A Micellar based Preconcentration Method for The Extraction of Erichrome Blue Black R Dye Using An Adsorptive Miceller Flocculation Technique and Determination of Thermodynamic Parameters

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***Abstract*:- A modern, simple and low budget method for extraction and preconcentration of Erichrome blue black R (EBBR) have been determined by an Adsorptive micellar flocculation (AMF) method using Sodium dodecyl sulphate(SDS) and aluminium sulphate. Different parameters, such as pH, surfactant (SDS) concentration, aluminium sulphate (flocculant) concentration, equilibrium temperature, and time have been studied to maximise efficiency. The calibration range and detection limit were 0.0-41.63µg/mL and 37.40 ng/mL of EBBR dye respectively. Thermodynamic parameters such as changes in Gibbs free energy, enthalpy and entropy were also calculated, and the outcomes shown that the AMF of EBBR dyes were spontaneous, feasible, and endothermic in the temperature range of (10–30)°C. The effect of temperature, surfactant concentration and dye concentration on various thermodynamic parameters was investigated, and it was found that ΔG^0 values increased with temperature but decreased with surfactant and dye concentration. ΔH^0 and ΔS^0 values increased as surfactant concentration increased and decreased as dye concentration decreased. The developed method has been confirm to be a cost efficient and environmental benefit method to extract MG and EBBR dyes from tap and sea water samples and more than 97% extraction was obtained for both the dyes.**

Keywords:* *Erichrome blue black R, adsorptive micellar flocculation, Thermodynamic parameters.

INTRODUCTION

A number of methods are reported for wastewater treatment such as adsorption [1, 2], coagulation-flocculation [3, 4], reverse osmosis [5, 6], ion-exchange [7, 8], biodegradation [9-10], advanced oxidation process [11-14] reduction [15], irradiation [16-18], etc. but their high price, the formation of detrimental byproducts, operational complexity and finite usage led to development new methods.

Adsorptive Micellar Flocculation (AMF) is a potential technique that has been reported for the removal and recovery of water-soluble pollutants of organic nature. It is a modification of the coagulation-flocculation (CF) technique which involves anionic surfactants. The production of bigger micellar-flocs that can collect organic contaminants is the basis of adsorptive micellar flocculation. In contrast to previous approaches, AMF has gained prominence as a potentially effective, simple, and environmentally acceptable technology for the removal of a variety of pesticides, dyes, and other organic substances such as phenol, polychlorinated biphenyls (PCBs), and others. It can remove fifty times more contaminants than admicellar solubilization per unit mass of surfactant. It uses fewer surfactants than other surfactant-based approaches, such as MEUF, and filtration is simple.

The major aim of the current study associated to the preconcentration and extraction of MG and EBBR dyes in water samples (tap and sea water) by using AMF method and thermodynamic parameters like Gibbs free energy, enthalpy and entropy during AMF has been reported.

2. EXPERIMENTAL

2.1. Apparatus

A Shimadzu UV-VIS Spectrophotometer (UV-1800) with 10mm matched quartz cells was used to measure the optical densities of the solutions. For all pH measurements a systronics digital 335 pH meter was used. Centrifuge, RHB model (Germany) was used for the AMF methodology. Thermostat was used to maintain the desired temperature.

2.2. Materials

All chemicals were used in this work were of analytical grade .In addition, double distilled water was used throughout. A 0.2M of Aluminum sulphate ($Al_2 (SO_4)_3.16H_2O$ Sigma- Aldrich, USA) solution was prepared by dissolving 63.038g of aluminum sulphate in 500-mL volumetric flask, standardized with standard EDTA solution. A stock solution of 1×10^{-3}M Erichrome blue black R **(**sodium; 4 - [(2-hydroxynaphthalen-1-yl) hydrazinylidene=] -3-oxonaphthalene-1-sulfonate**)** were prepared. A 0.2MSDS (Sodium dodecyl sulphate, Sigma-Aldrich, USA) solution was prepared by dissolving 28.837g of SDS in 500-mL volumetric flask. Buffer solutions were prepared by adding 1M KCl and 1M HCl the resultant pH was measured using pH meter.

