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THE SYNERGETIC EFFECT OF \(\alpha\)-HYDROXYCARBONYLS MIXTURES USED AS GREEN REDUCING AGENT ON THE INDIGO DYEING PROCESS

Article Highlights

• Development of a clean process for indigo dyeing
• Substitution of conventional sodium dithionite by green alternatives in reducing indigo
• Study of synergy effect of mixture \(\alpha\)-hydroxycarbonyls in reducing indigo
• Determination of the optimum mixture of \(\alpha\)-hydroxycarbonyls for reducing indigo

Abstract

Textile industries use different chemicals in dyeing processes, consuming large quantities of water and producing large volumes of wastewater. For the particular case of indigo dyeing processes, its reduction is performed chemically by the addition of sodium dithionite. However, this is considered environmentally unfavorable because of the resulting contaminated wastewaters. Therefore, it is important to replace sodium dithionite with other alternatives in order to achieve cleaner processes. \(\alpha\)-hydroxycarbonyls have been suggested as possible environmentally friendly alternatives to reduce indigo. However, each one applied alone is unable to attain the dyeing performances offered by the conventional reductant. Thus, the study of the synergy of some selected \(\alpha\)-hydroxycarbonyls was proposed. In this paper, a mixture design of experimental (DOE) methods was used to determine the optimum combination of \(\alpha\)-hydroxycarbonyls to be applied in the indigo reduction process. Based on the design expert software, quadratic models were established as functions of \(\alpha\)-hydroxycarbonyls ratios. The diagnostics of models were investigated by using mixture contour plots. Finally, a model was proposed to predict the optimum conditions leading to dyeing performances exceeding those obtained from the reduction of indigo by the conventional sodium dithionite.

Keywords: green reducing agent, \(\alpha\)-hydroxycarbonyls, synergetic effect, mixture design, clean process.

As a vat dye, indigo is considered the oldest dye known to man. It is an organic compound with a distinctive blue color. Historically, it was naturally extracted from plants, and this was important economically because blue dyes were rare. Nearly all indigo dyes produced today - several thousand tons each year - are synthetic. Indigo and other vat dyes consumption reaches about 33×10^6 kg annually [1]. This situation is expected to stay unchanged in the near future mainly due to the high performances of this dye group [1,2]. The use of indigo in textile dyeing requires its reduction to water-soluble leuco form before being absorbed by fibers. Chemically, indigo is a conjugated dicarbonyl system, which is reduced with a change in conjugation. The reduction is a two-electron change and the resultant reduced form (leuco-indigo) can then be easily reoxidized [3,4]. The process of reducing indigo to leuco-indigo is used on a large scale worldwide [5]. It is performed using sodium dithionite as a reducing agent [6], and is applied to all vat dyes at temperatures above 30 °C [7]. The use of sodium dithionite is known to offer an effective reduction of indigo, as well as other vat

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dyes, and it enables very short fixing times in various dyeing methods [2]. Nevertheless, sodium dithionite has many issues such as low stability, it is easily oxidized by atmospheric oxygen [8], and risks of fire and health hazards during storage. Besides, the stability of its alkaline solutions decreases with the increase of temperature, even in the absence of oxygen. Hence, large amounts of dithionite and sodium hydroxide are needed over the stoichiometric requirements of the reduction process. Furthermore, the oxidation of byproducts causes various problems with wastewater disposal. In fact, sulphate, sulphite, and thiosulphate ions resulting from the oxidation of sodium dithionite during the reducing process have harmful effect on the environment due to their toxicity, as well as their corrosive effect on the waste lines. In addition, sodium dithionite affects the aerobic processes in wastewater treatments and toxic hydrogen sulphide can be generated anaerobically from the sulphate present in wastewaters [2,7]. The improvement of this type of process by eliminating or minimizing the production of inorganic waste from chemical reducing agents, can be made by many methods, such as the use of iron (II) complexes (gluconic acid complexes) [9], organic reducing agents [10], biological reduction [11], and electrochemical reduction [1,2,5]. However, most of these methods are not deemed satisfactory because of technical and economic limitations.

Recently, the reduction of indigo with $\alpha$-hydroxycarbonyls has been studied as possible environmentally friendly reducing agents [12,13]. In a previous study [14], reduction of indigo was achieved by the eco-friendly $\alpha$-hydroxycarbonyls, the oxidation products of which are biodegradable [15], but it is also known that applying $\alpha$-hydroxycarbonyl alone in the reducing indigo process would not achieve the same dyeing performances offered by the conventional reduction processes. Therefore, we propose the use of a mixture of only some selected $\alpha$-hydroxycarbonyls and to study their synergy effect in order to optimize conditions and, if possible, attain the conventional reducing power and dyeing performances. We use a mixture design via Minitab [16]. The $\alpha$-hydroxycarbonyls compounds used in this study are: acetal, acetoin and glucose.

