Removal of Reactive Blue 19 using nonionic surfactant in cloud point extraction


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**A R T I C L E   I N F O**

Article info

Received 15 May 2014
Received in revised form 6 October 2014
Accepted 8 October 2014
Available online 22 October 2014

**Keywords:**
Reactive Blue 19
Nonionic surfactant
Cloud point extraction
Coacervate phase
Langmuir isotherm

**A B S T R A C T**

Textile wastewater represents a serious environmental issue due to the presence of toxic dyes. The cloud point extraction, which involves the application of nonionic surfactants at temperatures above the cloud point, was applied in this research to remove Reactive Blue 19 dye from a synthetic wastewater. Nonylphenol with 9.5 ethoxylation degree was used as nonionic surfactant. Dye removal was evaluated considering the influence of surfactant concentration, temperature, and initial dye concentration. Equilibrium data followed the Langmuir isotherm model. Negative Gibbs energy, enthalpy, and entropy showed that the process was spontaneous and exothermal. Dye removal reached 91% when using 7.5 wt% surfactant, at 65.0 °C. Cloud point extraction can be used as an efficient alternative for treating textile wastewater containing Reactive Blue 19.

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1. Introduction

Because of the changing characteristics of the wastewater, studies of wastewater treatability are increasing, especially with reference to the treatment of specific constituents [1]. The textile industry is one of the major sources of water pollution. It uses a huge quantity of water and produces substantial volumes of colored wastewater. The removal of color from wastewater, due to the presence of unused synthetic dyes, is one of the most difficult tasks faced by the textile industry [2,3].

A dye is a natural or synthetic coloring substance with affinity to bind to a substrate, e.g. fabric. It is usually applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibers [4]. Dye classes include basic, acid, cationic, direct, reactive, sulfur, azoic, and disperse, with reactive being the most widely used in the textile industry.

Around 1 million tons of synthetic dyes, including reactive dyes, are produced every year worldwide and 5–15% of this amount is discharged as textile wastewater [5,6]. The main problem associated with the use of reactive dyes is their low affinity for textile material, with up to 50% of them present in the discarded bath [7,8]. Reactive dyes, in their original or hydrolyzed forms, are difficult to degrade biologically and are highly toxic to animals and humans [9]. In the case of Reactive Blue 19 (RB19), fixation efficiency in cotton ranges between 75% and 80%, due to the competition between the formation of vinyl sulfone and that of 2-hydroxyethylsulfone [10], Fig. 1 shows the molecular structure of Reactive Blue 19, explaining the formation of vinyl sulfone and 2-hydroxyethylsulfone [11]. According to Weber and Stickney [11], the hydrolysis of the vinyl sulfone moiety before the formation of a covalent bond between dye and fiber is the major problem associated with dye technology, because, after hydrolysis, this dye loses its affinity for the textile fiber.

It is difficult to remove dye from wastewater using conventional treatment systems [12]. A number of techniques have been developed in search of efficient alternatives to treat dye-bearing wastewater, including electro oxidation [13], adsorption [4,14], ionic-liquid-based aqueous two-phase systems [6], sonochemical degradation [7], and ozone application [15]. Oxidative processes can be complicated for Reactive Blue 19, since its anthraquinone aromatic structure, highly stabilized by resonance, makes it very resistant to chemical oxidation [16].

Surfactants are applied in many industrial separation processes. A solution of nonionic surfactant becomes cloudy at a certain temperature, known as cloud point temperature. Above this temperature, the solution will separate into two phases: an aqueous phase containing surfactant at a concentration slightly above its critical micelle concentration (cmc) and the other, a surfactant-rich one, called coacervate phase. When organic solutes are present in the solution, they separate along with the surfactant to the coacervate phase, in a process known as Cloud Point Extraction (CPE).
interaction occurs due to adsorption of the solute on the surface of the micelles or some others sites within micelles. This phenomenon can be suggested by the monolayer coverage of the solute on the surface of the micelles [17]. Cloud point extraction, as observed by several authors, is an effective technique for removing dissolved organic contaminants from wastewater and groundwater [17–23].