2.3. General procedure

Adsorptive micellar flocculation (AMF)

In a 15ml graduate test tube 0.1MPotassium chloride –0.1M Hydrochloric acid buffer of desire pH=2.1, 0.8 mL of 0.2M of aluminum sulphate, 1.6mL of 0.2M SDS and 24.983µg/mL of EBBR dye was added. The remaining volume of the graduated test tube was filled with double distilled water upto 10.0 ml and placed in a thermostatic bath at room temperature for one hour then centrifuged at 250rpm for 5minutes. The separation of the two phases was achieved by filtration (aqueous phase and floc). The floc obtained from filtration was dissolved in 30% methanol and the spectrophotometric analysis was carried out at (λ_{max}) 520 nm using a spectrophotometer (Shimadzu, UV-1800) EBBR dyes respectively. The experiment was repeated at different concentrations of dye, concentrations of SDS and different concentrations of aluminum sulphate for optimization.

For the determination of thermodynamic parameters, different concentrations of EBBR dye (12.49, 16.65, 20.81, 24.98, 29.14, 33.31µg/mL) and different concentrations of SDS [0.032, 0.04, 0.05M] were taken and conducted the experiment at different temperatures 283, 293, 303 K, respectively.

3. RESULTS AND DISCUSSIONS

The maximum absorbance of EBBR was found to be 520nm. Therefore all the experiments carried out at these wavelengths. So, the effect of various parameters like effect of pH, effect of concentration of aluminum sulphate (flocculant), effect of concentration of SDS, effect of temperature and contact time were optimized. The optimum conditions are discussed below.

Factors effecting adsorptive micellar flocculation (AMF)

Effect of pH

The effect of pH on recovery of EBBR dye was studied. Various buffers corresponding to pH range 1 to 8 were used. Maximum recovery was obtained for EBBR dye at pH 2.1(0.1M KCl-0.1MHCl) respectively. High pH causes unavailability of flocculant ion (Al^{+3}ion) [28] which results in resolubilization of dye molecules, hence maximum efficiency was observed at pH 2.1 for EBBR dye. This pH was maintained for the rest of the study, and the details are presented in Fig.1 (a).

Effect of Concentration of SDS

In the present study, one of the anionic surfactant SDS was chosen for the removal of EBBR dye. It has high solubilization capacity for the solute, readily biodegradable, aggregation number and less expensive. The percentage recovery EBBR dye increases with increase in SDS concentration. Beyond a certain concentration the presence of excess SDS in the solution results in solubilization of adsorbed EBBR dyes which ultimately decreases the percentage of recovery of EBBR dye.The recovery of EBBR dye were examined in the concentration range of SDS from 0.0 to 0.06M. Thus, the optimum concentration of SDS was 0.032M for EBBR dye and the details are presented in Fig.1 (b).

Effect of concentration of Aluminum sulphate (flocculant)

For flocculation of micelles and complexation of pollutants, aluminum salts (Al^{+3}) were considered. Micelles contain charged regions called diffused and stern layers .The Stern layer has the majority of cations tightly bound with micelles. When the micelle Stern and diffuse layer surface binds with Al^{+3}. The recovery of EBBR dye was studied by changing the concentration of aluminum sulphate from 0.0-0.06M. In EBBR dye the recovery increases up to 0.016M and then decreases. The mechanism of AMF depends on the three factors

1. Interaction between the Flocculant and the dye
2. Flocculant – micellar interaction
3. Micelle- dye interaction

A combination of all the three factors results in maxima of efficiency followed by decrease of recovery and the details are presented in Fig.1 (c).

Effect of Temperature and contact time

Temperature has a significant effect on the rate of adsorption. The percentage recovery of dye initially increases and then decreases with temperature due to CMC of the surfactant undergo initial decrease and favoring micellization. Maximum recovery of EBBR dye was obtained at room temperature. Removal of the dye depends on formation of micelles (CMC). As temperature increases, CMC increases which results in inefficient floc formation. Hence maximum recovery was obtained at30^{0}C. Effect of contact time on recovery of EBBR dye was optimized. Contact time between 10 to 90 minutes was optimized. Removal efficiency, in general, approaches 90% within first few minutes. But since the dye is water soluble, longer contact time (> 60 min) makes the dye molecules unable to remain bound to the micellar flocs.

