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Cloud Point Extraction for Spectrophotometric Determination of Acid Blue 29 Dye in Water Samples

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Abstract

A simple and fast Cloud Point Extraction (CPE) preconcentration of Acid Blue 29 (AB 29) dye was developed prior to its spectrophotometric determination. The suggested procedure was successfully applied for the determination of AB 29 dye in different water samples with high recoveries. Optimization of experimental conditions such as surfactant type and volume, pH, stirring, and centrifugation conditions were studied. The effect of interfering ions was also studied. The calibration curve was in the range of 0.4-10 µgmL^{-1} with a limit of detection and limit of quantitation of 0.35 and 1.1 µgmL^{-1}, respectively. Furthermore, the method is free of the interference of common ions present in water.

Keywords: Acid Blue 29, Cloud point extraction, Nonionic surfactant, Spectrophotometry.

Introduction

Synthetic dyes are widely used in different industries, such as textiles and paints, leading to the release of huge amounts of different dyes each year [1]. Some of these dyes are hazardous to humans and other living beings due to the discharge of different dyes in water environments [2].

The accumulation of such effluents, mainly on the surface of water bodies, results in significant destruction to the ecosystems as a results of decreasing the penetration of sunlight into the water, then affecting the photosynthetic process and marine life [3]. The contamination of aquatic organisms causes severe dysfunction in the food chain of various ecosystems and may lead to the deficiency or extinction of many organisms [4].

UV-VIS spectrometry is a method widely used for the determination of dyes, but due to the problem of their low concentration and matrix effect. These problems can be overcome using different preconcentration or separation steps achieved prior to introducing the sample to the analytical instrument. These methods involve: solvent extraction [5], solid phase extraction (SPE) [6,7], molecularly imprinted solid phase extraction [8,9], dispersive liquid-liquid microextraction (DLLME) [10,11], and cloud point extraction (CPE) [12-15].

CPE was developed as an active and alternative method for the separation and preconcentration of different species, such as dyes [14-16], toxic heavy metal ions [17-19], and pharmaceutical products [20, 21]. CPE is an analytical technique that uses non-ionic surfactants instead of common organic solvents. These surfactants usually form micelles in aqueous solutions, leading to a turbid mixture of aqueous and non-aqueous phases at a certain temperature called the cloud-point temperature. Above or below this temperature, the micellar solution separates into two phases: the surfactant-rich phase usually has a small volume that primarily contains the hydrophobic components, and a diluted aqueous phase containing a small amount of surfactant of a critical micellar concentration (CMC). The implementation of CPE as an extraction technique has several advantages, including easiness, low cost, and use of nontoxic surfactants, such as Triton derivatives (Triton X-100 and Triton X-114) are examined in this study due to their low-cost, low toxicity and high purity [22].

Acid Blue 29 (AB 29) is a textile diazo dye (Fig. 1) that may be present as a pollutant in different water samples, the dye has toxicity, and there are efforts to remove it from water sites [23]. To our knowledge, there is no simple preconcentration method for the determination of the dye in water samples. In the present study, we have proposed a simple, fast, and green CPE coupled with a spectrophotometric procedure using a non-ionic surfactant (Triton X-114) to determine AB 29 dye in different environmental water samples. The effects of different experimental factors such as pH, surfactant nature and amount, temperature, and incubation time, on the efficiency of CPE of AB 29 from aqueous samples were studied and evaluated.

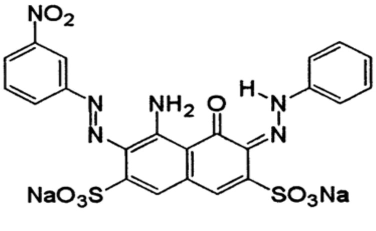

Figure 1. **Chemical structure of Acid blue 29 dye**

Materials and Methods

All chemicals used were analytical grade, and solutions were prepared with deionized water. AB 29 was purchased from Sigma Aldrich (40%), Triton X-100, Triton X-114, Brij 35, and Tween 80 were purchased from Merck. 5% solution NaCl and different surfactants were prepared in deionized water, and phosphate buffer was used to adjust the pH of the solutions.