MATERIALS AND METHODS

Chemicals and materials used

Indigo (Bezema AG, Switzerland), glucose (Sigma, France), acetal (Fluka, Germany), acetoin (SAFC, USA) and sodium hydroxide (CDM, Germany) were used for the reduction without further purification. Commercially bleached but unfinished cotton fabric with the following specifications was supplied from Sitex, Tunisia; plain weave; ends per inch, 33.02; picks per inch, 38.1; warp count, 10.5 Open End; weft count, 15 Open End; weight, 204 g m$^{-2}$.

The process in the absence of indigo (white bath)

A solution containing 12 g L$^{-1}$ of sodium hydroxide and 0.055 mol of the studied reducing agent were prepared by adding them to 200 ml of distilled water. This solution was brought up to the appropriate temperature (50, 70 or 90 °C) for 120 min. The reaction was carried out in the laboratory autoclave machine (Ahiba Datacolour International, USA) where the duration and temperature of the reduction were programmed ahead of time. The redox potentials and the pH of the medium were recorded at the end of the process. All the redox potential measurements were given in mV (vs. Ag/AgCl, 3 mol L$^{-1}$ KCl) [17].

The reduction process of indigo

The same procedures previously used were repeated here but in the presence of 2 g L$^{-1}$ of indigo. The reduction reaction was carried out in the laboratory autoclave machine (Ahiba Datacolour International, USA), the redox potential and pH measurements were taken at the end of process. The redox potentials of the medium were recorded at the end of the process. All the redox potential measurements were given in mV (vs. Ag/AgCl, 3 mol L$^{-1}$ KCl).

Continuous dyeing process

The reaction medium obtained from the reduction process was used as a dyeing bath after the decrease of the medium temperature to 25 °C (this step lasted about 10 min before the beginning of the dyeing process). The dyeing process was continuous; it consisted mainly of “6-dip-6-nip” in order to achieve deep shades. After that, the dyed samples were hand washed with hot water for 5 min at 70 °C, followed by a cold rinsing, and finally drying at room temperature.

Conventional indigo dyeing process

In the conventional process of dyeing cotton by indigo, basic dyebath formulations include generally 2 g L$^{-1}$ of indigo, 4 g L$^{-1}$ of sodium hydroxide with a reduction temperature around 50 °C. The dyeing process is carried out using a 6-dip-6-nip padding operation at 25 °C. A complete 1-dip-1-nip cycle consists of dipping fabric in dye liquor for 1 min then airing it for 2 min. After that, the dyed samples were subjected to a hand washing with hot water for 5 min at 70 °C,
followed by a cold rinsing, and drying at room temperature [18,19].

Dyeing quality evaluation

The dyeing quality was evaluated using a colour yield parameter \( K/S \). The reflectance of the dyed samples was measured at 660 nm on a SpectroFlash SF300 spectrophotometer with dataMaster 2.3 software (Datacolor International, USA). Then, \( K/S \) value was determined according to the Kubelka-Munk equation [20]:

\[
K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}
\]

where \( R \) is the decimal fraction of the reflectance of dyed fabric, \( R_0 \) is the decimal fraction of the reflectance of undyed fabric, \( K \) is the absorption coefficient and \( S \) is the scattering coefficient.

Fastness testing

The dyed samples were tested according to ISO standard methods. The specific tests were for colour fastness to washing ISO 105-C06: 2010, colour fastness to rubbing ISO 105-F09:2009 and colour fastness to light ISO 105-B02:1999.

Mixture design model (DOE)

A three component constrained simplex lattice mixture design was used. The mixture consisted of acetol (A), acetoin (B) and glucose (C). Component proportions were expressed as fractions of the mixture with a sum (A + B + C) equal to one. The mixture plan was accomplished and statistical analyses of data was achieved using commercial software (Minitab, version 15, State College, PA, USA).

RESULTS AND DISCUSSION

The effect of temperature on the reducing power of \( \alpha \)-hydroxycarbonyls mixtures

The purpose of this part is to study the reducing power of different mixtures of \( \alpha \)-hydroxycarbonyls reducing agents according to an increase of the reducing temperature and to the presence or absence of the indigo dye in the medium [17] in order to compare them to the reducing power of the conventional reduction process. The studied reduction mixtures and their symbols are described in Table 1.

