REDUCING POLLUTION IN REACTIVE COTTON DYEING THROUGH WASTEWATER RECYCLING

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The study tries to elucidate the feasibility of Fenton-like oxidation treatment as a water recycling process in cotton fabrics preparation. Two commercial dyes, Reactive Blue 19 and Reactive Red 243, have been analysed. First, the wastewater produced during dyeing (individual dyes and dye mixture) at different dye concentrations and the wash-off wastewater have been decolorized. The effectiveness of the treatment was indicated by the colour removal degree, both reactive dyes showing good discoloration during the oxidative process. Further on, the treated wastewater was reused, either as such or mixed with fresh water (1:1), in preparation processes, namely cotton scouring and bleaching. Scouring with discoloured wastewater led to high hydrophilicity, for both individual dyes and dye mixtures. It was found out that dyeing and wash-off wastewater can be recycled only at low dye concentration, after discolouration and mixing with fresh water, in a new bleaching process, without affecting the final quality of the fabric. It was concluded that the studied Fenton-like process could be effective in recycling wastewater in cotton fabrics preparation.

Keywords: discoloration, Fenton-like system, reactive dyeing and washing wastewater, water recycling

INTRODUCTION

Water is one of the most valuable resources of this planet. Although it looks like available in sufficient amounts, as it covers over two thirds of the Earth's surface, the water suitable for drinking, agricultural and industrial purposes becomes more and more scarce and hence, more expensive.[1]

In the textile industry, water is intensely used in almost every step of various processes, both to transport the needed chemicals and to wash them out at the end of the process, thus acquiring various and numerous chemical additives that pollute the environment. At present, because of the growing resource limitations and severe environmental requirements, the textile industry has to assume a sustainable approach, and all wastes (wastewater included) must be perceived as unutilised resources.

A solution to make textile technologies more sustainable is wastewater recycling, as it brings about significant environmental benefits, reducing pollutants discharge and water consumption and diminishing the costs of depuration processes.[2]

Cotton, the world's most commonly used fibre, requires numerous operations for its processing, such as pre-treatment, dyeing and/or printing and finishing, each of them involving high water consumption and significant chemical pollution.[3] Thus, cotton finishing wastewater contains surfactants, sizing agents, solids, dyes, oil, halogenated organics from bleaching and finishing additives. The colour of the textile dyes makes them extremely visible if present in wastewater, even in small concentration. Besides the aesthetic deterioration, colour is responsible for obstructing the penetration of atmospheric oxygen and sunlight into natural watercourses.[4] Consequently, the industry is required to minimize environmental release of colour, even in cases in which a small but visible release might be considered as quite inoffensive toxicologically.

A preliminary treatment is usually sufficient to reduce BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), TSS (Total Dissolved Solids), and pH to an acceptable level, yet without removing the colour of wastewater.

Many physical and chemical methods can be used to remove wastewater colour, such as advanced oxidation processes that use hydrogen peroxide (like Fenton's regents – H_2O_2 and Fe^{2+}), ozonation, coagulation-flocculation using lime, alum, polyelectrolyte and ferrous salts, adsorption, etc.

Advanced oxidation processes (AOPs) appears as highly effective in treating many hazardous organic pollutants present in water, dyes included.[5] One of the most efficient and advanced oxidation methods is Fenton oxidation, based on a catalytic process that produces hydroxyl radicals from hydrogen peroxide after an electron transfer between H_2O_2 and metal ions.[6] The method has proved to be both inexpensive, as no energy input is necessary to activate hydrogen peroxide and easy-to-handle reagents are used, and efficient, because the generated hydroxyl radicals are very strong oxidizing agents that can react with many organic compounds. Lately, the heterogeneous Fenton catalyst obtained by impregnating metal oxide in resins or clays has proved to be highly active, assuring low metal leaching.[7,8]

The mechanism of reaction in a Cu(II) and H_2O_2 Fenton-like system, like the one used in the present research, is not completely elucidated. There are indications of a radical-chain mechanism that generates hydroxyl radicals HO•:[9]

$$Cu(II) + H_2O_2 \rightarrow Cu(I) + HO_2^{\bullet} + H^+ \quad (1)$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + HO^{\bullet} + OH^- \quad (2)$$

Other possible reactions are:[10]

$$2Cu(II) + H_2O_2 \rightarrow 2Cu(I) + HO_2^{\bullet} + H^+ \quad (3)$$

$$HO_2^{\bullet} \rightarrow O_2^{\bullet} + H^+ \quad (4)$$

$$2O_2^{-\bullet} + 2H^+ \rightarrow H_2O_2 + O_2 \quad (5)$$

$$Cu(II) + O_2^{-\bullet} \rightarrow Cu(I) + O_2 \quad (6)$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + {}^{\bullet}OH + OH^- \quad (7)$$

The aim of this work was to evaluate the efficiency of cotton reactive dyeing wastewater recycling in new preparation stages (scouring and bleaching) after oxidative discoloration, using a Fenton-like system composed of a 30% solution of hydrogen peroxide and a resin functionalized with amines and saturated with a Cu(II) catalyst.

