TEXTILE DYEING IN SUPERCRITICAL CARBON DIOXIDE

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Synthetic and natural textiles were dyed in supercritical carbon dioxide ($scCO_2$) with a reactive dichlorotriazine dye. Experiments were carried out on polyester, silk, wool, cotton and aminated cotton. Pressure and temperature were varied from 225 to 278 bar and from 100 to 116°C. In the experiments a small quantity of water was added as enhancer of reactivity and/or accessibility of the natural fibres. Polyester was dyed well, with fixation percentages in the order of 95% and the color yield increased with pressure but not with temperature. Silk and wool were dyed with a color yield independent of pressure and temperature. Fixation percentages on silk (76%) and wool (70%) were almost independent of pressure and temperature. Comparison of the experimental results with literature data shows that silk can only be dyed in $scCO_2$ when a small amount of water is dissolved in the $scCO_2$ and in the silk. Cotton was dyed poorly under all conditions. Aminated cotton was dyed better than cotton but not as good as silk and wool. Fixation on aminated cotton was 87%. It was concluded that dichlorotriazine dye can react in moist $scCO_2$ with amino groups of protein textile (e.g. silk and wool) but not with hydroxyl groups of cellulosic textiles (e.g. cotton).

1. INTRODUCTION

In conventional textile dyeing large quantities of wastewater are produced. This environmental and economical burden is avoided when supercritical carbon dioxide is used as dyeing medium instead of water. Separating residual dye from the CO_2 and recycling of CO_2 are easy. Energy is saved because textiles do not need to be dried after the dyeing process. An additional advantage of $scCO_2$ is the high diffusivity and low viscosity that allow the dye to diffuse faster towards and into the textile fibres. This results in a faster dyeing process.

Textiles can be classified into non polar, synthetic polymers (e.g. polyester) and polar, natural textiles. The second category can be divided into polymers built from amino acids (e.g. silk and wool) or cellulose (e.g. cotton).

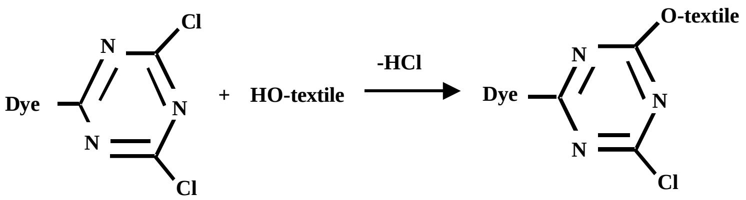
In polyester dyeing, $scCO_2$ penetrates and swells the fibres, thereby making them accessible for dye molecules. Upon depressurization, the dye molecules are trapped inside the shrinking polyester fibres. Polyester dyeing in $scCO_2$ has been studied by several researchers [1,2,3].

In natural textiles, the dye molecules can be fixed by either physical (e.g. Van der Waals) or chemical (e.g. covalent) bonds. Since the dyes used in a $scCO_2$-dyeing process are non-polar and natural fibres are polar the affinity between dyes and textiles is low so physical bonds are weak. Therefore, a dyeing process must be developed for dyeing natural textiles in $scCO_2$ with reactive dyes that create covalent dye-textile bonds.

So far, several reactive dyes known from conventional dyeing in water have been investigated in $scCO_2$:

- vinylsulphone dyes have been successfully used for silk and wool [5],
- 2-bromoacrylamide dyes have been successful in dyeing wool and cotton [6],
- dichlorotriazine dyes have been tested on silk and cotton but showed insufficient fixation [6].

In this work a dichlorotriazine dye was used that can react with a textile amino group of proteins (e.g. silk and wool) or a hydroxyl group of cellulose (e.g. cotton) via nucleophilic substitution as shown in reaction 1 for hydroxyl containing textile:



(1)

In the experiments discussed below, a small amount of water was added to the $scCO_2$. This was done because it has been shown [5] for vinylsulphone dyes that water facilitates the dyeing reaction and/or enhances the accessibility of the fibres by acting as a swelling agent. The water concentration in this work was so low that all the water was dissolved in the $scCO_2$ and the textile. No liquid water was present in the dyeing vessel.

Four factors play a role in reactive dyeing of natural fibres in $scCO_2$:

1. Solubility of the dye in the $scCO_2$ at the process pressure and temperature.
2. Accessibility of the porous fibre structure to allow diffusion of dye molecules into the pores.
3. Affinity or substantivity between the textile and the dye so that dye molecules can approach the textile surface close enough for the reaction to take place.
4. Reactivity of dye with the textile. The dye has to form a covalent bond with amino groups of proteins or with hydroxyl groups of cellulose.

Since pressure has an influence on dye solubility and temperature has an influence on at least solubility and reactivity, both parameters were investigated.