Compared to the conventional reducing agent, using \( \alpha \)-hydroxycarbonyls at a reducing temperature of 50 and 70 °C is not enough to obtain a reducing power similar to the conventional one. When just increasing temperature at 90 °C, the reducing power of a mixture of \( \alpha \)-hydroxycarbonyls could attain and exceed even the reducing power of the conventional reducer without altering the uniformity of the dyed samples (for three points at the same dyed sample, \( \Delta E < 1 \)).

<table>
<thead>
<tr>
<th>Conventional reducing agent</th>
<th>Reducing ( \alpha )-hydroxycarbonyls, %</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dithionite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>66.7</td>
<td>RM1</td>
</tr>
<tr>
<td>0</td>
<td>16.7</td>
<td>RM2</td>
</tr>
<tr>
<td>0</td>
<td>33.4</td>
<td>RM3</td>
</tr>
<tr>
<td>0</td>
<td>16.7</td>
<td>RM4</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>RM5</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
<td>RM6</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>RM8</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>RM9</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>RM10</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>D</td>
</tr>
</tbody>
</table>
The effect of the reducing temperature on the dyeing quality

At a reducing temperature of about 50 °C, when comparing conventional dyeing qualities and those resulting from reducing indigo by a α-hydroxycarbonyls mixture, it is clear that the conventional one is the best. For α-hydroxycarbonyls mixture reducing indigo, when increasing the temperature to 90 °C, the best dyeing quality is achieved even in comparison with conventional dyeing. However, when observing the results obtained for a reducing temperature of about 70 °C, it could be deduced that acting under this condition is enough to achieve better results than conventional dyeing (see Figure 3). Besides, at 70 °C, the resulting fastness is similar to those obtained with conventional dyeing (see Table 2).

Modeling and optimisation of a mixture design

Based on the previous study (see Section “The effect of temperature on the reducing power of α-hydroxycarbonyls mixtures”), it is deduced that acting at a reduction temperature of 70 °C is enough to reach and exceed the dyeing quality offered by conventional reducers. So, it would be interesting to model and optimize mixed α-hydroxycarbonyls reducing agents at these conditions via a mixture design plan (see Table 3).

Mixture design plan

Mixture experiments are a special class of response surface experiments in which the product under investigation is made up of several components or ingredients. Designs for these experiments are useful because many product design and development activities in industrial situations involve formulations or mixtures. In these situations, the response is a function of the proportions of the different ingredients in the mixture [21].

Figure 1. Effect of reducing temperature on the reducing power of α-hydroxycarbonyl mixtures analyzed in a reducing medium in absence of indigo in comparison with that using sodium dithionite as conventional reducing agent (see Table 1 for description of different symbols).

Figure 2. Effect of reducing temperature on the reducing power of α-hydroxycarbonyl mixtures analyzed in a reducing medium in presence of indigo in comparison with the conventional reducing agent.
Figure 3. Effect of reducing temperature on the dyeing quality resulted from indigo continuous dyeing reduced by the different α-hydroxycarbonyl mixtures analyzed in comparison with the conventional dyeing.

Table 2. The fastness properties for the dyed samples with both the continuous dyeing resulting from a reducing process at 70 °C and a conventional dyeing process.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reducing agent, %</th>
<th>Symbol</th>
<th>Wash</th>
<th>Light</th>
<th>Rubbing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetol</td>
<td>Acetoin</td>
<td>Glucose</td>
<td>RM1</td>
<td>RM2</td>
</tr>
<tr>
<td>Continuous dyeing</td>
<td>66.7</td>
<td>16.7</td>
<td>16.7</td>
<td>15,7</td>
<td>14,82</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>16.7</td>
<td>66.7</td>
<td>19,97</td>
<td>18,59</td>
</tr>
<tr>
<td></td>
<td>33.4</td>
<td>33.4</td>
<td>33.4</td>
<td>23,24</td>
<td>22,03</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>66.7</td>
<td>16.7</td>
<td>20,59</td>
<td>19,82</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>23,24</td>
<td>22,03</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>20,59</td>
<td>19,82</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>23,24</td>
<td>22,03</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>20,59</td>
<td>19,82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RM1</td>
<td>RM2</td>
</tr>
<tr>
<td>Conventional dyeing</td>
<td>Sodium dithionite</td>
<td>D</td>
<td>4</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3. Composition of reducing agents mixture in a simplex mixture design for a reducing temperature of about 70 °C.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Reducing agents proportions, %</th>
<th>Responses</th>
<th>PR WB 70, mV</th>
<th>PR BB 70, mV</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetol</td>
<td>Acetoin</td>
<td>Glucose</td>
<td>PR WB 70, mV</td>
<td>PR BB 70, mV</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>66.7</td>
<td>16.7</td>
<td>16.7</td>
<td>-862</td>
<td>-879</td>
</tr>
<tr>
<td>2</td>
<td>16.7</td>
<td>16.7</td>
<td>66.7</td>
<td>-830</td>
<td>-851</td>
</tr>
<tr>
<td>3</td>
<td>33.4</td>
<td>33.4</td>
<td>33.4</td>
<td>-825</td>
<td>-843</td>
</tr>
<tr>
<td>4</td>
<td>16.7</td>
<td>66.7</td>
<td>16.7</td>
<td>-844</td>
<td>-863</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>-821</td>
<td>-839</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>-837</td>
<td>-858</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>-818</td>
<td>-837</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>-815</td>
<td>-828</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>-808</td>
<td>-809</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>-812</td>
<td>-815</td>
</tr>
</tbody>
</table>
Establishing models