Instrumentation and Techniques

Absorbance measurements were made using CARY 100 BIO UV-VIS spectrophotometer (USA) using 1-cm glass cells. A centrifuge with calibrated 10 mL tubes with a speed rate of 3500 rpm was used to accelerate the separation between the two phases. pH measurements were performed using a Hanna 8521 digital pH meter, and a STUART model Vortex mixer was used for stirring.

Sampling and sample preparation

Tap water samples were taken in our laboratory and analyzed immediately after collection by the suggested procedure without any other treatment. The mineral water samples, which differ in total dissolved solids over a wide range were purchased from a local supermarket in Amman-Jordan and stored in a refrigerator at 4°C. Well water samples were obtained from a well located south of Amman city. Water samples were degassed in an ultrasonic bath for 20 min and then spiked with appropriate amounts of the dye for analysis.

Procedure

5.0 mL of aqueous solution containing appropriate amounts of (AB 29 dye) was transferred into a 10 mL graduated centrifuge test tube with conical bottom, 1.0 mL of 5% (v/v) Triton X-114 was added, the pH was adjusted using 0.5 mL phosphate buffer, followed by adding 1.0 mL 5% (w/v) NaCl solution. The solution mixture was diluted to 10.0 mL with deionized water. After that, the mixture was vortex stirred for 1 min, the solution became cloudy, then it was centrifuged at 3500 rpm for 10 min. The surfactant rich phase containing the dye was settled down, and 500 µL of the precipitate was transferred into a micro cuvette and diluted to 3 mL using methanol and mixed manually. Finally, the absorbance of the dye was measured at 606 nm.

Results and Discussion

Due to their advantages, such as simplicity, speed, and sensitivity, CPE was chosen as a pre-concentration process using a non-ionic surfactant. In order to obtain high extraction efficiency with low extraction time and high recovery, it is convenient to study the effect of all the parameters that would affect the extraction performance, such as the type and volume of surfactant, pH, salt concentration, vortex time and centrifuging conditions.

The principle of CPE using non-ionic surfactant depends on the formation of a neutral form of dye under certain conditions that result in one homogeneous cloudy phase, consequently centrifuged, and the surfactant rich phase was formed concentrated with the targeted dye that can be determined spectrophotometrically. The absorbance of the dye was measured at 606 nm during the experiments, as shown in Fig. 2.

Condition optimization

In order to find the optimum values of different variables that affect the separation efficiency of the suggested method, the univariant method was performed as follows:

Effect of pH

The pH of the dye solution plays a significant role in the cloud point formation since it is to obtain the dye in a neutral form so that it forms a stable micelle with the surfactant [6]. The pH of the dye solutions was adjusted using phosphate, and finally, the absorbance of the extracted dye was measured at 606 nm. It was absorbed that pH=5 is the best recovery to form CPE of AB 29 dye (Fig. 3).

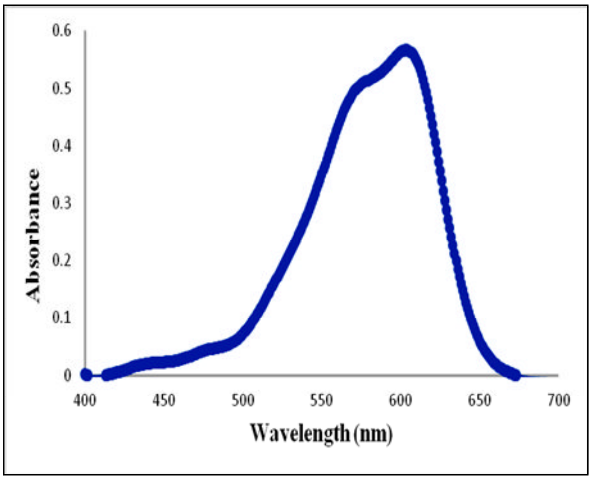

Figure 2. **UV-VIS spectrum of Acid blue 29 dye: 20.0 µgmL^{-1} in deionized water**

