COLOURED NANOPARTICLES FOR ECOLOGICAL DYEING OF WOOL, SILK AND COTTON

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CARE FOR THE ENVIRONMENT

- The textile industry uses an enormous quantity of water, a scarce resource, which in many cases is disposed to the environment with inadequate treatment.

- Another major environmental problem for many years is the effluent from the dyeing process.
  - Colour in the effluent
  - Heavy metals
  - Dyeing auxiliaries (ethoxylated and non-biodegradable)
  - High concentration of salts

- Therefore new concepts have to be evaluated. Dyeing with coloured nanoparticles (CNPs) can be a viable alternative.
WORK OBJECTIVES

- Using Coloured Nanoparticles as a novel method of dyeing fibres.
  - Coloured Silica nanoparticles (CNPs) combine the properties of small molecule textile dyes
    - bright colours
  - with the advantages of silica
    - insolubility in water
    - affinity for natural fibres
    - physical trapping in fibres.
  - As the dye is adsorbed inside the silica matrix, silica provides an effective barrier keeping the dye from the surrounding environment, with positive consequences:
    - it might improve lightfastness,
COLOURED NANOPARTICLES PREPARATION

- CNPs were prepared using a modified sol-gel emulsion, with anionic dyes. By changing the dye, different coloured CNPs can be obtained. CNPs medium size: 200 nm.

Using appropriate synthesis conditions and by careful selection of dyes, a large number of dye molecules can be incorporated inside a single silica particle.
DYEING WITH COLOURED NANOPARTICLES (CNPs)

- **WOOL DYEING** (Exhaustion Process)
  - 10g/L of cationic levelling agent
  - 10g/L of the CNPs emulsion (0.15% o.w.f dye)
  - Liquor to fabric ratio of 10:1
  - 105°C
  - Diferente pH's

- **SILK DYEING** (Exhaustion Process)
  - 10g/L of cationic levelling agent
  - 100g/L of the CNPs emulsion (1.5% o.w.f dye)
  - Liquor to fabric ratio of 10:1
  - 90°C
  - pH 8

- **COTTON DYEING** (Exhaustion Process)
  - 10g/L of the CNPs emulsion (0.15% o.w.f dye)
  - Liquor to fabric ratio of 10:1
  - 80°C
  - pH 8
RESULTS AND DISCUSSION

- **WOOL DYEING**

Table: Comparison of wool fabrics dyed with a conventional dye and with CNPs

<table>
<thead>
<tr>
<th>Samples</th>
<th>ΔE</th>
<th>ΔL</th>
<th>Δa</th>
<th>Δb</th>
<th>Colour uniformity (σΔE)</th>
<th>K/S</th>
<th>Wash fastness</th>
<th>Wash shade change</th>
<th>Staining on wool</th>
<th>Staining on cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.089</td>
<td>3.15</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>4.69</td>
<td>4.06</td>
<td>1.10</td>
<td>2.07</td>
<td>0.074</td>
<td>2.70</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.119</td>
<td>4.57</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>19.53</td>
<td>11.64</td>
<td>9.83</td>
<td>12.23</td>
<td>0.123</td>
<td>1.75</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.028</td>
<td>3.62</td>
<td>4-5</td>
<td>5</td>
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<tr>
<td>F</td>
<td>2.29</td>
<td>1.81</td>
<td>-1.10</td>
<td>0.88</td>
<td>0.087</td>
<td>4.09</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
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</tr>
</tbody>
</table>
Conclusions for wool

- The highest colour intensity on the samples was when wool was dyed at pH 8.
  - It is possible that these particles do not fit easily into the fibre’s cell membrane complex and other low sulphur regions (the gap in between the scales of the wool cuticle), which are known to be the preferred diffusion pathway in the keratin fibres.
  - Alkaline conditions promotes higher fibre swelling, facilitating the diffusion of CNPs through the fibre.
- The results show that the colour uniformity and the fastness to washing and to staining of wool samples dyed with CNPs, were at least as good as those obtained by the reactive dye. All samples dyed with CNPs exhibit good fastness to washing and to staining.
RESULTS AND DISCUSSION

- SILK DYEING

Silk dyed with a reactive dye (G) and with CNPs (H) at pH 8

- CNPs diffusion is improved at pH 8 (previous work), there are some degradation of the silk fibres (it might be due to the size of the CNPs)

- For comparison silk was also dyed with reactive dye, under the same dyeing conditions.
Results for Silk

Table 2: Comparison of silk fabrics dyed with a conventional dye and with CNPs

<table>
<thead>
<tr>
<th>Samples</th>
<th>ΔE</th>
<th>ΔL</th>
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<th>Δb</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wash shade change</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.008</td>
<td>10.57</td>
<td>4</td>
</tr>
<tr>
<td>H</td>
<td>4.69</td>
<td>3.88</td>
<td>3.40</td>
<td>3.00</td>
<td>0.082</td>
<td>6.70</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2. All samples exhibit good uniformity and good fastness to washing and to staining.
RESULTS AND DISCUSSION

- COTTON DYEING

The dyeing process was a one stage process (all-in), at high temperature (80°C), and without adding salt. For comparison, cotton was also dyed with reactive dye, under the same dyeing conditions, but adding salt, and having a wash-off process in order to remove the unfixed, hydrolysed dye,
Results for cotton: intensity of colour

<table>
<thead>
<tr>
<th>Samples</th>
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<th>ΔL</th>
<th>Δa</th>
<th>Δb</th>
<th>Color uniformity (σΔE)</th>
<th>K/S</th>
<th>Wash fastness</th>
<th>Wash shade change</th>
<th>Staining on wool</th>
<th>Staining on cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.209</td>
<td>0.79</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>J</td>
<td>2.85</td>
<td>-1.96</td>
<td>1.66</td>
<td>-1.23</td>
<td>0.189</td>
<td>0.75</td>
<td>4-5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

- The K/S, the colour uniformity and the fastness to washing and to staining of cotton samples dyed with CNPs, were at least as good as those obtained by reactive dye.
Conclusions for cotton

- The affinity of the silica in cotton fibres is favourable at pH 8 (similar results of high affinity were obtained with other silica nanoparticles)
- For low intensity of colour (present results) the fastness is good.
- For strong colours recent results show that some NCPs are lost, leading to some colour alteration.
  - It is possible that a saturation limit is reached at 1.5% colour intensity.
ECOLOGICAL ISSUES

Figure: Separation of the aqueous phase from the solid phase (CNPs).
Ecological Issues: conclusions

- The dyeing of wool fibres with CNPs does not require ethoxylated dyeing auxiliaries to obtain a level dyeing.

- It does not require salt in the case of cotton, lowering the conductivity of the effluent.

- Using this technology, the effluent resulting from dyeing with CNPs has no free soluble dye.

- The CNPs that were not absorbed by the fibres, after an hour settle to the bottom of the “tank”, allowing the separation of the solid phase (NPCs), from the aqueous phase (water), as shown in the figure.

- After phase separation is possible to reuse the water in a new bath dyeing.

- Or another approach is to reuse the CNPs bath as it is, for further dyeing (on-going work).
FINAL CONCLUSIONS

- Wool fibres, silk fibres and cotton fibres were successfully dyed with CNPs, when using anionic dyes for obtaining the CNPs.
- Wool, silk and cotton fabrics, showed good fastness to washing and to staining, and showed good colour uniformity.
- The process is greener than traditional dyeing and allows the possibility to recover and reuse water and CNPs from previous dyeing.
THANK YOU FOR YOUR ATTENTION!