In the present research, experiments were developed to remove Reactive Blue 19 dye by CPE using a nonionic surfactant widely used in Brazil, despite its known toxicity [24]. Its residual concentration in the process after phase separation is very low, in the order of the cmc, which can still be resolved by recovery of solvent [20,21]. The removal efficiency was evaluated considering the influence of temperature, dye initial concentration, and surfactant concentration. The thermodynamic parameters were evaluated (enthalpy, entropy and Gibbs energy) and the Langmuir isotherm model was used to fit the equilibrium data.

2. Materials and methods

2.1. Material

Nonylphenol polyethoxylate with an average number of 9.5 ethylene oxide units per molecule (NP9.5EO) was used as nonionic surfactant (weight = 617 g mol\(^{-1}\), complete solubility in water, viscosity 230–270 mPa s at 25 °C, density 1060 kg/m\(^3\), cloud point 56 °C in aqueous solution at 1% m/m). Reactive Blue 19 (RB19) was used to obtain the synthetic dye wastewater (Dystar; molar weight = 626.54 g mol\(^{-1}\); \(\lambda_{\text{max}}\) = 592 nm, blue). All reagents were acquired commercially and used without further purification.

2.2. Methods

2.2.1. Cloud Point Experiments (CPE)

In CPE, the NP9.5EO concentration was varied in 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5% (m/m). The initial RB19 concentration was varied in 10, 25, 50, 75, 100, 125, 150, and 200 ppm. Five temperatures were chosen (65.0, 67.5, 70.0, 72.5, and 75.0 °C). First, in 100 mL – graduated test tubes (±1 mL), 100 mL solutions of NP9.5EO and RB19 were prepared by dissolving them in distilled water at different concentrations, according to each experimental run. The tests were performed in a thermostatic bath (Koehler Instrument Company, Inc., USA) at a constant temperature and stirring rate (500 rpm), for five minutes to assure homogenization. After, the samples were left at rest for two hours to allow phase separation. The volumes of the dilute and coacervate phases were visually measured in the graduated test tubes. Dye concentration in the dilute phase was determined with a UV–Vis spectrophotometer (Varian Analytical Instruments, Cary 50 Conc, USA). Dye removal efficiency was calculated by using Eq. (1):

\[
\% \text{Efficiency} = \frac{C_{\text{RB19, initial}} - C_{\text{RB19, dilute}}}{C_{\text{RB19, initial}}} \times 100
\]

where \(C_{\text{RB19, initial}}\) is the initial dye concentration and \(C_{\text{RB19, dilute}}\) is the dye concentration in the dilute phase.

2.2.2. Adsorption isotherm

To describe equilibrium data, dye concentrations between aqueous and coacervate phases were fit to the Langmuir isotherm model. The linear expression for the Langmuir model is given by Eq. (2):

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_L C_e}
\]

where \(q_e\) is the equilibrium adsorption capacity (g of RB19/g of NP9.5EO), \(C_e\) is the equilibrium concentration in the dilute phase (g/L), \(q_m\) the maximum adsorption capacity (g of RB19/g of NP9.5EO) and \(k_L\) is the Langmuir parameter (L/g of RB19).

3. Results and discussions

3.1. Dye removal efficiency

In order to maximize dye removal efficiency by CPE, the influences of surfactant concentration and temperature were first evaluated, maintaining constant the initial dye concentration (100 ppm). Surfactant concentration was fixed between 3.0 and 7.5% (m/m), since preliminary tests showed that dye removal was very low at concentrations below 3% and concentrations above 7.5% were not considered economically viable. Two factors were conside to determine temperature range, as follows: temperatures above the cloud point (56.0 °C), in order to guarantee phase separation, and work in a temperature range close to that found in the textile effluent which can reach 70 °C [25]. Fig. 2 shows the extraction efficiency for different temperatures and initial surfactant concentrations.

In Fig. 2 one can observe that removal efficiency decreases with increasing temperature and increases with increasing surfactant concentration, especially in the surfactant concentration range between 3.0 and 6.0% (m/m). An increase in surfactant concentration outside this range will not cause a significant increase in dye removal efficiency. This behavior was expected because the number of micelles rises with increasing surfactant concentration,
resulting in greater solubilization of dye molecules [21]. According to Purkait et al. [26] at constant temperature and dye concentration, the fractional coacervate phase volume increases with surfactant concentration. This increase in the volume of coacervate phase occurs because the surfactant concentration in this phase remains constant at constant temperature, consequently, to maintain material balance, the phase volume increases. As there is more surfactant in micellar form present in the coacervate phase, an increase in dye solubilization and also in extraction efficiency is verified.

