A cloud point extraction approach using Triton X-114 for the separation and preconcentration of Maxillone Golden Yellow (MGY) dye in waste samples

M. Askari, M. Alizadeh*, S. Alipour
Department of Chemistry, Azad Islamic University, Gachsaran, (IRAN)
E-mail: mehdi.alizadeh85@yahoo.com
Received: 23rd May, 2009; Accepted: 2nd June, 2009

ABSTRACT
Cloud point extraction (CPE) is carried out to extract Maxillone Golden Yellow (MGY) dye from aqueous solution using non-ionic surfactant, TX-114. The effects of different operating parameters, e.g., concentrations of surfactant, dye and salt, temperature, pH on extraction of both dye and surfactant have been studied in detail. The extraction of dye increases with temperature, surfactant concentration and salt concentration. It has been observed that 95.3-90.01 percent MGY is possible for the feed dye concentration of up to 500 ppm using pH 11, 0.7% of Triton X-114 (W/V), and 0.6(M) of salt (KCl) at 65 °C for 15 min. It is concluded that the cloud point extraction techniques for the dye removal may be an alternative to the present dye removal processes.

1. INTRODUCTION

Above the cloud point temperature, aqueous solution of a non-ionic surfactant separates into two phases, namely a surfactant rich phase, which has small volume compared to the solution and is called coacervate phase and the other is dilute bulk aqueous phase containing surfactant concentration slightly above the critical micelle concentration (CMC)\(^1\). The solute molecule present in aqueous solution of non-ionic surfactant is distributed between the two phases above the cloud point temperature\(^2\). This phenomenon is known as cloud point extraction (CPE). This process is schematically described in Figure 1.\(^3\)

Several authors proposed various mechanisms for phase separation of non-ionic surfactants above cloud point. Following are some of the widely accepted hypotheses for cloud point phenomena: (1) micellar interactions which are repulsive at lower temperature become attractive at higher temperature\(^4,5\); (2) dehydration occurs in the external layer of the micelles at higher temperature\(^5,6\). The dielectric constant of water decreases at elevated temperature and water becomes a poor solvent for the hydrophilic part of the surfactant.

Figure 1 : Schematic of cloud point extraction process.
molecules leading to phase separation; (3) at higher temperature, micellar aggregation number and micellar size increases causing to phase separation\textsuperscript{7,8}. In our laboratory, CPE has been successfully used for the removal of MGY dye using TX-114 as the non-ionic surfactant.

Color removal from effluent is one of the most difficult requirements faced by textile finishing, dye manufacturing, paper industries. Among the various types of dye, MGY dye is used in textile, wood and leather. The effluents containing dyes are highly colored resulting in major environmental problems. So these colored wastes need to be treated before disposal.\textsuperscript{9}

Many investigators have studied different techniques for the removal of colored dye from wastewater, e.g., (a) different membrane separation processes like reverse osmosis (RO)\textsuperscript{10}, nanofiltration (NF)\textsuperscript{11}, micellar enhanced ultra filtration (MEUF)\textsuperscript{12,13} and membrane-wet oxidation\textsuperscript{14}; (b) adsorption on to (i) agricultural solid waste\textsuperscript{15}, (ii) different bentonites\textsuperscript{16}, (iii) various types of activated carbon\textsuperscript{17} and (iv) surfactant impregnated montmorillonite\textsuperscript{18}, etc.: (c) several oxidation processes\textsuperscript{19}; (d) ozonations\textsuperscript{20}. Cloud point extraction (CPE) may be an effective method for removing dye from aqueous solution\textsuperscript{21,22}.

In the present work, cloud point extraction has been adopted to remove cationic dye (MGY) from wastewater using TX-114 as nonionic surfactant. The effect of pH, temperature, concentrations of surfactant and salt on extraction of dye has been studied.

2. EXPERIMENTAL

2.1. Instruments

The absorption of MGY was performed with a 160A shimadzu spectrophotometric UV-VIS. The instrumental parameters were those recommended by the manufacturer. A Metrohm691 pH/Ion meter with a combined glass. Calomel electrode was used for adjustment of test solution pH.

2.2. Reagents

All Chemicals used water of analytical grade and double distilled water was used throughout. A solution of Triton X-114 was prepared by dissolving 12 g of Triton X-114(Merck) in Water and diluting to 100 mL in a volumetric flask. A stock solution of 500 mg L\textsuperscript{-1} of MGY was prepared by dissolving 0.5 g of the MGY in water and diluting to 100 mL in a volumetric flask. More diluted were prepared daily using this stock solution. A solution of potassium chloride (KCl) 2.0 mol L\textsuperscript{-1} was prepared by dissolving 14.91 g of KCl (Merck) in water and diluting to 100 mL in a volumetric flask. Doubly distilled water was used to prepare all the solutions.

2.3. General procedure

An aliquot of the MGY, 0.7% of Triton X-114 (W/V), 15 mL of 2 mol L\textsuperscript{-1} KCl were added to a 50 mL volumetric flask and diluted to the mark with water. The resultant solution was transferred to a 50 mL tube and equilibrated at 65°C in a thermostat bath for 15 min. After complete phase separation, the tube was removed from the temperature bath and cooled to room temperature. The concentration of MGY in the dilute phase was measured by spectrophotometric method.

3. RESULTS AND DISCUSSION

The absorption of MGY in aqueous solution showed a maximum absorption band at 439 nm. Therefore, all the measurements were carried out at this wavelength.

