SOL-GEL TECHNOLOGY FOR ECOLOGICAL DYEING CELLULOSIC OF FIBRES

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1. INTRODUCTION

The textile industry has been considered an activity of high impact on the environment
mainly due to the effluent having high concentrations of organic compounds and visible coloration.[1] The wet processes of the textile industry (pre-treatment, dyeing and finishing) consume wide amounts of water and energy. The used chemical products are varied, from inorganic composites to polymers and organic composites. [1]
The costs of using water or treating waste in industrial processes like conventional dyeing of textiles is a serious concern for textile manufacturers and finishers.
Of all dyed textile fibres, cotton occupies the number-one position, and more than 50% of its production is dyed with reactive dyes, owing to their technical characteristics. Unfortunately, this class of dyes is also the most unfavourable one from the ecological point of view, as the effluents produced are relatively heavily coloured, contain high concentrations of salt and exhibit high BOD/COD values. Dyeing 1 kg of cotton with reactive dyes requires an average of 70–150 L water, 0.6 kg NaCl and 40 g reactive dye. The composition of the dyebath contains solid particles (cotton fibres), dyeing auxiliaries (organic compounds), hydrolyzed reactive dyes, substantial quantities of alkalis (sodium carbonate and soda ash) and very high concentration of sodium chloride or sodium sulphate. [2]
Using appropriate synthesis conditions and by careful selection of dyes, a large number of dye molecules can be incorporated inside a single silica particle. Moreover, as the dye is trapped inside the silica matrix, which provides an effective barrier, keeping the dye from the surrounding environment such as photodegradation. Since it is applied in the liquid form, allergy and potential cancer risk phenomena for the workers using the dyes can be minimized[3].Beyond simply combining the properties of the dye and silica, this combination has been shown to actually enhance the stability of the dyes, compared to the free dye solution.
In previous work coloured silica nanoparticles were applied to wool fibres with good results on the washfastness and the levelness[4]. Preliminary studies were also done on silk and cotton with light to medium colours.
The present work has led to a novel method of dyeing cotton fibres in the absence of salt using sol-gel containing silica coloured nanoparticles for darker colours. The sol-gel was prepared using a modified Stöber [5,6] synthesis method.

2. EXPERIMENTAL

2.1 Materials

The material used was a woven 100% cotton fabric.
Dyes were supplied by *Dystar*. All products were applied as received, without any previous purification.

2.2 Nanoparticles preparation and characterization

Silica nanoparticles have been obtained using a modified method of producing silica microcapsules (hollow spheres) [4,5,6]. In this work silica nanoparticles were obtained from a typical sol-gel reverse emulsion (W/O) with an aqueous dye solution. The process was an adaptation of the Stober method. The dye was fixed to the nanoparticles with a crosslinking agent. The ionic particles were characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 transmission electron microscope.

2.3 Coloured Nanoparticles Dyeing

Cotton fabric was dyed in a solution containing 100 g/L of the CNPs emulsion at liquor to fabric ratio of 10:1. The cotton CNPs dyeing experiments (1,5% o.w.f dye) were performed at 80ºC and at pH 11, and were carried out in a Linitest machine. For the control experiments, wool, silk and cotton fabrics were dyed using the same conditions described above, except that instead of using CNPs, reactive dyes at the same concentrations were used. Dyes were selected having the same chomophore groups as the dyes trapped inside the silica nanoparticles.

2.4 Dye uptake

CIELAB and colour yield (K/S) values were measured using a Datacolor SF600 instrument at λ_{max} using illuminant D65 and 10º observers. Colour uniformity was calculated based on the standard deviation ($\sigma\Delta$) around the mean ΔE value of replicate measurements over the same fabric specimen.

2.5 Wash fastness testing

The wash fastness properties of the cotton fibres were measured according to ISO 105 CO6-C1.

3. RESULTS AND DISCUSSION

3.1 Nanoparticles preparation

A stable sol-gel of coloured nanoaprticles was obtained. The dye was entrapped inside the nanoparticles by electrostatic bond between anionic (acid) dye and NPs. The crosslinker promotes the linkage between the hydroxyl groups of the nanoparticles and the amine groups of the acid dye. From fig.1 we can see that nanoparticles have a medium size of 200nm.