It is important to observe that, as temperature increases, dye removal efficiency declines. This is also related to the volume of the coacervate phase, which decreases with increasing temperature.

After defining the best conditions for temperature and surfactant concentration, it was assessed the influence of dye concentration in CPE process. It was observed that the best results were obtained using 6 wt% surfactant, at 65.0 °C. To better evaluate dye removal efficiency, it was decided to vary surfactant concentration in the range of 5–7 wt% and dye initial concentration in the range of 10–200 ppm, as can be observed in Fig. 3.

Fig. 3 shows that removal efficiency increases until a maximum value is achieved and, then, decreases. The highest removal efficiency was observed when using 100 ppm RB19, reaching 86.67% for a surfactant concentration of 7.0 wt%. The initial increase in removal efficiency occurs due to the solubilization of dye molecules in the micellar core. As the concentration of surfactant remains constant, the removal efficiency declines at dye concentrations above 100 ppm due an insufficient amount of surfactant to solubilize excess dye molecules, that remain unsolubilized in the dilute phase, thus decreasing dye removal efficiency [27]. Fig. 4 shows that the ratio between the dye concentration and the surfactant concentration is another factor that affects the process.

Fig. 4 shows that the RB19/NP9.5EO ratio between 1.0 and 2.0 provides better removal of dye, one should take into account this parameter in the process.

### 3.2. Fractional coacervate phase volume

In cloud point extraction another important point to analyze is the fractional coacervate phase volume (FV), which is defined as the ratio between the coacervate phase volume and the total solution volume. The following three process variables affect the coacervate phase volume: initial dye concentration, surfactant concentration, and temperature. Fig. 5 shows the fractional coacervate phase volume as a function of surfactant concentration and temperature.

In Fig. 5 one can observe that the fractional coacervate phase volume increases with surfactant concentration. This occurs because in the dilute phase surfactant concentration is always close to the cmc, and all remaining surfactant is directed to the coacervate phase, increasing its volume. It can also be observed that the fractional coacervate phase volume declines when temperature rises. This occurs because at high temperatures the interaction between surfactant molecules and water decreases, leading to the dehydration of the outer layers of the micellar aggregates, thus reducing the volume of the coacervate phase [20].

From the experimental data it was possible to obtain a model that describes the behavior of the fractional coacervate phase volume at different surfactant concentrations and temperatures (Eq. (3)), with correlation coefficient ($R^2$) equal to 0.9916.

$$\%FV = 86.625 - 1.2T + 4.5(\%NP9.5EO) - 0.125(\%NP9.5EO)^2$$

(3)

where %FV is the fractional coacervate phase volume, %NP9.5EO is percentage of surfactant and $T$ (°C) is the temperature.
3.3. Partition coefficient

The partition coefficient (D) is the ratio between solute concentration in the coacervate and dilute phases. Fig. 6 shows the partition coefficient as a function of surfactant concentration for all studied temperatures.

In Fig. 6 one can observe that the partition coefficient increases with surfactant concentration and declines with temperature. When the concentration of surfactant increases, the volume of the coacervate phase also increases, thereby increasing the solubilization of dye in this phase. However, at high surfactant concentrations, there is a tendency toward stabilization of the distribution coefficient value. This occurs because extraction efficiency approaches its maximum value and the addition of more surfactant will only increase the size of the coacervate phase, without representing gain in efficiency. Considering the effect of temperature, it can be observed that a rise in temperature cause a decrease in the partition coefficient. This can be explained by the equilibrium of the chemical potential ($\mu$) of the dye between the coacervate ($\mu_{RB19,c}$) and dilute ($\mu_{RB19,d}$) phases (Eq. (4)).

$$\mu_{RB19,c} = \mu_{RB19,D}$$

where,

$$\mu_{RB19,c} = \mu_{RB19,c} + RT\ln(\gamma_{RB19,c}x_{RB19,c})$$

$$\mu_{RB19,D} = \mu_{RB19,D} + RT\ln(\gamma_{RB19,D}x_{RB19,D})$$

where $\mu_o$ is the standard-state chemical potential in a given reference state, $R$ is the universal gas constant ($8.314 \times 10^{-3}$ kJ/mol K), $T$ is the temperature (K), $\gamma$ is the activity coefficient, and $x$ is dimensionless concentration. Given that the dye concentration in both of these phases is very small, $\gamma_{RB19,c}$ and $\gamma_{RB19,D}$ are equal to unity. Thus,

$$\Delta G^o = \mu_{RB19,D}^o - \mu_{RB19,c}^o$$

where $\Delta G^o$ is the standard-state Gibbs free energy. The partition coefficient (D) is a function of the temperature, as shown in Eq. (8).

