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ADSORPTIVE MICELLAR FLOCCULATION AND CLOUD POINT EXTRACTION AS PRE-CONCENTRATION METHODS FOR THE DETERMINATION OF PHENOSAFRANINE DYE IN AQUEOUS SOLUTIONS

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ABSTRACT
A micellar-based preconcentration method for the extraction of Phenosafranine (PS) dye was developed by using adsorptive micellar flocculation (AMF) and cloud point extraction (CPE) techniques. In the case of AMF, aluminum sulphate (flocculant) and sodium dodecyl sulphate (SDS) were taken in 1:2 ratios for the extraction of PS dye. The parameters affecting the AMF and CPE were optimized. The calibration range and detection limits were 0.0-8.07 μg/mL and 4.182 μg/mL respectively for AMF. The calibration range and detection limits were 0.0-9.684 μg/mL and 2.272ng/mL respectively for CPE.s The methods presented were used to extract PS dye from aqueous samples.
Keywords: Phenosafranine**,** Adsorptive Micellar Flocculation**,** Cloud Point Extraction, Aluminium Sulphate, Sodium Dodecyl Sulphate.
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INTRODUCTION

One of the major difficulties for an analytical chemist in the analysis of environmental samples in trace amounts is sample preparation, purification, and pre-concentration. Methods like solvent extraction[1-2] and liquid-solid extraction[3-5] techniques are generally used to segregate the analytes from the original matrix and eliminate other impurities. All these methods of chemical analysis require large amounts of organic solvents, reagents, and energy and they also generate a lot of waste. The aim of Green Chemistry is to reduce the undesirable side effects.[6-8] To overcome these difficulties, different surfactant-mediated pre-concentration techniques like cloud point extraction (CPE)[9-11] and adsorptive micellar flocculation (AMF)[12-13] have been employed. Both CPE and AMF are simple, inexpensive methods for removing analytes from aqueous solution and obey green analytical chemistry principles. This is because inexpensive solutions of low concentrations which generate low amounts of harmless residues are used. AMF is a good modification of the coagulation-flocculation[14-16] method which involves surfactants. Large micellar flocs are formed which can capture the analytes. It is a pre-concentration technique that makes use of the adsorption tendency of pollutant anions onto the surface of flocs. On the other hand, CPE is a new promising environmentally benign technique based on phase separation behavior exhibited by an aqueous solution of certain surfactant micelles. In general, the CPE procedure has been established well using non-ionic surfactants, but very few mixed micellar CPE methods are found in literature.[17-19] The percentage recovery of dye increases by using mixed micelles when compared to single micelles.[20-22] The main aim of the present study includes pre-concentration and separation of PS dye from aqueous solutions using AMF and CPE methods.

EXPERIMENTAL

Analytical reagent-grade chemicals and distilled water were used all through the study. The solution of 5×10^{-4} phenosafranine (3, 7–di amino-5-phenyl phenazine-5-ium chloride) was prepared. A stock solution of 0.2 M of aluminum sulphate ($Al_2(SO_4)_3).16H_2O$) (Sigma-Aldrich, USA) was prepared and

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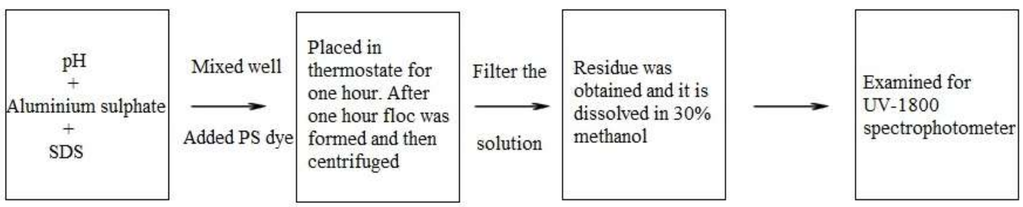
standardized with a standard EDTA solution. A stock solution of 0.2 M SDS (Sodium dodecyl sulphate, Sigma-Aldrich, USA) solution was prepared for the AMF experiment. Stock solutions of 10 % (w/v) Triton X-114 (Sigma-Aldrich, USA), 10 % (w/v) SDS and 30 % (w/v) sodium chloride was prepared for CPE experiment.
The absorbance of the solutions was measured using a Shimadzu UV-VIS spectrophotometer (UV-1800) (10mm quartz cells).

