Polyester Dyeing and its Environmental Impact

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Abstract. Dyeing and printing of textiles are responsible for 30% of the pollutants contained in the effluents. The impact of textile dyeing processes on environment is highly variable, most important issues being the colour, the organic charge, and the solids in suspension. The present study investigates the characteristics of the polyester dyeing process in what concerns the environmental issues. Disperse dyes are non ionic, have very limited solubility in water at room temperature and have substantivity for polyester fibre. Two disperse dyes were used, and dyeing were performed at different concentrations. The exhaustion degree, the volume of wastewater used in the process, the specific flow, pH, temperature and chemical oxygen demand of the wastewater, the total residuum, volatile substances and the biological oxygen demand were determined in all the cases. The data obtained showed that the global pollutant content of the wastewater from disperse dyes dyeing is high (more than two times higher than those obtained in the case of dyeing with acid dyes). Absorption spectra of the initial and exhausted dyebath were determined, in order to evaluate the dilution degree needed to make wastewater colour acceptable.

1. Introduction

Most of the pollutants contained in the effluents from textile chemical processing are caused by preparation processes (about 70%). For the remaining 30% dyeing and printing are responsible [1-10]. Complete dye exhaustion in the dye bath is not possible for most dyeing systems. This is because there is a balance in dyeing and washing, which always leaves some of the dye in the wastewater. In commercial processes, there can be from almost none to more than 50% of the total dye left in the residual dyeing bath. In the textile sector, about 10-20% of the used dyes are lost in the wastewater through incomplete exhausting and washing process [11-18]. In addition to dyes, wastewater from textile dyeing contains significant amounts of auxiliaries, such as salt, acids, equalizing agents, etc., and this is why the textile dyeing is considered as one of the most environmentally unfriendly industrial processes [19-25].

The impact of dyes on environment is highly variable, but the colour they generate is of great interest. Even though colour is one of the key attraction of any textile material, the dyes may cause threats to environment and living beings [26-28]. While coloured organic substances generally impart only a small degree of the total organic load in a wastewater, the high degree of colour is easily detected (human eye can detect some dyes at concentrations as low as 0.005 mg/L) and detracts from the aesthetic value of streams, rivers, etc. These small quantities of dyes that are visible in water give rise to worries. Most dyestuffs have a mammalian toxicity low enough so they do not cause problems, but, as long as the public is concerned, the presence of coloured wastewater is often more important.
than the presence of the soluble colourless organic substances which usually contribute to the major fraction of the biochemical oxygen demand.

Polyester fibre is currently the most used fibre in the textile industry, due to its physical properties, price, recyclability and versatility, advantages unmatched by any other fibre. Also polyester can be successfully blended with cotton with various proportions. Since 1990, the consumption of polyester fibres has increased at a sustained rate of almost 7% per year globally.

Figure 1. Evolution of fibre demand [29].

Because the polyester fibres are characterized by a very compact structure, with a high crystallinity and without defined dyeing areas, only disperse dyes, applied from a stable aqueous dispersion, are used for their dyeing. Besides polyester, disperse dyes are the main water-insoluble dyes for cellulose acetate fibres [4-5].

Disperse dyes are non ionic, have very limited solubility in water at room temperature and have substantivity for polyester fibre [30-37]. As disperse dyes have very limited solubility in water, some particulate disperse dye may still be on fibre surface after the dyeing phase has completed, and these dyes particles have to be removed from the surface as it will considerably reduce the wet fastness, wash fastness, sublimation and dry cleaning fastness, as well as making the shade become dull. The usual procedure for removing this unwanted dye is called reduction clearing, and it generates supplemental pollution to the wastewater [38-41].

2. Experimental

The paper investigates the characteristics of the polyester dyeing process in what concerns the environmental issues.

We have used commercial samples of two disperse dyes: Disperse Blue 19 and Disperse Black 9. The dyeings were made on 100% polyester fabric under HT conditions. Different concentration dyeings were produced in sealed dye pots of 300 cm³ capacity, housed in a laboratory-scale dyeing machine, using a 20:1 L:R, at a maximal temperature of 130°C. The dyeing recipes are showed in Table 1.