$$D = \frac{x_{RB19,c}}{x_{RB19,D}} = \frac{e^{\frac{\Delta H^o}{RT}}}{\gamma}$$

where $\Delta H^o$ is the change in enalphy and $\Delta S^o$ is the change in entropy. Therefore, if temperature rises, the partition coefficient tends to decline.

3.4. Adsorption equilibrium

In this study the experimental data were fitted to the Langmuir model, as can be observed in Fig. 7 and Table 1.

The values of $q_m$ and $k$ were obtained from the slope and intercept of each isotherm shown in Fig. 7. Table 1 shows the values of maximum adsorption capacity ($q_m$), Langmuir constant ($k$), and correlation coefficient ($R^2$). It can be noticed that $R^2$ values are close to 1, indicating that the experimental data fitted well to the Langmuir model. In addition, although the adsorption capacity is constant [28], the value obtained in this work ranged around 2.14–3.12 mg/g, with a tendency to decrease with temperature, which explains the decrease in removal efficiency. Purkait et al. showed functions representing the variation of $q_m$ with temperature on CPE [26].

The Langmuir constant ($k$) was used to calculate the separation factor ($R_l$), which is a dimensionless constant. The $R_l$ value indicates the nature of the adsorption process: the process is unfavorable if $R_l > 1$; a favorable adsorption is observed when $0 < R_l < 1$; linear if $R_l = 1$; and irreversible if $R_l = 0$. The separation factor was calculated using Eq. (9):

$$R_l = \frac{1}{1 + kC_{RB19,initial}}$$

From the data shown in Table 1, it can be observed that the $R_l$ values were greater than 0 but less than 1, indicating a favorable adsorption process.
Dis the amount of solubilized dye (mg) per g of NP9.5EO, \( \frac{C_0}{C_0 + C} \) correlation coefficient (\( R \)) for concentrations. Gibbs free energy of adsorption (kJ/mol) for different temperatures and surfactant concentrations.

### Table 2
Adorption enthalpy and entropy for surfactant concentrations ranging from 3.0 to 7.55 m/m.

<table>
<thead>
<tr>
<th>NP9.5EO concentration (wt%)</th>
<th>( \Delta H^o ) (kJ mol(^{-1}))</th>
<th>( \Delta S^o ) (kJ mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>-53.50</td>
<td>-0.15</td>
</tr>
<tr>
<td>3.5</td>
<td>-74.97</td>
<td>-0.21</td>
</tr>
<tr>
<td>4.0</td>
<td>-77.29</td>
<td>-0.22</td>
</tr>
<tr>
<td>4.5</td>
<td>-80.00</td>
<td>-0.22</td>
</tr>
<tr>
<td>5.0</td>
<td>-80.79</td>
<td>-0.22</td>
</tr>
<tr>
<td>5.5</td>
<td>-91.10</td>
<td>-0.25</td>
</tr>
<tr>
<td>6.0</td>
<td>-87.96</td>
<td>-0.24</td>
</tr>
<tr>
<td>6.5</td>
<td>-77.79</td>
<td>-0.21</td>
</tr>
<tr>
<td>7.0</td>
<td>-71.72</td>
<td>-0.19</td>
</tr>
<tr>
<td>7.5</td>
<td>-66.71</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

### 3.5. Thermodynamic analysis of adsorption

Gibbs free energy (\( \Delta G^o \)), entropy (\( \Delta S^o \)) and enthalpy (\( \Delta H^o \)) were calculated to determine the behavior of the system with modifications in temperature and surfactant concentration. Thermodynamics parameters were obtained using Eqs. (10) and (11) [29]:

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]

\[
\log(q_e/C_e) = \frac{-\Delta S^o}{2.303R} + \frac{-\Delta H^o}{2.303RT}
\]

where \( q_e \) is the amount of solubilized dye (mg) per g of NP9.5EO, \( C_e \) is the dye equilibrium concentration (mg/L), \( a \) is the adsorbent dose level (g NP9.5EO/L), and \( T \) is the temperature in Kelvin. The data for enthalpy and entropy are shown in Table 2 and the Gibbs energy in Table 3.

