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Enhanced separation of toxic Blue BG dye by cloud point extraction with IL as an additive: Effect of parameters, solubilization isotherm and evaluation of thermodynamics and design parameters

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ABSTRACT

Cloud point extraction (CPE) was adopted for removal of Blue BG dye from aqueous solution using tetraethyl ammonium tetrafluoroborate [TEA(BF_4)] ionic liquid (IL) as an additive with non-ionic surfactant Triton X-114 (TX-114). The effect of different operating parameters such as temperature, time, concentration of surfactant; IL and dye on extraction of dye have been studied in detail to find out optimum conditions. The extraction efficiency was found to increase significantly with temperature, time, surfactant concentration and IL concentration. A developed Langmuir isotherm was used to compute the feed surfactant concentration required for the removal of Blue BG dye up to an extraction efficiency of 90%. The effect of temperature and concentration of surfactant on various thermodynamic parameters, like change in Gibbs-free energy (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°) were examined. It was found that ΔG° increased with temperature but decreased with surfactant concentration whereas ΔH° and ΔS° increased with surfactant concentration.

Introduction

The removal of color from effluent is one of the most difficult requirements faced by the textile finishing, dye manufacturing, paper and pulp industries. The dyes present in waste water cause major environmental problems. Therefore, these colored wastes need to be treated before disposal [1]. Among the type of dyes, Blue BG dye is a disperse dye used for dyeing textiles and leather. The treatment of wastewater containing disperse dyes is a challenge because of their low water solubility and high capacity to form suspensions that inhibit the most advanced oxidation processes.

A number of researchers have studied various techniques for the removal of colored dye from wastewater such as, nanofiltration [2], polyelectrolyte or micelle-enhanced ultrafiltration [3,4], waste material adsorption [5] and various advanced oxidation processes [6,7]. Each method has its certain advantages and drawbacks. For example, due to low biodegradability of dyes, conventional biological wastewater treatment cannot efficiently remove these dyes [8]. In membrane separation processes, care is needed to avoid membrane fouling. Therefore, physical and chemical methods are implemented for dye wastewater treatment [9]. Adsorption is a common dye wastewater treatment method, but is usually costly and sometimes generates large amounts of waste sludge [10]. In the last decade, increasing interest on the use of aqueous micellar solution has been originated in the field of separation science. Cloud point extraction (CPE) is a potentially better alternative treatment method. Advantages of CPE are the use of relatively nontoxic surfactants instead of toxic organic solvent, lower cost, modest energy consumption, higher extraction efficiency, experimental convenience etc. In recent times, the application of CPE for wastewater treatment has rapidly progressed. Some examples of dyes that have been separated using this method are toxic Congo red, Eosin [11], Nitrobenzene [12], Malachite green [13], Sunset yellow [14], Rhodamine B [15], and Chrysoidine [16].

An aqueous solution of a non-ionic surfactant gets separated into two phases above the cloud point temperature. The dilute bulk aqueous phase contains surfactant concentration slightly above the critical micelle concentration (CMC) and the other phase is surfactant rich phase, which is also known as coacervate phase and has a small volume compared to the solution. The dye molecules present in aqueous solution of non-ionic surfactant are allocated between the two phases above the cloud point temperature [17]. This phenomenon is known as cloud point extraction.

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Recently, application of inorganic salts in enhancement of the CPE efficiency of non-ionic surfactants has been reported in a number of studies [1,11,12,16]. However, literature review revealed that very few reports are available for the use of ILs as additives with non-ionic surfactants in CPE for metal separation [18,19] but no report is available for dye removal. The distinctive physical and chemical properties of ILs make them the most suitable candidates as additives with non-ionic surfactants in CPE [20]. ILs have large number of applications in the area of organic synthesis [21], catalysis [22], electrochemistry [23] and chemical separation [24]. Furthermore, ILs are considered as "green solvents" due to their non-volatile nature with an added advantage of tuning their physical and chemical properties by a suitable selection of cation, anion, and substituent.

In the present work, we have demonstrated a novel application of IL as an additive to non-ionic surfactants for CPE of toxic Blue BG dye. The effect of various operating parameters such as time, temperature, concentrations of surfactant, dye and IL on the CPE of dye has been studied in order to establish optimum conditions. Detailed study on dye solubilization and evaluation of thermodynamic parameters have been carried out. Further, the design parameters at different temperatures were also developed to find out the dosage of surfactant concentration required for different feed concentration of the Blue BG dye.

Experimental

Materials

All reagents used were of analytical grade and were used without further purification. Octyl phenol poly(ethylene glycol ether) commercially known as Triton X-114 was received from Sigma–Aldrich, India. The Blue BG dye used in the present study was obtained from Colourtex Pvt. Ltd., (India). The [TEA(BF_4)] IL with high purity was received with compliments from Tatva Chintan Pharma Chem. Pvt. Ltd. (India). The aqueous solutions of all samples have been prepared using deionized water (Millipore Elix 3, USA) with surface tension $72 \pm 0.2\,mN\,m^{-1}$ and specific conductivity order $10^{-3}\,mS\,cm^{-1}$.