EXPERIMENTAL

Materials

200 grams per square meter of 100% cotton fabric were used for all experiments: in raw form for scouring, scoured for bleaching and in scoured and bleached form for dyeing, respectively. Two reactive dyes from the same commercial range (Bezactiv) were tested: Reactive Blue 19 and Reactive Red 243. The chemical structures of the dyes are shown in Figures 1-2. The dyes, supplied by Bezema, were used without previous purification.

All chemicals were of analytical grade and were used without any further purification. Distilled water was used to prepare all dye solutions.

Wastewater discoloration

The wastewater was obtained from dyeing 100% previously scoured and bleached cotton fabric with the two previously mentioned dyes (indvidual and mixed). For each dye and for the dye mixture, two common dyeing concentrations were used: 1 and 3% o.w.f. – percent on weight of fabric, respectively. The dyeing process flow diagram is shown in Figure 3.

The amounts of alkaline agents and electrolyte as to dye concentration are listed[11] in Table 1.

The unfixed hydrolysed dye left over in the fabric was removed by a 4 stage washing process: 3 stages at boiling temperature for 15 min and a final one at room temperature for 10 min. The dyeing wastewater and washing-off wastewater were collected separately and treated to remove colour.

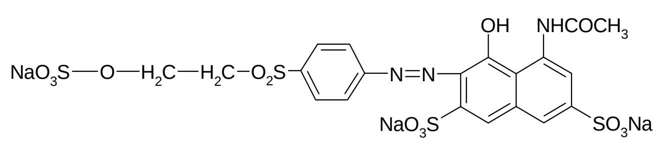

Figure 1: Chemical structure of Reactive Blue 19

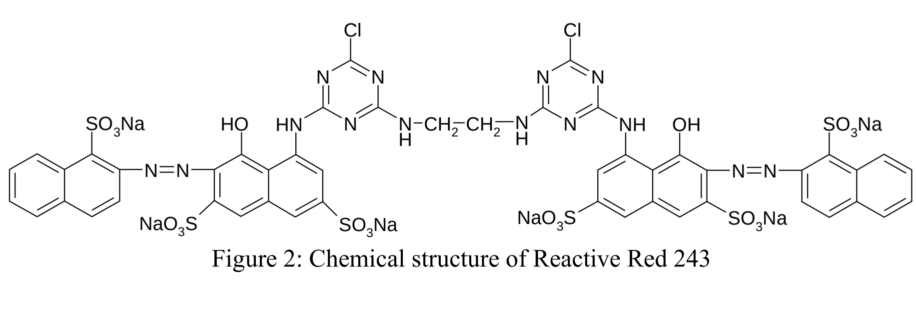

Figure 2: Chemical structure of Reactive Red 243

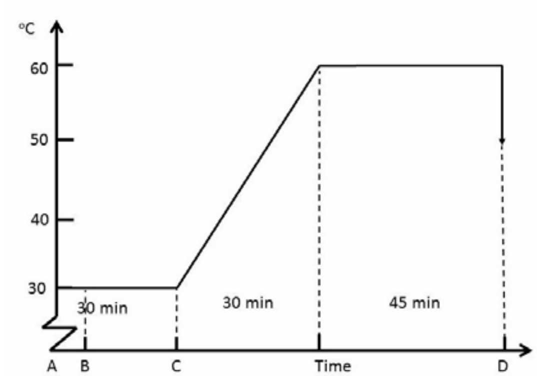

Figure 3: Reactive cotton dyeing process flow diagram: A – adding of dyestuff; B – adding of electrolyte (sodium chloride); C – adding of alkalis; D – discharge of residual dyeing bath

Table 1
Composition of reactive dyeing bath

Dye, %	Electrolyte, g/L	Sodium carbonate, g/L	Sodium hydroxide, 38° Be ml/L
1%	40	5	2
3%	60	5	3

Table 2
Codification of recycling experiments

Variant	Dye concentration, % o.w.f.	Wastewater type	Recycling method*
2	1	dyeing	a
3			b
4		wash-off	a
5			b
6	3	dyeing	a
7			b
8		wash-off	a
9			b