General Procedure

Adsorptive Micellar Flocculation (AMF)

In a 10 mL graduate test tube, Hydrochloric acid-Potassium chloride buffer of pH 1.6, 0.6 mL of 0.2 M of aluminum sulphate, and 1.0 mL of 0.2 M of SDS were added followed by the addition of 4.84 µg/ mL of PS dye. The remaining volume of the graduated test tube was filled with water to get a 10 mL overall solution and placed in a thermostatic bath at room temperature for one hour and then centrifugation at 250 rpm for 5 minutes. The separation of an aqueous phase and floc was accomplished by filtration. The floc obtained from filtration was dissolved in 30 % methanol and the absorbance was measured at (λ_{max}) 550 using a spectrophotometer (Shimadzu, UV-1800). The AMF procedure is represented in Scheme-1.



Scheme-1: Representation of Adsorptive Micellar Flocculation Procedure

Cloud Point Extraction (CPE)

In a 10 mL volumetric flask, a pH of 4.0 (acetate buffer), 4.8 µ g/ mL of PS dye, 2.0 mL of Triton X–114 (10 % w/v), 0.12 mL of SDS (10 % w/v) and 0.6 mL of NaCl (30 % w/v) were added and the rest of the volumetric flask was filled with double distilled water. The solution was heated to 70^0 C for 20 min. The phases (bulk aqueous phase and surfactant phase) were separated by centrifugation for 5 minutes, and the entire system was cooled for 20 minutes. Then the bulk aqueous phase was separated by decantation and 20 % methanol was used to dissolve the surfactant phase containing PS. The amount of the dye was determined spectrophotometrically at a wavelength of 550 nm which is the wavelength of maximum absorbance for PS.

RESULTS AND DISCUSSION

The various analytical parameters affecting adsorptive micellar flocculation and cloud point extraction (CPE) are discussed below.

Factors Affecting Adsorptive Micellar Flocculation (AMF)

Effect of pH

The variation of pH was evaluated because the stability of anionic surfactant is greatly affected by pH. Thus, it is essential to adjust the pH of the medium. Various buffers of pH range 1 to 5 were used to monitor the effect of pH on the recovery of PS dye. Recoveries were found to be maximum at pH 1.6 for PS dye. The efficiency of PS dye confirms that acidic buffer (KCl-HCl) was chosen for the pre-concentration of PS dye at a pH of 1.6 (Table-1 and Fig.-1a).

Effect of Concentration of SDS

The effect of SDS has been studied on the recovery of PS dye. The percentage recovery of PS dye increases with the rise in SDS concentration due to the significant number of micelles formed at high surfactant concentrations. The presence of excess SDS in the solution causes resolubilization of adsorbed PS dye which ultimately decreases the percentage of recovery of PS dye. SDS concentration was changed from 0.0 to 0.04 M and the recovery was determined. Maximal recovery was observed at 0.02 M of SDS (Table-1 and Fig.-1b).

Effect of Concentration of Aluminum Sulphate (Flocculant)

Substances bind with the floc either through complexation with Al^{+3} at the surface of the micelle. The recovery of PS was optimized in the concentration of aluminum sulfate from 0.0-0.20 M. The recovery increases up to 0.012 M and then decreases. Maximum recovery of PS dye was observed at 0.012 M of aluminum sulphate (Table-1 and Fig.-1c).

Effect of Temperature and Contact Time

The temperature has a significant effect on the rate of adsorption. The percentage recovery of dye increases and then declines with temperature and encouraging micellization. Maximum recovery PS dye was obtained at room temperature. The effect of contact time on the recovery of PS dye was optimized. Contact time between 10 to 90 minutes was optimized. Maximum recovery was observed at 60 minutes then after recovery decreased.