The aim of this work is firstly to test the applicability of a dichlorotriazine dye for polyester, silk, wool, cotton and aminated cotton in moist $scCO_2$ and secondly to determine the influence of pressure and temperature on the dyeing process.

2. EXPERIMENTS

2.1 Materials

The used (purple) dichlorotriazine dye was designed and synthesized for textile dyeing in $scCO_2$. The textiles were dyed as pieces of woven cloth, with no pretreatment except in the case of cotton that was received mercerized (treated with sodium hydroxide to increase the accessibility [7]). The aminated cotton was received containing 4% indosol E-F, this is an aliphatic polyamine. The carbon dioxide was purchased from Hoek Loos and was 99.97% pure.

2.2 Equipment and procedure

A 4 liter autoclave was used, preheated by oil flowing through a heating jacket. Dye powder (0.2 g) was placed at the bottom of the autoclave in a filter to prevent entrainment of undissolved dye particles. A piece of cotton (20 g) was wetted with water (20g) and folded around pieces (0.2 g) of silk, wool, aminated cotton and polyester and placed in the autoclave. The apparatus (figure 1) was pressurized to 200 bar and $scCO_2$ was circulated through the dye filter and the textile at a rate of 0.10 (±0.02) m^3/h during 2 hours. In the first hour, temperature and pressure increased due to heating of the $scCO_2$. During the second hour, pressure and temperature were constant. Experiments were done at different pressures and temperatures.

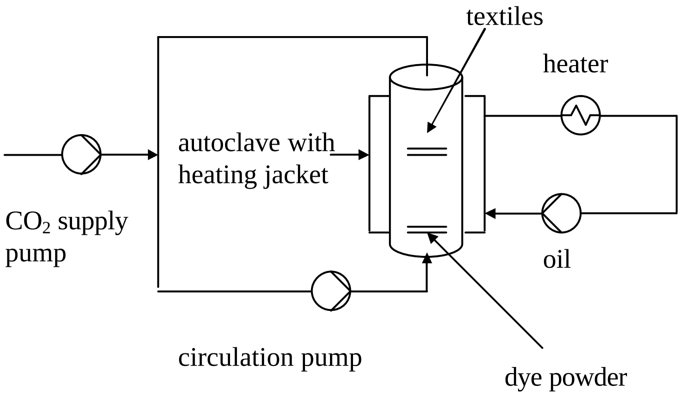


Figure 1. Equipment for dyeing textiles in supercritical carbon dioxide.

2.3 Colour analysis

Dyed textile samples were analysed by measuring the reflectance curve between 350 and 750 nm with a spectrophotometer. The minimum of the curve (R_{min}) was used to determine the ratio of light absorption (K) and scatter (S) via the Kubelka-Munk function [8]:

$$\left(\frac{K}{S}\right)_{dyed} = \frac{(1 - R_{\min})^2}{2R_{\min}}$$

(2)

Since the ratio *K*/*S* is proportional to the concentration of dye molecules in textile, it is a measure for the coloration of the textile.

After this analysis, each sample was stripped of unfixed dye by Soxhlet extraction with a 50 weight% solution of acetone in water for 30 min. The *K/S*-value of the extracted textile $(K/S)_{extr}$ was determined and used to calculate the percentage of dye molecules that was fixed to the textile (*F*):

$$F = \left(\frac{K}{S}\right)_{extr} \Big/ \left(\frac{K}{S}\right)_{dyed} * 100\ \%$$
(3)

3. RESULTS

The fixation percentages were calculated with equation (3) and it was found that the fixation on polyester was independent of pressure (ranging from 225 to 278 bar) and temperature (ranging from 100 to 116°C). The fixations on silk, wool and aminated cotton decreased slightly with pressure and with temperature. Because only small differences in fixation were measured, only the fixation percentages found in the experiment at 250 bar and 100°C are given in table 1. The *K/S*-values for cotton before and after Soxhlet extraction were low and the samples were stained so that the fixation percentage was unreliable and left out of table 1.

Table 1. Typical fixations of textiles dyed in moist scCO_2 at 250 bar and 100°C.

textile	F(%)
Polyester	95
Silk	76
Wool	70
Aminated cotton	87

In figure 2 the $(K/S)_{extr}$ -values that were measured after extraction are given for all textiles at different dyeing pressures (225 to 278 bar). In all cases, the dyeing time was two hours, the temperature was 100°C and the amounts of textile and water were the same. The coloration of polyester is good and increases with pressure. Although less than polyester, silk, wool and aminated cotton were dyed well and the coloration was found to be independent of pressure. The coloration of cotton was negligible.