Methods

In a typical CPE process, various aqueous solutions of TX-114, [TEA(BF_4)] IL and Blue BG dye of different concentrations were prepared by dissolving accurate amounts of surfactant, IL and dye, respectively. The concentration of TX-114 varied as 0.05, 0.1, 0.15, 0.2 and 0.25 M. The concentration of dye varied as 1.31×10^{-4}, 2.63×10^{-4}, 3.95×10^{-4} and 5.27×10^{-4} M. The effect of amount of IL on CPE of dye was studied using various concentration of IL as 0.01, 0.04, 0.07, 0.1, 0.5 and 0.9 wt.%. Each experiment was performed in a gradate test tube placed in a constant temperature bath ($\pm 0.1\,^{\circ}C$) for the different span of time (30, 45, 60 and 75 min) and at four different temperatures (318.15, 323.15, 328.15 and 333.15 K). The complete phase separation occurs during the given time and then gradate test tube was removed from the temperature bath and cooled for 2–5 min to attain room temperature. The prepared micellar phases are stable up to 6–8 h after phase separation. The top layer (aqueous phase) was collected using micropipette and the concentrations of both dye and surfactant have been determined spectrophotometrically (VARIAN Cary 50). In order to study the thermodynamics and design parameters, the volume of both phases (aqueous and coacervate phase) were measured. The calibration curves of Blue BG and Pure TX-114 solution have been developed for different concentrations at maximum absorption wavelengths of 529 and 223 nm, respectively, using standard method [25].

Results and discussion

A new cloud point extraction methodology using IL as an additive for the enhancement in extraction efficiency of toxic Blue BG dye was developed in this study. The factors that affect the CPE such as temperature, time, concentrations of TX-114, dye and IL were investigated in order to achieve optimized conditions. The nature of solubilization isotherm at different temperature has been discussed and practical applicability of this method was also evaluated for the aqueous and waste water samples. The detailed thermodynamic study for CPE at different temperatures and surfactant concentration has also been carried out.

For CPE, the efficiency of extraction is defined as below:

$$\text{Efficiency of extraction}(E) = \left(1 - \frac{C_d}{C_0}\right) \times 100 \qquad (1)$$

where C_0 and C_d are the initial and dilute phase concentration of Blue BG, respectively.

Optimization of the CPE conditions

Effect of surfactant concentration on extraction

The effect of TX-114 concentration on the extraction of Blue BG is demonstrated in Fig. 1a. It reveals that the dye extraction increases sharply with TX-114 concentration up to 0.1 M and thereafter remains nearly constant for both the cases (i.e., presence and absence of IL). The extraction efficiency found in absence of IL is about 61% and it increases significantly up to 98% with the addition of small amount of IL (0.1 wt.%). As surfactant concentration increases, the concentration of the micelles increases in the solution which resulting in more dye solubilization in the micelles. Hence, the extraction efficiency of dye increases with surfactant concentration. The optimum surfactant concentration of 0.1 M of TX-114 has been selected in order to achieve maximum possible extraction for further study.

Effect of dye concentration on extraction

The effect of dye concentration on the extraction of Blue BG is presented in Fig. 1b. It shows that the extraction of Blue BG decreases with an increment in dye concentration for both cases. It has been established that the compounds (formamide, urea etc.) which have water structure breaking characteristics can increase the CMC of non-ionic surfactant [26]. The presence of structure-breaking ions can hinder the self-aggregation of water molecules. This will enhance the extent of hydrogen bond formation between water molecules and ether groups in non-ionic surfactants. In the present study, the Blue BG dye has similar active functional group. So, it may be presumed that CMC of the non-ionic surfactant increases in the presence of dye. It also entails that the number concentration of the micelles decreases with dye concentration. Hence, decline in extraction efficiency with increment of feed dye concentration is owing to the increment of unsolubilized dye molecules in the dilute phase.

Effect of IL concentration on extraction

The effect of IL concentration on the extraction of Blue BG is demonstrated in Fig. 1c. The results reveal that the extraction of Blue BG increases significantly up to 0.1 wt.% and afterwards it becomes steady. Considering this, all the further experiments for the design and thermodynamic parameters were carried out with 0.1 wt.% IL. Our previous studies confirmed that, [TEA(BF_4)] IL act as a salting-out agent and decreases the cloud point of the surfactant and it supports the dehydration of the ethoxy groups on the outer surface of the micelles [27]. Furthermore, accumulation of IL increases the phase separation, micellar size and specific viscosity.