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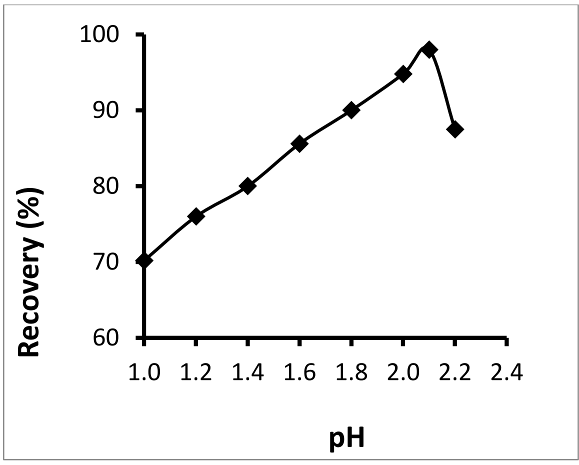

Fig. 1(a)

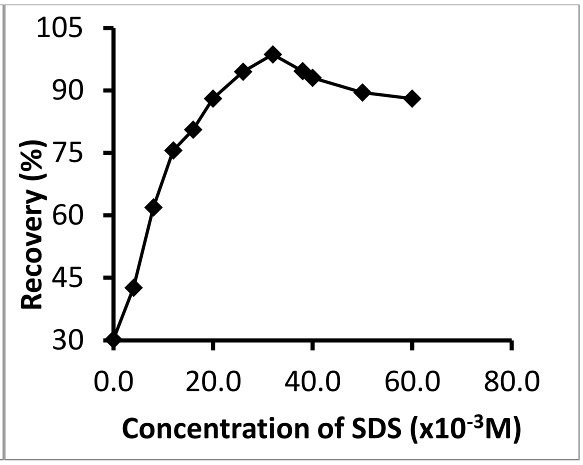

Fig. 1(b)

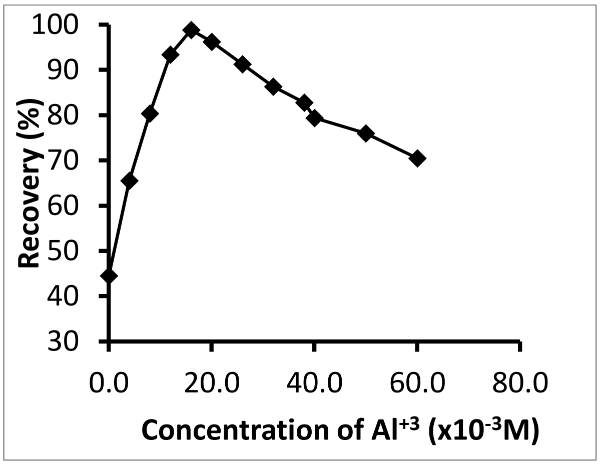

Fig. 1(c)

Thermodynamic parameters:

The extraction of EBBR dye was studied in the temperature range from 283 to 303 to determine Gibbs free energy (ΔG), Enthalpy of solubilization (ΔH), and Entropy of solubilization (ΔS) of AMF method respectively, by using following equations.

$$\Delta G = \Delta H - T \times \Delta S$$

$$\log(\frac{q}{C_e}) = \frac{\Delta S}{2.303R} + \frac{(-\Delta H)}{2.303RT}$$

ΔH and ΔS values are obtained from the slope and intercept of plot log (q/Ce) against 1/T. ΔG values were calculated by using above equation. The negative value of ΔG indicates the spontaneous nature and confirmed affinity of adsorbent for the dye.

Effect of surfactant concentration and dye concentration on the change of enthalpy (ΔH^0) of AMF:

Thermodynamic systems to total energy can be calculated by enthalpy. The variations of enthalpy change (ΔH^0) during AMF method of EBBR dyes at different concentrations of surfactants and dyes are shown in Fig.2 (a) and 2(b). From the figures the value of ΔH^0 increases with the SDS concentration but decreases with the dye concentration because it is due to decrease in the amount of dye solubilization per mole of surfactant. Here the positive values of ΔH^0 indicate that the solubilization of dye is endothermic in nature.

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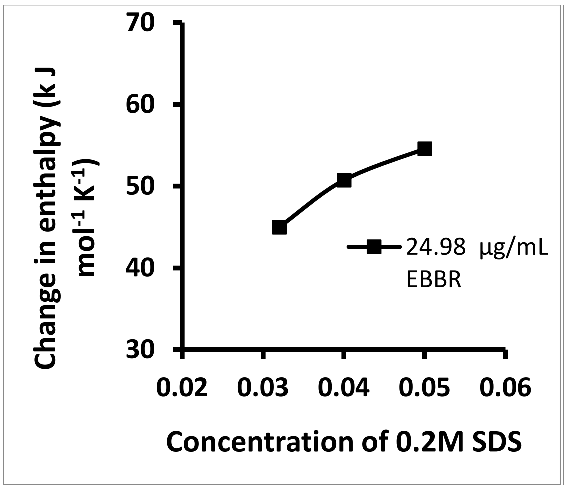