*a – as such; b – mixed with fresh water (1:1 w/w)

To remove the colour, a hydrogen peroxide solution (Merck, 30% w/w) was used. To activate hydrogen peroxide decomposition, resins functionalized with amines and saturated with Cu(II) catalyst was used. In a previous work,[12] the colour removing efficiency of this Fenton-like system has been analysed and discoloration experiments were carried out according to the methodology providing optimal results: 2.5 mL hydrogen peroxide (30%), activated with 0.2 g catalyst, have been added to 250 mL of wastewater samples (adjusted with H_2SO_4 to pH 4) and the treatment continued for 60 min.

The colour removal degree, expressed percentually, was calculated from the relative decrease of absorbance, determined as the ratio of the difference between the absorbance of the initial and final solution to the absorbance of the untreated solution. Colour intensity was measured on a UV/VIS Camspec M501 spectrophotometer. The maximum absorbance wavelength was used for all absorbance readings (593 nm for Reactive Blue 19 and 517 nm for Reactive Red 243).

Discoloured wastewater recycling

The discoloured wastewater was used in the new cotton fabric preparation stages (scouring and bleaching), as such or mixed with fresh water. Codification of the experiments is detailed in Table 2.

The scouring process was based on the following recipe: 3% NaOH o.w.f., 0.3% surfactant o.w.f., 0.2% sequestrant o.w.f., for 1 h at 98 °C, followed by thorough rinsing.[13] Finally, the samples were dried in ambient conditions.

After scouring, wettability was investigated. To evaluate cotton fabric wettability after treated wastewater scouring, the Sinking Time Test was applied. This method consists in measuring the time required for 4 cm x 4 cm fabric samples to totally sink in distilled water, at room temperature. Every sinking time was the average of 10 measurements.[14]

In the bleaching process, the scoured samples were treated[15] using the following recipe: 1 g/L NaOH 38° Be, 3 cm^3/L H_2O_2 30% and 4.5 cm^3/L Na_2SiO_3 (d = 1.44), liquor ratio 20:1, 30 min at 85-90 °C. After 30 min, the samples were removed, thoroughly rinsed in hot and cold water and finally dried.

The whiteness degree of the cotton samples bleached with recycled water was measured according to the AATCC method 110-2005 (ISO 105-J02).[16] The colour parameters and the whiteness degree (W CIE) were measured using a DATACOLOR Spectroflash SF-300 spectrophotometer in D65 – daylight standard illumination conditions, large area of view, specular included, CIE 1964 Supplemental Standard Observer (10°). To obtain opacity, each sample was folded twice. DataColor software Micromatch was used to calculate directly the whiteness degree and the colour parameters differences to the standard. Every measurement was based on an average of 5 readings. The colour parameters of the CIELAB colour space that have been determined are: L*, which represents the lightness of the colour and is the vertical coordinate of a three-dimensional system of colours, taking values from 0 (black) to 100 (white), a* – the horizontal coordinate, ranging from green to red, and b* – the horizontal coordinate, ranging from blue to yellow.[17]

RESULTS AND DISCUSSION

The colour removal degree of the dyeing and wash-off wastewater is listed in Table 3.

It can be seen that the discolouration process efficiency is high, especially for Reactive Blue 19. 1% Reactive Red 119 dyeing wastewater shows significant colour removal, as well. The dye mixture leads to colour removal degree values close to those obtained for Reactive Blue 19.

The analysis of the raw cotton samples scoured with discoloured wastewater shows that hydrophilicity is high for all analysed variants, both for individual dyes and dye mixtures (Table 4). If the raw material shows a sinking time exceeding 30 min, all samples scoured with treated wastewater recorded a sinking time of 1 to 2 s. It has been concluded that the presence of the electrolyte in the recycled wastewater had no influence on scouring process efficiency.

The whiteness degree of the discoloured wastewater bleached fabrics, as a function of the recycling variant, are shown in Figure 4 for Reactive Blue 19, in Figure 5 for Reactive Red 243 and in Figure 6 for the dye mixture, respectively. The observation has been made that, in the control sample, the whiteness degree is high (75.4%), none of the various wastewater recycled bleaching variants showing equal results. However, it can be seen that variants 3 and especially 5 produce very similar whiteness degrees, in all studied cases.