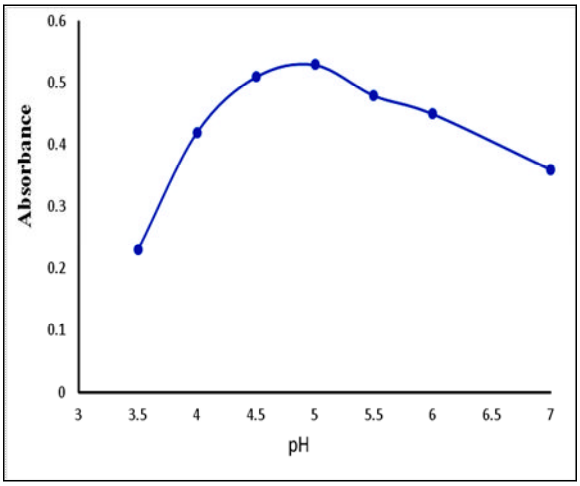

Figure 3. **Effect of pH on the CPE preconcentration performance. Conditions: 5.0 µgmL^{-1} (AB 29) using phosphate buffer**

Effect of surfactants

The nature of nonionic surfactants is a key factor in forming a stable micelle. As a result, different nonionic surfactants (Triton X-100, Triton X-114, Brij 35, and Tween) were used at different volumes. The best improvement of the extraction was obtained using Triton X-114, as shown in Fig. 4. The volume of the selected surfactant was also studied, as shown in Fig. 5.

Selectivity of Triton X-114 for CPE with AB 29 dye because of high purity, stability, non-volatile, and environment friendly.

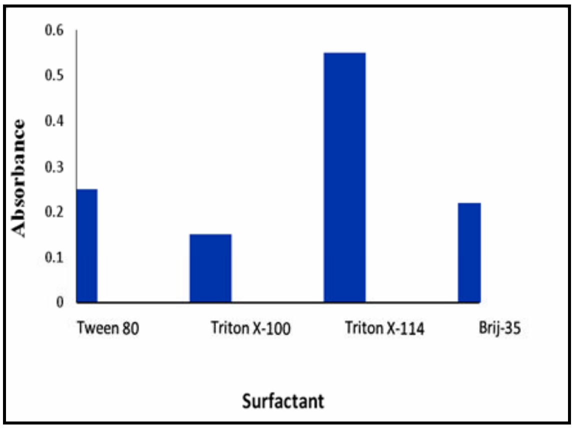

Figure 4. **Effect of adding 1.0 ml of 5% surfactant on separation efficiency, pH 5.0 and using 5.0 µg mL^{-1} (AB 29)**

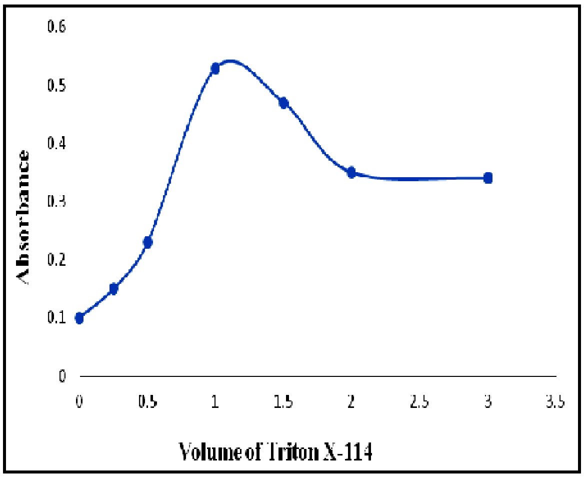

Figure 5. **The influence of the volume of Triton X-114, pH 5.0 on the analytical signal. Conditions: 5.0 µg mL^{-1} (AB 29)**

Effect of temperature

The optimum temperature is necessary to complete the reaction and achieve phase separation. The performance of the separation was tested at room temperature (25°C), then the temperature effect was studied in the range of (20-40°C). As a result, there was no appreciable change in the results, which enabled the application of the method at room temperature.

