS) and non-ionic surfactant Triton X-114 (TX-114) for the pre-concentration and extraction of basic fuchsin (BF) dye in water samples was determined with spectrophotometry at a pH of 3.8. The optimal conditions like pH, surfactant concentrations (both SDS and TX-114), salt concentration, equilibrium temperature and equilibrium time were optimized for the best recoveries of the dye. Under the optimized conditions the analytical characteristics such as limits of detection, liner range and pre-concentration factor are 0.04763µg mL^{-1}, 0.0-4.05 µg mL^{-1}and 16.6 respectively. The present proposed method was successfully applied for the extraction of BF dye in tap and sea water samples. The recoveries were found to be in the range of 81.18 - 91.08 %.

Graphical Abstract



Keywords: Cloud point extraction (CPE), Spectrophotometry, TX-114, SDS

INTRODUCTION

Synthetic dyes are used in textile, leather, paper, pharmaceutical and food industries which are continuously entering into the ecosystem. These dyes are hazardous in nature and therefore monitoring of environmental samples for trace determination of organic dyes [1-2] and their removal [3-4] is very important in the recent times. Due to the low concentration of dyes in water and to obtain accurate quantification results, it is necessary to eliminate the unwanted matrix effects and hence pre-concentration is required before subjecting the samples for instrumental analysis. Some pre-concentration techniques include solid phase extraction [5], dispersive liquid-liquid micro extraction (DLLME) [6-8] and cloud point extraction (CPE)[9-12].

Among these techniques CPE is recognised as an efficient technique for hydrophobic species in solution phase. The aqueous solution of surfactants are heated and at a certain temperature they become turbid and separate into two distinct phases, aqueous phase and surfactant rich phase. Depending on the solubility of a solute in the surfactant it is entrapped in the surfactant rich phase during separation. The two phases are separated by centrifugation and thus the solute pre-concentration is achieved. The concentration of the solute present in the surfactant rich phase is then determined by different analytical methods. This method is called cloud point extraction method (CPE) and the temperature is called cloud point temperature.The CPE method has been well investigated using single pure surfactant like TX-114 [13-14] but CPE methods are only slightly explored in the presence of mixed micelles. Mixed micelle cloud point extraction based on mixing either cationic or anionic surfactants with non-ionic surfactants exhibit better performance and synergism compared to single surfactant due to higher surface activity.

In this work a simple and new mixed micelle cloud point extraction procedure for the extraction and pre-concentration of basic fuchsin (BF) dye using TX-114 and SDS is reported.

MATERIALS AND METHODS

Reagents and Solutions: All the chemicals used were of analytical reagent grade. Stock solution of 10% w/v TX–114 (Polyethylene glycol *tert*-octylphenyl ether, Sigma-Aldrich, USA) was prepared by dissolving 10g of TX–114 in double distilled water and 10% w/v SDS(sodium dodecyl sulphate ,Sigma-Aldrich, USA) was prepared by dissolving 10g of SDS in double distilled water. Stock solution of basic fuchsin dye (1×10^{-3} mol L^{-1}) was prepared by dissolving 0.0337g of basic fuchsin dye in 100 mL double distilled water. Stock solution of sodium chloride 30% w/v was prepared by dissolving 30g of sodium chloride in 100 mL double distilled water.

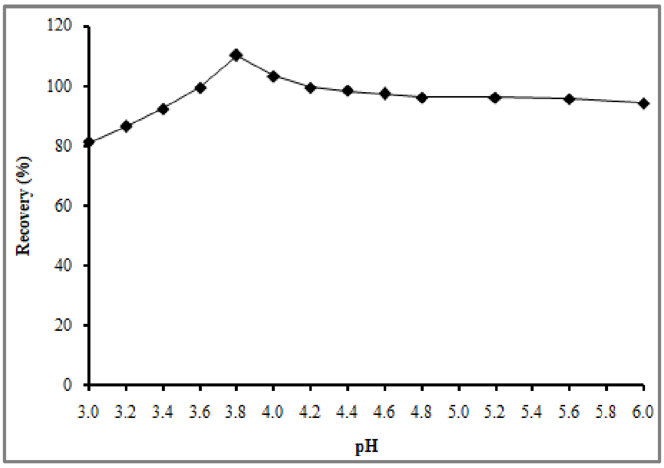
Equipment: A double beam UV-vis spectrophotometer (UV–1800, Shimadzu, Japan) was used for measuring the absorbance and recording the spectra. A Systronics digital pH meter 335 was used for pH measurements. A Remi R–24 was used for centrifugation of samples.