Table 3
Colour removal degree for various types of wastewater

Dye	Dyeing wastewater	Wash-off wastewater
1% Reactive Blue 19	91.78	81.56
3% Reactive Blue 19	91.56	82.89
1% Reactive Red 243	86.4	82.6
3% Reactive Red 243	82.35	80.9
0.5% Reactive Blue 19 – 0.5% Reactive Red 243	90.68	80.72
1.5% Reactive Blue 19 – 1.5% Reactive Red 243	90.12	81.45

Table 4
Sinking time for recycled wastewater scoured 100% cotton fabric

Raw fabric	Recycled wastewater		
Recycling variant	Reactive Blue 19	Reactive Red 243	Dye mixture
2	1.4	1.6	1.6
3	1.6	1.2	1.4
4	1.4	1.4	1.4
5	1.2	1.4	1.6
6	1.8	1.2	1.2
7	1.4	1.6	1.2
8	1.4	1.2	1.2
9	1.4	1.4	1.4

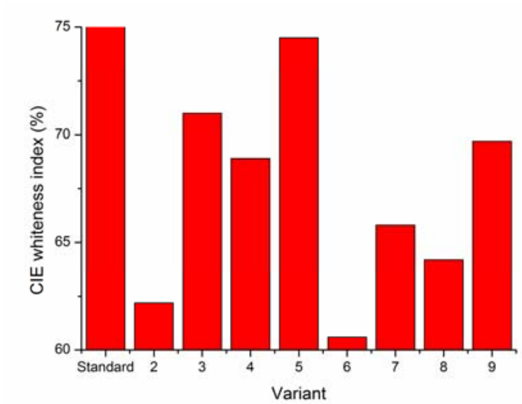

Figure 4: Whiteness degree of Reactive Blue 19 discoloured wastewater bleached fabrics depending on recycling variant

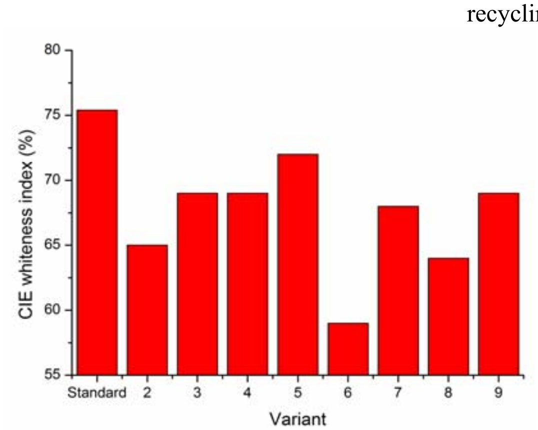

Figure 5: Whiteness degree of Reactive Red 243 discoloured wastewater bleached fabrics depending on recycling variant

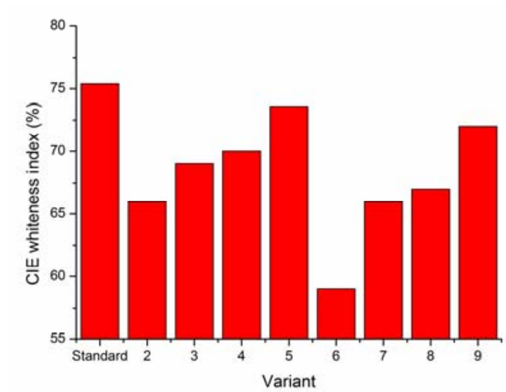

Figure 6: Whiteness degree of mixed dyes discoloured wastewater bleached fabrics depending on recycling variant

The best results are obtained for Reactive Blue 19, with a 74.6% whiteness degree for washing off discoloured wastewater mixed with fresh water, and with 73.8%, respectively, for the mixture of dyes, for the same recycling variant. In the case of 3% dyeing wastewater, only variant 9 led to acceptable whiteness degrees. Generally, the obtained results indicate a poor bleaching effect when using recycled dyeing wastewater, comparatively with conventional preparation. In fresh wastewater, good whiteness degrees are to be expected only for lower dyeing concentration (1%), after mixing.

Besides the whiteness degree, to identify colour deviations, the coordinates of the CIELAB colour space dL*, da* and db* deviations for the recycled wastewater bleached.samples were calculated, the result being shown in Figures 7-9.

Figure 7 plots colour shift for samples bleached with Reactive Blue 19 dyeing recycled wastewater. A tendency of colour shift towards smaller a* values and higher b* values may be observed. This indicates on the a* axis greener or less red and on the the b* axis – yellower or less blue, respectively. This tendency is insignificant for the variants using recycled wastewater mixed with fresh water, but it is very prominent for the other ones. A shift of lightness L to a darker magnitude, which is very significant for variants 6 and 2, may be also observed.