3.1. Effect of pH

The effects of the pH of the solution on the extent of MGY extraction are shown in Figure 2 for different concentration of MGY (5, 8 mg L\textsuperscript{-1}), 0.12% of Triton X-114 (W/V) and 80°C. Extraction of MGY is less in acidic pH. Hence, pH 11 was chosen as adequate pH value for further studies.

![Figure 2 : Effect of pH on extraction of dye using TX-114. Conditions: 50 mL of solution containing different concentration of MGY (5, 8 mg L\textsuperscript{-1}), 0.12% of Triton X-114 (W/V), Temp 80°C and time 20 min.](image-url)
3.2. Effect of Triton X-114 concentration

The effect of the Triton X-114 concentration on CPE efficiency of MGY is shown in Figure 3. For successful cloud point extraction of dye, it is desirable to use minimum amount of surfactant maximum extraction of dye. Therefore, the effect of the surfactant concentration was investigated in order to ensure maximum extraction efficiency. It has been observed from the figure that extraction of the dye increase sharply when TX-114 concentration increases from 0.03 to 0.7 % (W/V). Beyond 0.7 % (W/V), the extraction efficiency is almost constant.

Quantitative CPE efficiency was observed when the Triton X-114 concentration was above 0.7 % (W/V). The surfactant concentration of 0.7 % (W/V) was chosen as optimum.

3.3. Effect of equilibration temperature

The effect of the equilibration temperature (45-80°C) on the cloud point extraction was also investigated. The critical micelle concentration (CMC) of non-ionic surfactant decreases with temperature\[23\]. Moreover, non-ionic surfactant appear relatively more hydrophobic at higher temperatures, due to an equilibrium shift that favors dehydration of the ether oxygens. This leads to an increase in the number concentration of micelles. Therefore, the solubilization capability of the micellar solution increases with temperature leading to an increase in the dye extraction. The effects of the operating temperature on the extraction of MGY are clear from Figure 4. The extraction efficiency of dye increases with temperature. Quantitative CPE efficiency for MGY were temperature above when minimum 65°C were used. Thus a temperature of 65°C was selected.

3.4. Effect of equilibration time

Optimal equilibration time are necessary to complete reaction, and achieve easy phase separation as efficient as possible. The dependence of extraction efficiency upon equilibration time was studied for a time interval of 5-30 min (Figure 5.). An equilibration time of 15 min was chosen as an optimum value.

3.5. Effect of electrolyte

It has been reported that due to electrolyte salting-out effect, salts decrease the cloud point of the surfactant and it is promotes the dehydration of the ethoxy group on the outer surface of the micelles. The salting-out phenomena is directly related to the desorption of ions from the hydrophilic parts of the micelles, increasing inter-attraction between micelles and consequently leading to the precipitation of surfactant molecules\[24\].
Therefore, addition of electrolyte increases phase separation enhancing the micellar concentration in the coacervate phase, leading to solubilization of more dye. However, the effect of potassium chloride is important because the cost of the eventual process depends on the amount of heat needed to obtain the separation of phases.

The effect of potassium chloride as an electrolyte was studied. It is observed from Figure 6, the extraction efficiency of MGY was slightly increased in the presence of KCl and it was almost constant above 0.6 mol L\(^{-1}\) of KCl. Thus a 0.6 mol L\(^{-1}\) of KCl was selected for further studies.

**Figure 6 : Effect of KCl concentration on the CPE efficiency of MGY.** Conditions: 50 mL of solution containing different concentration of MGY (5, 8 mg L\(^{-1}\)), 0.7 % of Triton X-114 (W/V), pH 11, Temp 65\(^{\circ}\)C and time 15 min.

### 3.6. Effect of initial dye concentration

The effect of initial dye concentration on the extraction efficiency using above optimum concentration was investigated. The results presented in **TABLE 1**, show that up to 500 mg L\(^{-1}\) of MGY be removed (>90%) by CPE procedure. From Table observed that the extraction efficiency of dye decreases with the feed dye concentration. At a particular operating temperature and surfactant concentration, the surfactant concentration in both the dilute and coacervate phase remains constant. Hence, the dye solubilization capacity of the surfactant micelles remains almost invariant in the coacervate phase. Therefore, with the further increase in feed dye concentration, excess dye remains unsolubilized in the dilute phase, resulting in a decrease of the extraction efficiency.

### TABLE 1 : Effect of initial dye concentration on the CPE efficiency of MGY.

<table>
<thead>
<tr>
<th>Concentration (mg L(^{-1}))</th>
<th>CPE efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>95.3</td>
</tr>
<tr>
<td>8.0</td>
<td>95.0</td>
</tr>
<tr>
<td>15.0</td>
<td>96.7</td>
</tr>
<tr>
<td>20.0</td>
<td>94.3</td>
</tr>
<tr>
<td>25.0</td>
<td>96.0</td>
</tr>
<tr>
<td>50.0</td>
<td>95.2</td>
</tr>
<tr>
<td>75.0</td>
<td>94.8</td>
</tr>
<tr>
<td>150.0</td>
<td>94.0</td>
</tr>
<tr>
<td>200.0</td>
<td>94.6</td>
</tr>
<tr>
<td>500.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>

### 4. CONCLUSIONS

Cloud point extraction of MGY can be successfully used to remove color wastewater using TX-114 as non-ionic surfactant. The effects of pH, temperature, and time, concentration of KCl, TX-114 and MGY on the extraction efficiency have been studied in detail. It is observed that the extraction efficiency increases with temperature, TX-114 and KCl concentration. From the experimental, it is observed that for dye concentration up to 500 mg L\(^{-1}\), >90 percent of MGY dye is removed. Separated aqueous phase still contains some of dye, probably solubilized in the micelle of the surfactant.

### REFERENCES