Mechanism is as follows:

$$Al^{3+} + SDS^{-} \longrightarrow \underset{\textbf{Floc}}{Al^{3+}\text{-}SDS^{-}}$$

$$Al^{3+}\text{-}SDS^{-} + \text{Dye} \longrightarrow [Al^{3+}(\text{Dye})\,SDS^{-}]$$

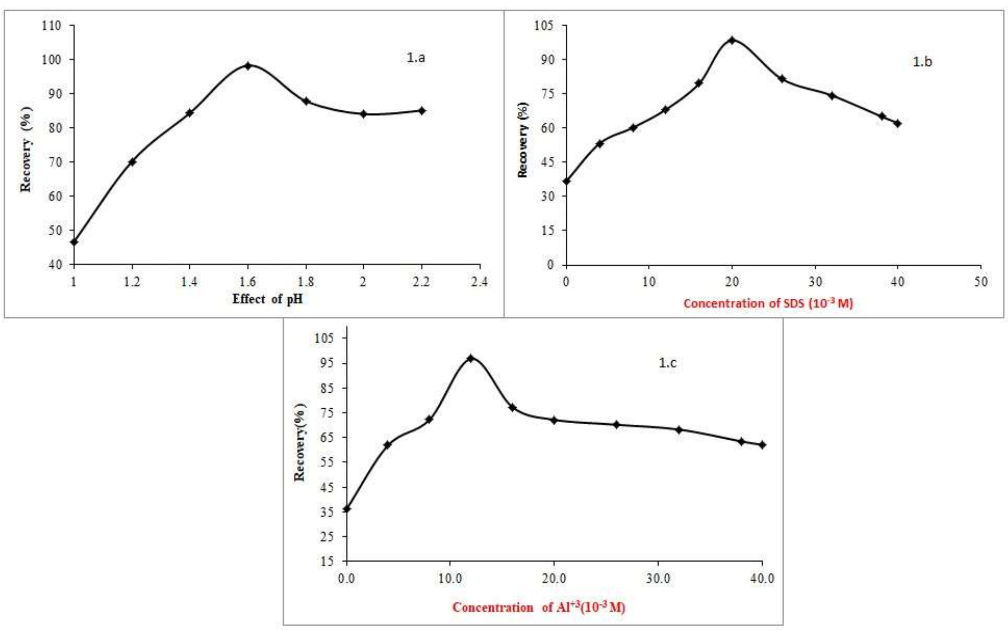


Fig.-1: Adsorptive Micellar Flocculation (a.) A Plot of pH Vs. Recovery of PS Dye, (b.) A Plot of Concentration Al^{3+} Vs. Recovery of PS Dye, (c.) A plot of Concentration of SDS Vs. Recovery of PS Dye

Factors Affecting Cloud Point Extraction (CPE)

Effect of pH

A change in the pH of the solution influences the recovery of charged analytes as it causes protonation (in acidic solutions) or deprotonation (in basic solutions) of the analyte which may result in a declining trend of extraction. Various buffers of pH range 1 to 8 were used to investigate the impact of pH on the recovery PS dye. Recoveries were found to be maximal at pH 4.0 (Fig.-2a).

Variation of Concentration of TX–114 and SDS

In the present study, TX-114 (non-ionic surfactant) was selected due to low cloud point temperature (23^0C-26^0C) near room temperature which makes easy phase separation. The extraction of the dye was found to be maximal at 2.0 % w/v of TX–114, thereafter the recovery decreased. Therefore, good extraction was obtained at 2.0 % w/v for PS dye (Fig.-2b). To magnify dye recovery, SDS was used along with TX-114. The addition of SDS raised the cloud point of TX-114 from 25^0C to 70^0 C. TX-114 was held at a constant concentration of 2.0 % w/v. and SDS concentration was varied between (0.0 -1.0) % w/v. Maximum recovery was observed at 0.12 % w/v of SDS and thereafter decreased (Fig.-2c).

Table-1: Optimized Conditions of PS Dye (Adsorptive Micellar Flocculation)

pH	0.2 M SDS (mL)	0.2 M Al^{+3} (mL)	5×10^{-4} M PS Dye (mL)	Recovery (%)
1.0	1.0	0.6	0.3	46.7
1.2				70.2
1.4				84.4
1.6				98.3
1.8				87.9
2.0				84.1
2.2				85.1
1.6	1.0	0.0	0.3	36.2
		0.2		61.9
		0.4		72.3
		0.6		96.8
		0.8		77.2
		1.0		72.2
		1.3		70.2
		1.6		68.3
		1.9		63.5
		2.0		62.1
1.6	0.0		0.3	36.8
	0.2			53.3
	0.4			60.2
	0.6			68.2
	0.8			79.6
	1.0			98.5
	1.3			81.5
	1.6			74.3
	1.9			65.1
	2.0			62.2