Table 2 shows that enthalpy variation is negative in all cases, confirming that the process is exothermic. The enthalpy values obtained in Table 2 can explain the temperature dependence of the extraction efficiency, which decreases with a rise in temperature, since extraction was found to be exothermic. Furthermore, it may be pointed out that dye molecules are organized in a less random form in the micelles than in a bulk solution.

### Table 3
Gibbs free energy of adsorption (kJ/mol) for different temperatures and surfactant concentrations.

<table>
<thead>
<tr>
<th>NP9.5EO concentration (wt%)</th>
<th>Temperature (°C)</th>
<th>65.0</th>
<th>67.5</th>
<th>70.0</th>
<th>72.5</th>
<th>75.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.37</td>
<td>-0.98</td>
<td>-0.59</td>
<td>-0.21</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>-2.88</td>
<td>-2.35</td>
<td>-1.82</td>
<td>-1.29</td>
<td>-0.75</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>-3.69</td>
<td>-3.15</td>
<td>-2.60</td>
<td>-2.06</td>
<td>-1.52</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>-4.53</td>
<td>-3.97</td>
<td>-3.41</td>
<td>-2.85</td>
<td>-2.30</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>-5.14</td>
<td>-4.56</td>
<td>-4.02</td>
<td>-3.46</td>
<td>-2.90</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>-5.85</td>
<td>-5.22</td>
<td>-4.59</td>
<td>-3.96</td>
<td>-3.33</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>-6.30</td>
<td>-5.70</td>
<td>-5.10</td>
<td>-4.49</td>
<td>-3.89</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>-6.42</td>
<td>-5.89</td>
<td>-5.36</td>
<td>-4.83</td>
<td>-4.31</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>-6.70</td>
<td>-6.22</td>
<td>-5.74</td>
<td>-5.26</td>
<td>-4.78</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>-6.91</td>
<td>-6.46</td>
<td>-6.02</td>
<td>-5.58</td>
<td>-5.14</td>
<td></td>
</tr>
</tbody>
</table>

In Table 3 one can observe that the \( \Delta G^o \) values were negative, indicating that the adsorption process was spontaneous, except at 75.0 °C and 3.0 wt% surfactant. It can also be noticed that the absolute value of the Gibbs energy is higher when the surfactant concentration increases and declines when the temperature is raised. These results are in agreement with those obtained by using the partition coefficient of the dye between coacervate and dilute phases.

### 4. Conclusion

In this study nonylphenol polyethoxylate with an average number of 9.5 ethylene oxide units per molecule (NP9.5EO) was used in a cloud point extraction process to evaluate reactive Blue 19 (RB19) removal from a synthetic wastewater. The main conclusions of this work are:

- The efficiency of dye extraction strongly depends on surfactant concentration, and to a lesser extent, on temperature and initial dye concentration.
- The partition coefficient increases with surfactant concentration and declines with temperature. This occurred because when the concentration of surfactant increases, the volume of the coacervate phase also increases, thereby increasing the solubilization of dye in this phase.
- A non-linear equation describes the behavior of the fractional coacervate phase volume at different surfactant concentrations and temperatures, which shows 0.9916 as correlation coefficient (\( R^2 \)).
- The experimental data were well fitted to the Langmuir model, and the maximum adsorption capacity was obtained at 65 °C, reaching 3.12 mg RB19/g NP9.5EO.
- The separation factor (\( R_L \)) showed values greater than 0 but less than 1, indicating a favorable adsorption process.
- The Gibbs free energy showed negative indicating that the process is spontaneous in nature.
- Extraction using the CPE process showed to be efficient, reaching values of more than 90% dye recovery, confirming that NP9.5EO can be used as surfactant for this type of treatment. It is important to evaluate surfactant recovery to prove the viability of the process.

### Acknowledgements

The authors are grateful to the Federal University of Rio Grande do Norte (UFRN), especially to the Chemical Engineering Post-Graduation Program, to the Center for Teaching and Research in Oil & Gas (NUPEG), and to the Textile Engineering Laboratory.

### References

electrodes in the electrooxidation of the Blue Reactive 19 dye in ultrasound assisted.