Cloud point extraction Procedure: A cloud point extraction experiment was been carried out using an aliquot solution containing appropriate amount of basic fuchsin dye solution having concentration from 0.0 to 4.05 µg mL^{-1}.To this add 1.4 mL of 10% w/v TX–114, 0.2 mL of 10% w/v SDS and 0.8 mL of 30% NaCl in a 10 mL centrifuge tube and diluted with double distilled water. The above solution was kept at 60°C for 25 min in a thermostatic bath. The separation into two phases (bulk aqueous phase and surfactant rich phase or coacervate phase) was achieved by centrifugation at 3000 rpm for 10 min. The whole system was cooled for 15 min in an ice bath in order to increase the viscosity of the surfactant rich phase. The bulk aqueous phase was readily separated by inverting the centrifuge tubes. The surfactant rich phase (SRP) was diluted to 4mL of 20% methanol to decrease the viscosity of surfactant rich phase prior to spectrophotometric detection at 549 nm.

RESULTS AND DISCUSSION

The maximum absorbance of basic fuchsin dye in aqueous solution was found to be 549 nm. Therefore, all the measurements were carried out at this wavelength. The dye was extracted into mixed micelles of TX–114 and SDS in the presence of sodium chloride. To attain higher sensitivity, selectivity and precision for the extraction of basic fuchsin dye , the effect of various parameters like concentration of TX-114, concentration of SDS, concentration of NaCl, equilibrium temperature and equilibrium time were optimized. The optimum conditions are discussed below.

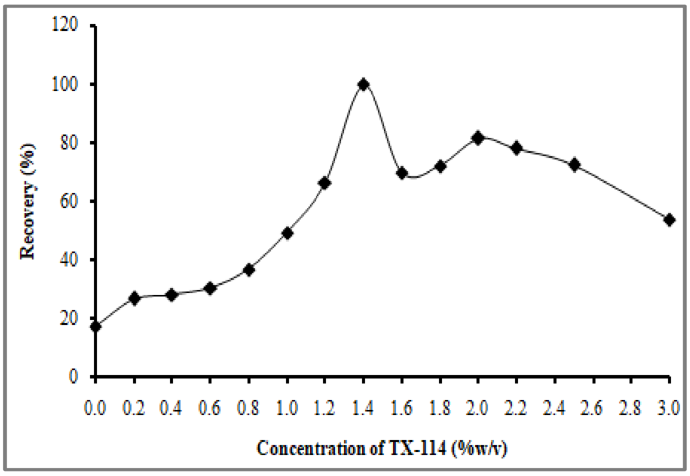
Optimization of pH: For optimization of pH, buffers in the pH range from 1 to 8 were used. A maximum recovery was observed for basic fuchsin dye with citrate buffer at a pH of 3.8. Therefore, pH 3.8 was chosen for the extraction of basic fuchsin dye in subsequent experiments (Figure 1).



(Experimental conditions: 1.4% w/v of TX–114; 0.2 % w/v of SDS; 2.4 % w/v of NaCl; equilibration temperature 60°C; equilibration time 25 min)

Figure 1. Effect of pH on the recovery of the basic fuchsin dye.

Optimization of concentration of TX–114): In the present study, one of the non-ionic surfactant TX-114 was chosen because it has low toxicity and cost, high purity, and high density of surfactant rich phase relatively low cloud point temperature (23^0C-26^0C) near to room temperature which makes easy phase separation. The recovery of basic fuchsin dye was studied in the concentration range of TX–114 from 0.0 % w/v to 3 % w/v. The recovery of basic fuchsin increased up to 1.4 % w/v of TX–114 and then decreased. Thus, the optimum concentration of TX–114 was 1.4 % w/v for basic fuchsin (Figure 2).

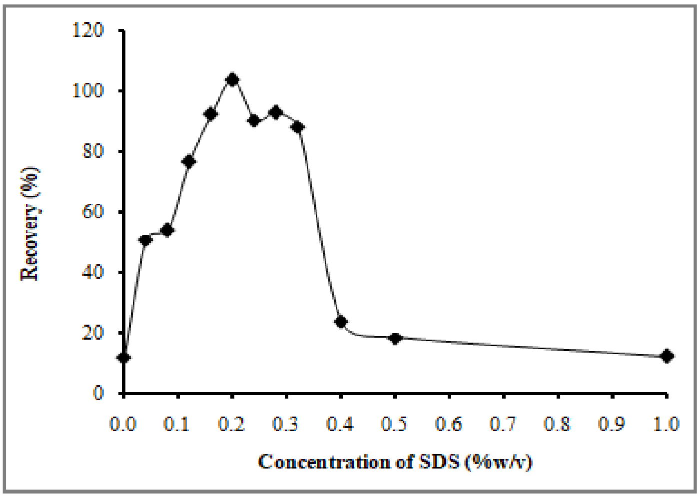


(Experimental conditions: pH 3.8; 0.2 % w/v of SDS; 2.4 % w/v of NaCl; equilibration temperature 60°C; equilibration time 25 min)

Figure 2. Effect of concentration of TX-114 on the recovery of the basic fuchsin dye.