Fig. 2(a)

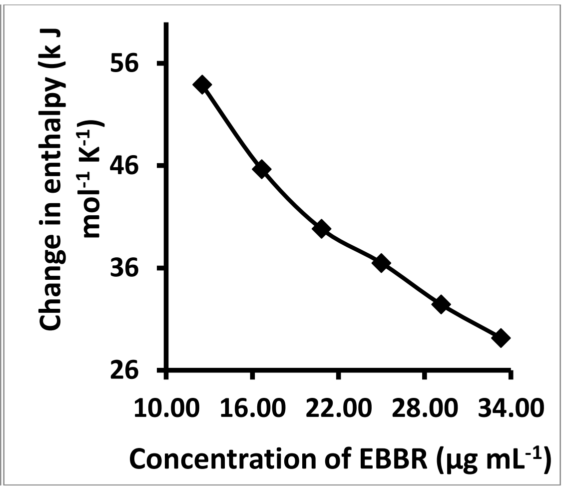

Fig. 2(b)

Effect of surfactant concentration and dye concentration on the change of entropy (ΔS^0) of AMF:

The change in entropy during AMF of EBBR dyes are shown in Fig. 2(a), and 2(d) (Table 2). From the figures the change in entropy (ΔS^0) increases with surfactant concentrations (SDS and TX-114) but decreases with the dye concentrations. Entropy depends upon the unsolubilized dye molecules and free surfactant molecules in the AMF system. The positive values of entropy indicate the greater affinity and well-coordinated analyte molecule in a random fashion in the floc and surfactant rich phase by AMF method.

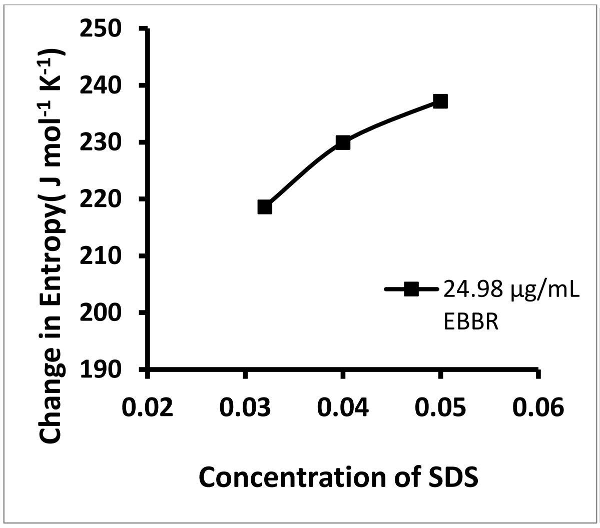

Fig. 3(a)

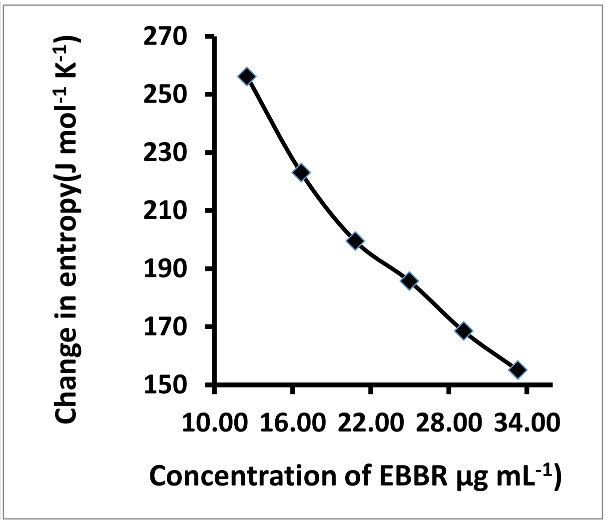

Fig. 3(b)

Effect of extraction change in Gibbs free energy (ΔG^0) of AMF:

By knowing the enthalpy of solubilization (ΔH^0), and the entropy of solubilization (ΔS^0) have been calculated the values of Gibbs free energy (ΔG^0). The change in Gibbs free energy during AMF method of EBBR dye was shown in Fig. 3(a) &3(b). The spontaneity of the AMF for EBBR dye indicated by negative values of Gibbs free energy. From the figures the change of the Gibbs free energy can be found to be linearly increased by the temperature and decreased by concentrations of SDS and dye. Negative values of (ΔG^0) represents the process of dye solubilization is thermodynamically favourable. And the dye adsorption was spontaneous.