When dyeing polyester with disperse dyes the levelness of the dyeing is determined by the dispersion stability, rate of dyeing and migration. An increase in migration demands longer dyeing times. The rate of dyeing and therefore the heating rate must be controlled in such a way that the dyeing is level from the beginning by means of controlled adsorption.
Table 1. Dyeing recipes.

| No. | Dyestuff       | Dye conc. % | Dispersant, g/l | pH* | Liquor: ratio | T°C | Time |
|-----|----------------|-------------|-----------------|-----|---------------|-----|------|
| 1   | Disperse Blue19| 1           | 2               | 4,5 | 1:20          | 130 | 1h   |
| 2   |                | 2           |                 |     |               |     |      |
| 3   |                | 3           |                 |     |               |     |      |
| 4   | Disperse Black 9| 8           | 2               | 4,5 | 1:20          | 130 | 1h   |
| 5   |                | 12          |                 |     |               |     |      |
| 6   |                | 16          |                 |     |               |     |      |

* with CH₃COOH

The HT dyeing process comprise the next phases:
• dyebath set at 50°C
• dyebath auxiliaries adding and running for 10 min
• dye adding and running for 10 min
• heating to 130°C at 1.5°C/min
• fixing for 60 min at the dyeing temperature
• rinsing and aftertreating.

The method used is shown in the figure below (Figure 2).

Figure 2. Polyester dyeing process.

After 40°C rinsing follows a reducing washing conforming to the recipe:
• soda ash: 6 ml/l, 36°Be
• sodium dithionite: 3g/L
• surfactant: 1g/L
• Liquor ratio = 1:20
• t° = 80°C
• time: 30'

The reductive washing process is schematised in the next diagram:

Figure 3. Reductive washing parameters.
The exhaustion degree, the volume of wastewater used in the process, the specific flow, pH, temperature and chemical oxygen demand of the wastewater, the total residuum, volatile substances and the biological oxygen demand were determined in all the cases.

We have determined the exhaustion degree for the analysed dyes by determining the absorbance of the dyestuff solutions with a spectrophotometer before and after the dyeing process. The cuvettes for the spectrophotometer were clear plastic and held one millilitre of sample. The spectrophotometer compared each sample to blank containing de-ionised water. The wavelength was selected so as to obtain maximum absorbance. The absorbance was converted into concentration using a calibration line.

The exhaustion degree was calculated using the relation:

\[
\text{Exhaustion degree} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100
\]

Where: \(C_{\text{initial}}\) represents the concentration of the initial dye solution; \(C_{\text{final}}\) represents the concentration of the dye in the exhausted bath.

The exhaustion degree for each dye and dyeing concentration is indicated in Table 2.

| Dye          | Variant | Dye concentration (%) | Exhaustion degree, (%) |
|--------------|---------|-----------------------|------------------------|
| Disperse Blue 19 | 1       | 1                     | 93.7                   |
|              | 2       | 2                     | 90.7                   |
|              | 3       | 3                     | 91.6                   |
| Disperse Black 9 | 4       | 8                     | 89.5                   |
|              | 5       | 12                    | 87.5                   |
|              | 6       | 16                    | 87.3                   |

The process of industrial dyeing of polyester with disperse dyes is a pretty long process (over 8 hours), takes place in enclosed system, at 130°C and uses in the final stage inorganic reductive products. During the dyeing and the washing stages there have been determined bath losses that reached about 10-12% in the dyeing process and about 5% in the reductive washing. Although the reductive wash uses sodium dithionite, it is improbable that sulphur compound are relieved in the atmosphere, especially because of the strong alkaline medium of the washing process.

Figure 4. Global water consume.
The wastewater is formed by the water that is used in the four stages of the process: the dyeing, first washing, reductive washing and final washing. Because of the significant duration between the dyeing process and the last washing (over 5 hours), we have studied the four categories of wastewater separately. The global water consume exceeds 110 L/kg, as it can be seen in Figure 4.

We have determined some of the most environmental relevant parameters of the wastewater. The Chemical Oxygen Demand (COD) value was determined according to the Romanian standard method: a sample of the wastewater (treated and untreated) is refluxed in strongly acidic solution with a known excess of potassium dichromate in the presence of silver sulphate. The organic matter that exists in the sample is oxidized by the potassium dichromate. The dichromate that exceeds the stoichiometric value was titrated with ferrous ammonium sulphate, using ferroin as an indicator. At equivalence point the colour of the solution changes from green blue to reddish blue. The amount of K₂Cr₂O₇ consumed is converted in the oxidizable matter that is calculated in terms of equivalent oxygen [42].

The 5 Days Biochemical Oxygen Demand (BOD₅) value was determined according to the Romanian standard method as well: filling with sample, to overflowing, an airtight bottle (300-mL bottles having a ground-glass stopper and a flared mouth) and incubating it at 20°C ± 1°C for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement [43].

To determine the Total Suspended Solids content, samples of 200 mL have been vacuum filtered using Glass microfiber filters. Finally the filters were dried one hour at 103-105°C, cooled in a desiccator and weighed [44]. The same sample was used to determine the Volatile organic compounds (VOCs) content. The filter have been introduced in a furnace and kept at 550°C ± 50°C for 30 minutes. In the end the samples were air cooled, desiccated and weighed [45].