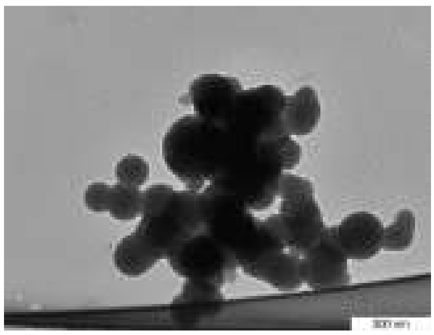

Figure 1: TEM picture of CNPs

3.2 Cotton dyeing

Having good results on dyeing wool and silk fabrics with sol-gel at pH 8, it was decided to dye cotton using the same pH. The dyeing process was a one stage process, at high temperature (80ºC), and without adding salt. A fixing agent was added for improving fastness. For comparison, Fig. 2, 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 (Table 3). 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,

Figure 2: Cotton dyed with reactive dye (I) and with CNPs (J) at pH 8

Table 3 Comparison of cotton fabrics dyed with a conventional dye and with CNPs

Samples	ΔE	ΔL	Δa	Δb	Color uniformity ($\sigma\Delta E$)	K/S	Wash fastness		
							Colour alteration	Staining on wool	Staining on cotton
I					0.209	0.79	5	5	5
J	2.85	-1.96	1.66	-1.23	0.189	0.75	4-5	5	5

In this work build-up of dye was studied and a limit of 1,5% was achieved. Darker colours are difficult to obtain due to saturation being higher with coloured nanoparticles than dyes (figure 2).

Figure 3. Fabrics dyes with sol-gel with different dye concentrations: 0.15% and 1,5%

3.3 Ecological issues

3.3.1. Dyeing with sol-gel

The method of dyeing with sol-gel has great environmental benefits compared to traditional processes. The dyeing of cotton does not require salt (in cotton) and washing off of the small amount of remaining hydrolysed dye requires much less water, since most of the dye is fixed to the fibre in the form of coloured particles.
However, the biggest advantage is to obtain an effluent with more ecological parameters, since most of the colour is in the form of silica nanoparticles and can removed by precipitation.

3.3.2. Dyeing with coloured silica nanoparticles

Sol-gel still has some loose dye left in its matrix. Even if it is a lot less dye left than when dying with reactive dyes, it still needs a washing off procedure so as

to obtain maximum fastness. By evaporating the solvent and filtering the aqueous dispersion obtained, coloured nanoparticles with no loose dye are obtained.
Using this technology, the effluent resulting from dyeing with CNPs has no free or hydrolyzed dye. From the waste water, the colour seen is due to the presence of CNPs that were not absorbed by the fibres, which 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 Fig. 5. After phase separation is possible to reuse the water and the CNPs in a new bath dyeing.

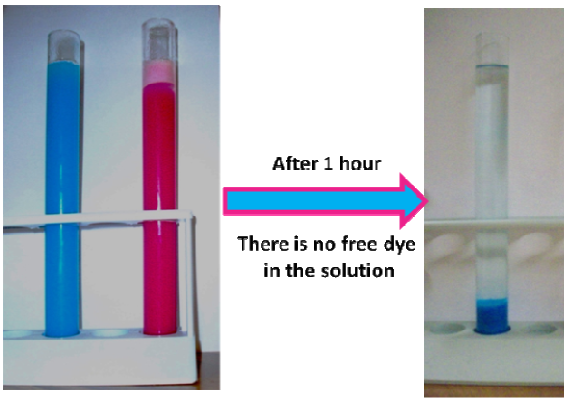

Figure 3: Separation of the aqueous phase from the solid phase (CNPs).

Since no dye is left in the effluent and it is easy to separate de Coloured nanoparticles from the dyeing bath, the Coloured nanoparticles and the water can be recovered and reused.

4. CONCLUSION

Cotton fibres were successfully dyed with sol-gel containing colored silica nanoparticles with no salt and with filtered coloured particles at medium/dark colours. Cotton fabrics showed good fastness to washing and to staining, and showed good colour uniformity. The process is greener than traditional dyeing, using no salt and less water, and with the new filtered coloured nanoparticles, there is the possibility to recover and reuse water and Coloured nanoparticles from previous dyeing.

5. REFERENCES

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