The results for the samples bleached with Reactive Red 243 dyeing recycled wastewater are shown in Figure 8. For all variants based on 3% dyeing wastewater, significant yellowing can be observed, correlated with important decreases in lightness. The other variants show smaller colour shifts, again with variant 5 presenting the best results. Figure 9 illustrates a colour shift for the samples bleached with the dye mixture dyeing recycled wastewater. The results are very similar to those obtained when using Reactive Red 243 dyeing recycled wastewater for bleaching. A very significant shift toward yellow may be observed for the variant using 3% dyeing wastewater.

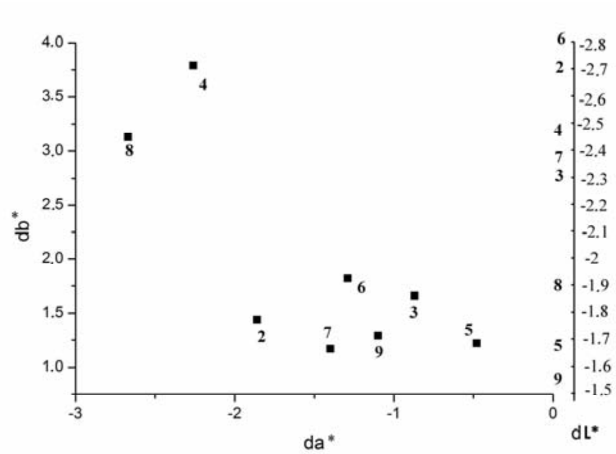

Figure 7: CIELAB dL*, da* and db* deviations for Reactive Blue 19 recycled wastewater

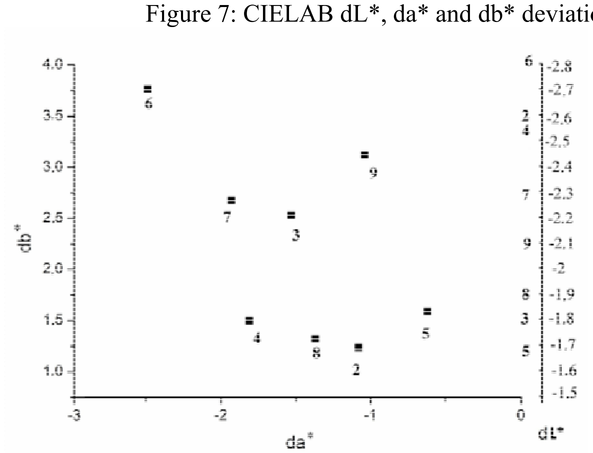

Figure 8: CIELAB dL*, da* and db* deviations for Reactive Red 243 recycled wastewater

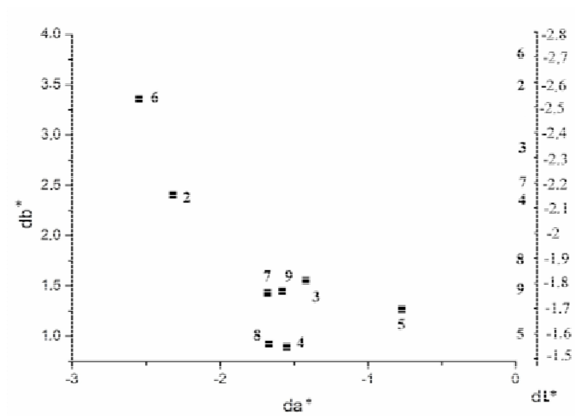

Figure 9: CIELAB dL*, da* and db* deviations for dye mixture recycled wastewater

CONCLUSION

The heterogeneous Fenton-like system used led to high colour removal degrees, especially for Reactive Blue 19. Reactive Red 119 dyeing wastewater shows significant colour removal only at 1% dyeing concentration. The dye mixture leads to colour removal degree values close to those obtained for Reactive Blue 19.

Using the discoloured wastewater in new scouring stages, a high hydrophilicity was obtained for all analysed variants, for both individual dyes and dye mixtures. In the bleaching experiments performed with treated dyeing wastewater, variants 3 and 5 produced whiteness degrees very similar to the standard. The results registered for the high concentration dyeing treated wastewater are not satisfactory, with the exception of variant 9 (washing off discoloured wastewater mixed with fresh water). For these variants, a significant colour shift towards yellow was observed. It can be concluded that, at low dyeing concentration, the dyeing and wash-off wastewater can be used after its mixing with fresh water in new bleaching processes, without affecting the final quality, thus reducing the amount of generated wastewater and, consequently, the load on the wastewater treatment system, as well as water consumption.

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