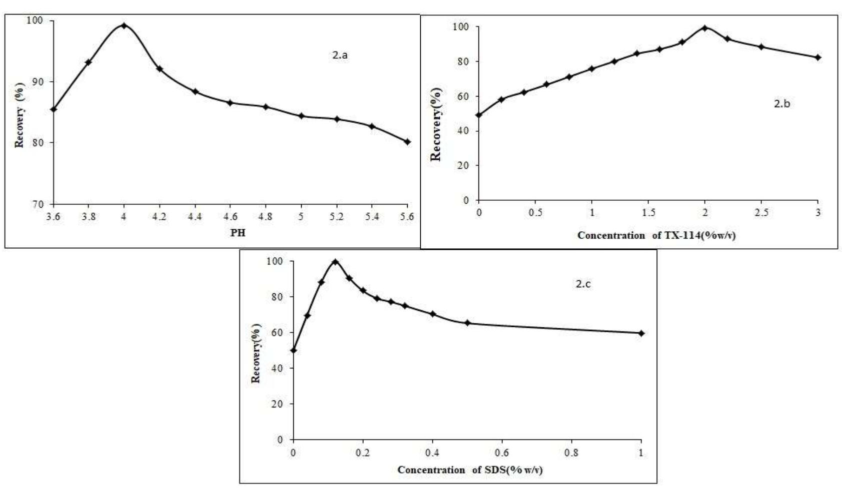


Fig.-2: Cloud Point Extraction (a.) A Plot of pH Vs. Recovery of PS Dye, (b.) A Plot of Concentration TX-114 Vs. Recovery of PS Dye, (c.) A Plot of Concentration of SDS Vs. Recovery of PS Dye

Optimization of Concentration of NaCl

Effect of various salts like NaCl, Na_2SO_4, and $NaNO_3$ was employed. Maximum recovery was observed in NaCl. Extraction of the dye was found to be maximal at 1.8 % w/v of NaCl when the NaCl concentration was changed from (0.0 to 6.0) % w/v.

Mechanism is as follows:

$$SDS^- + Dye^+ \longrightarrow [SDS^- Dye^+]$$

$$[SDS^- Dye^+] + [TX]_n \longrightarrow [SDS^- Dye^+] [TX]_n$$

The Summary of analytical data is show in Table-2. The proposed methods (AMF and CPE) were used for the extraction of phenosafranine (PS) dye in different aqueous samples. The spike recoveries for both methods were found to be around 100.0 % (Table-3).

Table-2: Summary of Analytical Data

Parameter	AMF	CPE
λ_{max} (nm)	550	550
Linear range (µg /mL)	0.0-8.07	0.0-9.684
Slope	0.1116	0.1027
Correlation coefficient (R^2)	0.9988	0.9995
Preconcentration Factor	10	12.5
Detection limit (ng/ mL)	4.182	2.272
The efficiency of extraction (%)	99.9	99.98

Table-3: Recovery of Phenosafranine (PS) Dye in Different Samples

Samples	AMF			CPE		
	Added/Spiked Dye in µg/mL	Observed Dye in µg/mL	(%) Extraction	Added /Spiked in µg /mL)	Detected (µg/mL)	(%) Extraction
Tap water	-	ND*	-	-	ND*	-
	2.42	2.42	100	2.42	2.43	100.41
	4.84	4.88	100.8	4.84	4.85	100.20
Seawater	-	ND*	-	-	ND*	-
	2.42	2.43	100.41	2.42	2.40	99.17
	4.84	4.92	101.65	4.84	4.82	99.58

CONCLUSION

- In the case of AMF, the maximum extraction efficiency of 99.98 % of PS dye was obtained using 1: 2 ratios of aluminum sulfate (flocculant) and SDS (anionic surfactant).
- In the case of CPE, the extraction efficiency of 99.98 % of PS dye was obtained using TX-114 (non-ionic surfactant) and SDS (anionic surfactant).
- High pre-concentration factors were obtained from CPE and AMF procedures for PS dye indicating that both the methods (AMF and CPE) are the best methods for the pre-concentration of PS dye.
- The developed extraction methods combined with spectrophotometry show that it is a sensitive, selective, economical, and accurate method for determining PS at the ng/mL level.

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