Regression quadratic analysis was used to investigate and model the relationship between the three continuous components in the mixture design. The most appropriate mixture regression models found for redox potential measured in a medium in the absence or presence of indigo and for the colour yield (K/S) parameter are as follows:

\[
WRP\,(mV) = -817A - 823B - 810C - 84AB - 34AC + 2BC - 1783AABC + 161ABBC + 521ABC
R^2 = 67\% \quad (1)
\]

\[
BRP\,(mV) = -830A - 841B - 811C - 107AB - 83AC + 27BC - 1196AABC + 136ABBC - 404ABCC
R^2 = 74\% \quad (2)
\]

\[
K/S = -16.47A + 17.95B + 15.38C + 11.21AB + 8.59AC - 1.284BC + 12.08AABC + 8.12AABBCC + 34.401ABCC
R^2 = 78\% \quad (3)
\]

where \(WRP\,(mV)\) is the redox potential measured in a reducing medium in the absence of indigo, \(BRP\,(mV)\) is the redox potential measured in a reducing medium in the presence of indigo, \(K/S\) is the colour yield parameter, \(A\) (%) is the acetol, \(B\) (%) is the acetoin, \(C\) (%) is the glucose and \(R^2\) (%) is the square of the multiple correlation coefficient.

\(R^2\) is the proportion of the variability in the response that is fitted by the model. In fact, if a model has perfect predictability, \(R^2 = 1\) (100%), whereas if a model has no predictive capability, \(R^2 = 0\). Thus, it could be deduced that models of the colour yield \((K/S)\) and the redox potentials measured in a medium with and without indigo, \((WRP and BRP)\) are described in Figure 4.

The dyeing performances determined by the colour yield parameter \((K/S)\) are shown by four different colours in Figure 5. Each colour corresponds to a level of dyeing quality.

Response optimization

Many designed experiments involve determining optimal conditions that will produce the “best” value for the response. The response optimizer provides an optimal solution for the input variable combinations.

According to Figure 6, it could be deduced that the best dyeing quality is obtained after a reduction process comprised of 43% acetol and 57% acetoin, as a reducing mixture agent of indigo. The colour yield could attain in this case a value of 20.06 with a desirability of 99%.

Validation of the model

Results obtained when applying the optimal combination offered by the response optimization via Minitab 15 in the previous part (3.3.7) is in agreement with the theoretical result. Indeed, an experimental value of 20.02 was obtained versus a theoretical value of 20.06 for the colour yield parameter \(K/S\) (see Table 4). Thus, the model suggested in this paper is confirmed.
CONCLUSION

The results of the present study showed that synergy between α-hydroxycarbonyls leads to a better reducing power than when using each one alone. Thus, such mixture would have great importance on improving the reducing process, and the synergy attained, and even to exceed the dyeing performances offered by conventional reduction methods without altering the uniformity of the dyed samples.

Statistically, optimal mixture design is shown to be effective and reliable in finding the optimal proportion of components in the reducing medium. The best dyeing performance was attained when the mixed proportions of acetol, acetoin and glucose were 43, 57 and 0%, respectively. We then conclude that the method used in this study is reliable and efficient. The optimal ecological mixture obtained in this paper could be expected to substitute the conventional environmentally unfavorable sodium dithionite.

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REFERENCES


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SINERGISTIČKO DELOVANJE SMEŠA α-HIDROKSIKARBONILA KAO ZELENOG REDUKUJEĆEG AGENSA U PROCESU INDIGO BOJENJA