Effect of time of stirring and centrifugation

In the proposed CPE method, stirring of the mixture was enhanced by using a vortex mixer, and it was found that the cloud point formation was obtained and stabilized after 1 min of stirring. Then, the separation of the enriched micellar and aqueous phases was enhanced by centrifuging the cloudy mixture for a different time at 3500 rpm. The time of centrifuge was studied between 3 and 15 min. The results show that centrifugation time lead to a higher volume of pure sediment phase and higher absorbance values after about 10 min. Therefore, on the basis of these considerations, we select 1 min stirring and 10 min centrifugation at 3500 rpm.

Analytical performance

Analytical figures of merit for the proposed CPE method obtained under the optimized conditions are shown in Table 1. Limit of detection (LOD) and limit of quantitation (LOQ) were calculated based on $3.3SD_a/b$ and $10\ SD_a/b$, respectively, where (SD) is the standard deviation of the intercept of the calibration curve and b is the slope. The preconcentration factor for the proposed method was calculated by the ratio of the sample volume (10 mL) to the final volume (0.5 mL) to be (20). Linear dynamic range was obtained in the range of (0.4-10 µg/mL) with an R^2 of 0.995.

Table 1. **Data showing analytical performance of the methods.**

Parameters	Proposed Method
Linear range (μg/mL)	0.4-10
Wavelength (nm)	606
Correlation coefficient (R^2)	0.995
Slope (b)	0.092
Intercept (a)	0.0341
SD of the intercept (SDa)	0.0098
LOD[a] (μg/mL)	0.35
LOQ[b] (μg/mL)	1.1

[a]Limit of detection, [b]Limit of quantitation, LOD = 3.3SDa/b; LOQ = 10SDa/b, where SD[a] refers to the intercept, and b is the slope.

Application to environmental water samples

To examine the reliability of the proposed method, the method was applied to determine the dye in tap water, Mineral water and Well water samples. Tap water was taken from the University of Jordan, mineral water samples were taken from local markets, and the well water was taken from Amman city. The samples were filtered through a 0.45 µm nylon membrane prior to analysis. Each sample was spiked with two levels of the dye and the recoveries were calculated according to the following equation;

R(%)= [*added concentration*/*Calculated concentration*]X100.

The results shown in Table 2 demonstrate the applicability of the procedure for the determination of the dye in different water samples.

Table 2. **Determination of AB 29 in different water samples.**

Sample	Amount of Dye added (µg/mL)	Amount found *(µg/mL)	Recovery (%)
Tap water	2.0	2.1	105± 3
	6.0	6.2	103±7
Mineral water	2.0	2.2	110±5
	6.0	6.1	102±3
Well water	2.0	2.2	110±4
	6.0	6.2	103±6

*average of three determinations ± standard deviation

Interferences

The effect of different cations and anions on the AB 29 recovery was studied by the present CPE procedure. The results are shown in Table 3. The tolerance limit which was calculated as the ion concentration causing a relative error smaller than ± 5%, related to the determination of AB 29. It was quantitatively recovered in the presence of large amounts of alkaline and alkaline earth ions and some transition metal ions. The matrix ion contents in the final solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

Table 3. **Tolerance ratio of some ions on the determination of 1.0 (µg/mL) AB 29**.

Ion	Tolerance ratio (w/w)
Na^+,K^+,Mg^{2+}, Ca^{2+}, Cl^{-1}, NO_3^-	1000
Zn^{2+}, CO_3^{2-}, SO_4^{2-}	500
Cu^{+2}	400
Ag^+	300
Fe^{3+}	200
Cd^{2+}, Hg^{2+}	100

Conclusion

A simple and inexpensive cloud point extraction method coupled with spectrophotometry has been developed for the determination of Acid Blue 29 dye in environmental water samples. The method showed good precision and sensitivity. The results obtained from this research revealed that the proposed method could be applied to analyze and monitor the studied dye in different water samples.

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Conflict of Interest

The authors declare that there is no conflict of interest.

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