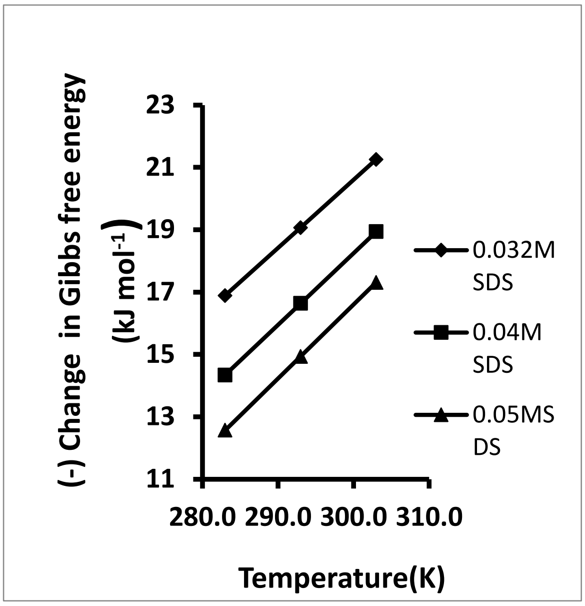

Fig. 4(a)

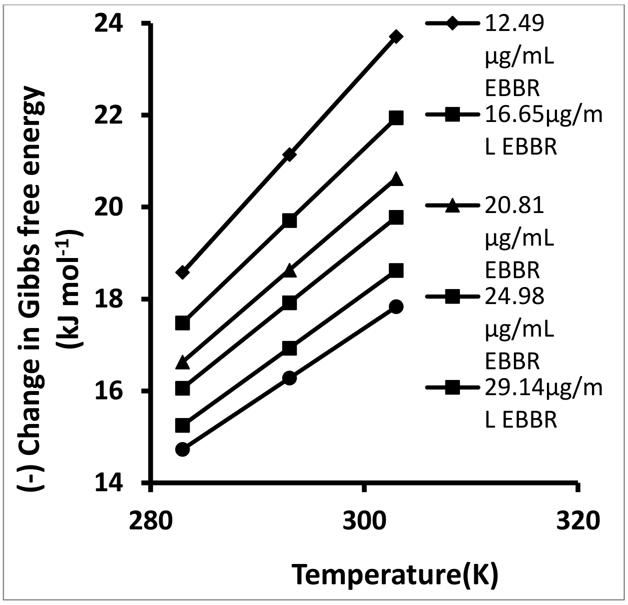

Fig. 4(b)

APPLICATION AND VALIDATION OF THE METHOD

The proposed adsorptive micellar flocculation method was successfully applied for the extraction of EBBR dye in different water samples. The spike recoveries were found to be in the range from 97.83% - 99.91% for EBBR dye in tap and sea water. The details are present in the given table 2.

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

Dyes	**Tap Water**			**Sea Water**		
	Spiked (μg mL^{-1})	**Detected (μg mL^{-1})**	**Recovery (%)**	**Spiked (μg mL^{-1})**	**Detected (μg mL^{-1})**	**Recovery (%)**
	–	ND*	–	–	ND*	–
Erichrome blue black R	12.49	12.45	99.72	12.49	12.21	97.83
	24.98	24.95	99.91	24.98	24.58	98.40

***Not Detected**

Table- 2: Analytical characteristics for the present proposed method

Parameter	**EBBR**
λmax (nm)	520
Linear range (μg /mL)	0.0-41.63
Slope	0.0222
Intercept	0.0
Correlation coefficient (R^2)	0.9932
Preconcentration Factor	12.5
Detection limit(ng/ mL)	37.40
Efficiency of extraction (%)	97.79

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CONCLUSIONS

- In case of AMF, maximum extraction efficiency of 97% for EBBR dye was obtained.
- High preconcentration factors were obtained from AMF procedures for EBBR dye (12.5).
- The effect of concentration of surfactants and dye on the change in Gibbs free energy, enthalpy, and entropy of dye extraction has been studied. The spontaneity of the EBBR dye extraction is governed by the negative values of ΔG^0.
- The developed extraction method combined with spectrophotometry shows that it is a versatile, simple, economical and accurate method for the determination of EBBR dye at ng /mL level.
- The conclusion was that the removal of dyes from aqueous solution is more efficient by adsorptive micellar flocculation with surfactant (SDS).

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