The reducer content in the wastewater has been analysed by means of an iodometric method.

The environmental relevant characteristics of the wastewater produced in the dyeing process with the two studied disperse dyes are shown in Tables 3 and 4.

The physical and chemical characteristics of the wastewater from the dyeing and washing process lead to the following conclusions:

- wastewater is intensely coloured and has a high suspension content (especially for Disperse Black 9).
- even if the dyeing concentration differs significantly, most of the parameters of the wastewater are comparable, probably because of the higher exhaustion degree of the black dye.

### Table 3. Environmental characteristics of the Disperse Blue 19 dyeings.

|        | Variant 1 |        | Variant 2 |        | Variant 3 |        |
|--------|-----------|--------|-----------|--------|-----------|--------|
| D      | RW        | FW     | D         | RW     | FW        | D      | RW     | FW     |
| 1      | 18        | 18.5   | 112.5     | 18     | 112.5     | 18     | 112.5  |
| 2      | 18.5      | 10.8   | 4.8       | 13.8   | 10.9      | 4.7    | 13.7   | 11     |
| 3      | 60        | 50     | 35-40     | 60     | 35-40     | 60     | 35-40  |
| 4      | 2560      | 1420*  | 400*      | 1430*  | 400*      | 2680   | 1430*  | 400*   |
| 5      | 2.9       | 7.2    | 3.1       | 7.6    | 0.3       | 3.1    | 7.6    | 0.3    |
| 6      | 55        | 4.7    | 26        | 61     | 7.4       | 30     | 62     | 6.9    |
| 7      | 358       | 32.7   | 41        | 353    | 31.9      | 32.0   | 351    | 29.7   |
| 8      | 1013      | 41.7   | 4.24      | 100.7  | 4.45      | 100.9  | 43.8   | 4.44   |

* values distorted due to reductive substances presence.

Where 1: Specific flow ratio (l/kg material) 2: pH; 3: t°C; 4: COD - Cr, mg/l; 5: Total residuum, mg/l; 6: VOC in the total residuum, %; 7: COD₂, mg/l; 8: Total reductive matter mval/l

The wastewater produced in the reductive wash process, with a strong alkaline reaction, shows a high degree or organical content. The values of COD were distorted by the presence of the ions S²⁻,
(S_2O_3)_2^-, (S_2O_4)_2^-, SO_3^2- as follows: (S_2O_3)_2^2-, 32 mg O_2/mval; (S_2O_4)_2^2-, 8 mg O_2/mval; (S_2O_3)_2^-, 40 mg O_2/mval; S^2- : 32 mg O_2 /mval.

Correlating these values with the COD values that we have determined, we can conclude that the reductive system is complex, containing a mixture of the indicated ions.

Table 4. Environmental characteristics of the Disperse Black 9 dyeings.

| Variant 1 | Variant 2 | Variant 3 |
|-----------|-----------|-----------|
| D RW FW   | D RW FW   | D RW FW   |
| 1 117 18  | 110 117 18 | 110 117 18 |
| 2 7.9 14.0 | 10.2 7.8 13.9 | 10.4 7.9 14.1 |
| 3 60 50 35-40 | 60 50 35-40 | 60 50 35-40 |
| 4 1621 864^1 | 185^1 3920 1270^1 | 240^1 4685 1400 264 |
| 5 2.6 6.8 1.2 3.2 7.4 1.9 5.3 9.6 3.1 |
| 6 65 75 9.9 77 51 11 81 65 12.3 |
| 7 842 90.4 82.8 1800 99.8 100.1 1985 102.7 100.9 |
| 8 102.2 51.3 3.11 189.2 53.9 3.96 199.2 56.7 4.51 |

Where: 1 – 8 have the same signification. In what concerns the biodegradability of the two dyes, important differences have been found. The BOD5/COD indicates a much better biodegradability in the case of the black dye, the blue dye having only modest biological degradation capabilities.

The values of the spectral absorbance quotient for the initial dyebath and the exhausted one are shown in Figures 5 and 6.

**Figure 5.** Spectral absorbance quotient for Disperse Blue 19.

**Figure 6.** Spectral absorbance quotient for Disperse Black 9.
It can be seen that important reduction of the spectral absorbance quotient is obtained in both cases, even if the blue dye proves to exhaust better.

3. Conclusions

The results that we have obtained indicate that the dyeing of polyester with disperse dyes in the HT process produces wastewater with high pollutant content, and large quantities of water are required. The alkaline reaction and the high content of sulphur salts of the reducing dyeing wastewater are other important environmental significant characteristics.

The washing process implies the use of reductive substances and consumes more than three quarters of the total water needed in the process, which means that the potential for environmental improvements in the rinsing procedures is in this way considerable.

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