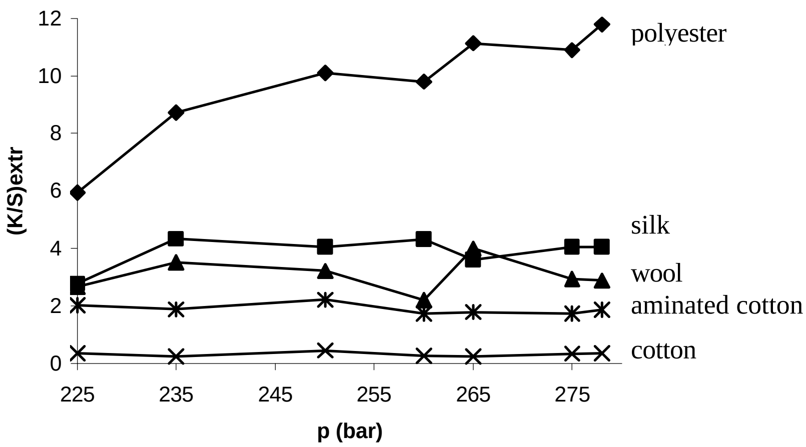


Figure 2: Coloration of textiles dyed in moist $scCO_2$ (100 °C, 2 hours) as a function of pressure.

The effect of temperature was investigated between 100 and 116°C. In all cases, the dyeing time was two hours, the pressure was 250 bar and the amounts of textile and water were the same. As can be seen from figure 3, the temperature had negligible influence on coloration.

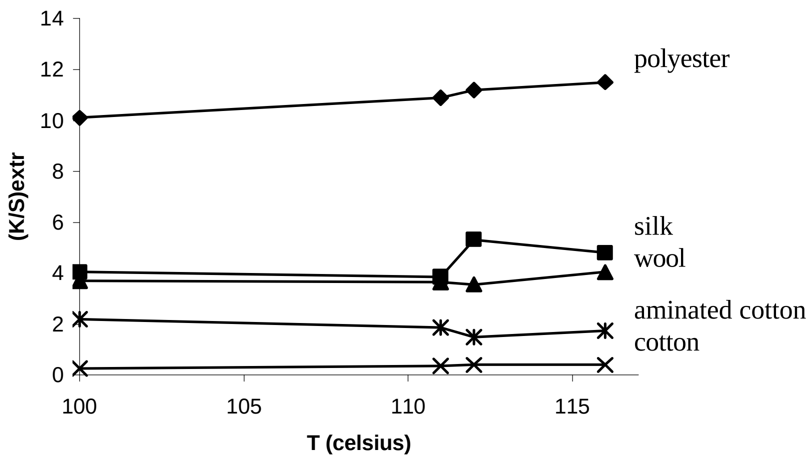


Figure 3: Coloration of textiles dyed in moist $scCO_2$ (250 bar, 2 hours) as a function of temperature.

4. DISCUSSION AND CONCLUSION.

Dichlorotriazine dye was used to dye textiles in $scCO_2$. Polyester yielded a good colouration and this is in accordance with literature [1,2,3]. This shows that there is enough dye dissolved in the $scCO_2$. The coloration of polyester increases with pressure because the solubility of the dye in the $scCO_2$ increases with pressure and because at higher pressure more CO_2 dissolves in the polymer matrix, i.e. the polyester is more swollen and therefore more accessible at higher pressure. Polyester coloration was independent of temperature.

As was discussed above, the four factors determining the supercritical dyeing process of natural fibres are dye solubility, fibre accessibility, dye-fibre substantivity and reactivity. The polyester results show that enough dye was dissolved in the $scCO_2$. Therefore, the lower coloration of the natural fibres (compared to polyester) can not be explained by limiting solubility. This is confirmed by the negligible influence of pressure on the coloration of natural fibres. The fact that temperature has no influence on the coloration of silk, wool and aminated cotton shows that also reactivity can be ruled out as a limiting factor. It can be concluded that either accessibility or substantivity limit the supercritical dyeing of silk, wool and aminated cotton under the dyeing conditions used in this work.

The coloration of silk and wool and their respective fixations of 76 and 70% are evidence that dichlorotriazine dyes can react with amino groups in moist $scCO_2$. Because Schmidt e.a. [6] found no fixation on silk dyed in dry $scCO_2$ with a dichlorotriazine dye it can be concluded that water is needed to dye silk in $scCO_2$.

Cotton was dyed poorly but aminated cotton was dyed better. This is caused by the lower polarity of aminated cotton or by the presence of amino groups that are able to react with dichlorotriazine.

It was shown that polyester, silk, wool and to a lesser extent aminated cotton can be dyed in $scCO_2$ with a reactive dichlorotriazine dye. The influence of pressure and temperature on coloration was negligible, except for polyester that showed increasing coloration with pressure. To create a covalent dye-silk bond, water is needed. Cotton was dyed poorly under all conditions.

5. REFERENCES

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