Optimization of concentration of SDS: To enhance the recovery of dye, an anionic surfactant SDS was used along with non- ionic surfactant TX-114. The concentration of TX-114 was fixed at 1.4 %

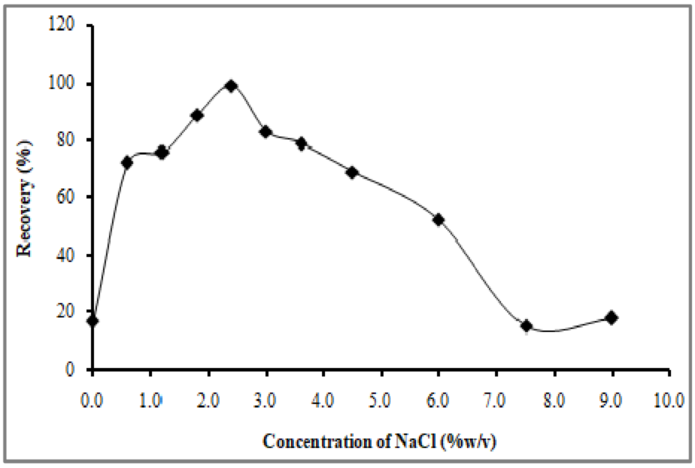
w/v and SDS was optimized in the range of 0.0%-1.0% w/v. The recovery increased up to 0.2 % w/v of SDS and then decreased. Thus, the optimum concentration of SDS was found to be 0.2 % w/v for basic fuchsin dye (Figure 3).



(Experimental conditions: pH 3.8; 1.4% w/v of TX–114; 2.4 % w/v of NaCl; equilibration temperature 60°C; equilibration time 25 min)

Figure 3. Effect of concentration of SDS on the recovery of the basic fuchsin dye.

Optimization of concentration of NaCl: The mixture of surfactants, TX–114 and SDS, which was used for the extraction of dye has a cloud point temperature around 90-100ºC. To reduce the cloud point temperature and to achieve the phase separation of mixed surfactants, a salting out agent was used. The effect of several salting out agents like NaCl, Na_2SO_4 and $CaCl_2$ was determined, and maximum recovery was observed in NaCl. The recovery of basic fuchsin dye was studied in the concentration range of NaCl from 0.0 % w/v to 9.0 % w/v. The recovery of dye increased with increasing the NaCl concentration upto 2.4% w/v and then decreased. The optimum concentration of NaCl was found to be 2.4 % w/v for basic fuchsin dye (Figure 4).



(Experimental conditions: pH 3.8; 1.4% w/v of TX–114; 0.2 % w/v of SDS; equilibration temperature 60 °C; equilibration time 25 min)

Figure 4. Effect of concentration of NaCl on the recovery of the basic fuchsin dye.

Optimization of equilibration temperature and time: The phase separation for the mixed micelles of TX-114 and SDS was not observed below 50ºC and the recoveries increased with increase in temperature up to 60ºC for basic fuchsin dye and then decreased. In the study of equilibration time, the recoveries increased up to 25 min and then decreased. Hence, the optimum equilibration temperature and time were found to be 60ºC for basic fuchsin dye and 25 min respectively.

Analytical characteristics of the method: The analytical characteristics of the proposed method were evaluated under the optimized conditions. Calibration graph was drawn for basic fuchsin dye under the optimum conditions, from which the observed linearity ranges for basic fuchsin was 0.0-4.05µg mL^{-1}. The calibration equations obtained were $A = 0.2498\ C_{BF}+0.01302$ with correlation coefficient of 0.9983. The corresponding limit of was 0.004763 µg mL^{-1}. The pre-concentration factor of the method was 16.6 and the extraction efficiency of the method was 87.90 %.

APPLICATION

The proposed mixed micellar cloud point extraction method was successfully applied for the extraction of basic fuchsin dye in tap and sea water samples. The spike recoveries were found to be in the range from 81.18 - 91.08 %. The results are given in table 1.

Table 1. Determination of basic fuchsin dye in the real samples and spike recoveries in the present proposed method

Samples	Spiked (µg mL^{-1})	Detected (µg mL^{-1})	Recovery (%)
	–	ND*	–
Tap water	1.01	0.82	81.18
	2.02	1.69	83.63
	–	ND*	–
Sea water	1.01	0.92	91.08
	2.02	1.71	84.65

*Not Detected

CONCLUSION

The mixture of TX–114 (1.4 % w/v) and SDS (0.2 % w/v) were taken to form mixed micelles of TX–114/SDS. These mixed micelles were used for cloud point extraction method for the extraction of basic fuchsin. The dye was extracted and the developed method was applied to different water samples. The proposed cloud point extraction method is sensitive, selective, low cost and accurate, which allows the determination of basic fuchsin dye at µg mL^{-1} level.

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