Assessment of toxicity of raw textile wastewater and after its reuse

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Abstract. Five consecutive dyeings were made using the treated effluent in every step. All photochemical treatments obtained decolourization efficiency (DE) above 90%, allowing the effluent to be reused in dyeings with fluorescent brighteners, from the first until the last treated effluent. In this proposed process, the rate of total organic carbon (TOC) presented after five consecutive dyeings achieved with treated effluent was 34 mg L⁻¹ compared with 435 mg L⁻¹ of the final effluent that was obtained after five conventional processes. The salinity of the final effluent obtained by this proposed process was 2.34 g L⁻¹ of NaCl compared with 25.00 g L⁻¹ presented in the effluent obtained by the conventional process. The values of the colour fastness to water showed no significant differences between the colours that were made by two processes. The average water consumption for a one-kilogram cotton dyeing after fifteen dyeings achieved by this proposed process was approximately 24 litres compared with the 70 litres that were consumed by the conventional process. However, the final treated effluent presented values of toxicity < 6.25% (EC₅₀, with 95% confidence interval) against 10.25% of the raw effluent. It means that in the sample concentration of the treated effluent presented 100% of Daphina similis mortality, indicating that this sample was more toxic than the raw effluent.

Keywords: toxicity, reuse of water, reactive dyestuff, dyeing of cotton, textiles
1. Introduction

The reactive dyestuff, which is the primary type of dyestuff that is used in Brazil and in all over the world [1,2], contains a reactive group forming a covalent bond with the fibre polymer and acts as an integral part of the fibre. This covalent bond is formed between the dye molecules and the terminal –OH (hydroxyl) group of cellulosic fibres or between the dye molecules and the terminal –NH2 (amino) group of polyamide or wool fibres. Moreover, textile processing effluents are often characterized by a high content level of dissolved organic dyes, resulting in large values of chemical and biological oxygen demands (COD and BOD) in the aquatic systems into which they are discharged. Moreover, reactive dyeing is the most commonly used coloration method for cotton, yet, it generates the most problematic effluents that are not only difficult to treat but also non-reusable. Such wastewater streams are a major environmental issue in developing countries [3-5].

It has been studied by researchers from many countries, including various types of treatments by photocatalysis. As example, Ben Younes et al [6] investigated the ability of Trametes trogii to decolorize azo and triarylmethane-dyes in the absence of redox mediators and studied various physico-chemical parameters in order to achieve maximum dye decolorization. Xia et al [7] investigated supported perovskite oxide (LaFeO3/SBA-15) for the first time as catalyst for the oxidation of organic dyestuff using hydrogen peroxide as oxidant, where tests indicate that LaFeO3/SBA-15 has large adsorption capacity, good catalytic performances, and wide working pH ranges (from 2 to 10) for the oxidation of dyestuff such rhodamine B, reactive brilliant red X-3B and direct scarlet 4BS.

Dias et al [8] evaluated the use of a residue-based catalyst for heterogeneous photo-Fenton of Reactive Black 5 dyestuff (RB5), preparing the catalyst by chemical vapor deposition of ethanol on a red mud residue, an important waste of the aluminum industry rich in iron oxide. Semeraro et al. [9] investigated the interactions between two industrial textile dyestuff in an aqueous solution and a series of different commercial cyclodextrins at 25 °C by spectrophotometric and electrochemical measurements to study their efficiency in the removal of colour from real textile wastewater in order to recover and reuse both clean water and dyes for other industrial processes, which is the same objective of this study.

Synthetic polyethylenimine and biopolymer chitosan were employed by Dasgupta et al. [10] in order to initiate the retention of anionic reactive red 120 (RR 120) from its aqueous solutions using polymer-enhanced ultrafiltration. In the ionizing radiation area, Borrely et al. [11] investigated colour and toxicity removal of C.I Reactive Blue 222 after radiation processing, which was conducted using a dynamitron electron beam accelerator. The best value of colour removal by radiation was 90%, with 2.5 kGy, in which Daphnia similis and Brachionus plicatilis were fitted well. All those factors mentioned before, such as water consumption, waste treatment, cotton fibre, reactive dyestuff and their effluents, were decisive for the development of this study.

2. Material and Methods

2.1. Reagents and materials

Sodium metasilicate 98% (Quimesp), nonionic detergent, nonionic levelling agent, fluorescent brightener and catalase (Golden Technology) were used in the processes of bleaching and white dyeings; hydrogen peroxide 50% (Quimesp) was used in the processes of bleaching, white dyeings and homogeneous photocatalysis; sulfuric acid 98% (Labsynth) was used for pH correction (Quimis pH metre); potassium titanium oxalate 0.1 mol L⁻¹ (Merck) was used to detect hydrogen peroxide (H₂O₂) residuals after bleaching and photocatalysis processes.

C. I. Reactive Yellow 145; C. I. Reactive Orange 122; C. I. Reactive Red 239; Azo chromophore group, heterobifunctional reactive groups type VS+MCT, 1136.32 g mol⁻¹ and CAS Registry Number 89157-03-9 (RR239) and C. I. Reactive Black 5, Azo chromophore group, homobifunctional reactive groups type VS+VS, 991.82 g mol⁻¹ and CAS Registry Number 12225-25-1/17095-24-8 (RB5) were provided by Golden Technology; sodium chloride 98%, sodium carbonate 98% and sodium hydroxide 98% (Quimesp) were used in the dyeings process; 100% cotton woven fabric, 180 g m⁻², 26 yarns 20/1 Ne per cm in the weft and 24 yarns 30/1 Ne per cm in the warp were also used.
2.2. Procedures

2.2.1. Bleaching. The bleaching process was executed in a jigger (Jigger Mathis) in 100 g samples with a liquor ratio of 10:1 using 1.0 g L\(^{-1}\) detergent; 1.0 g L\(^{-1}\) levelling agent and 0.5 g L\(^{-1}\) sodium metasilicate (Na\(_2\)SiO\(_3\)). In the case of H\(_2\)O\(_2\), bleaching was conducted with normal water with 4.0 mL L\(^{-1}\), and the bleaching achieved with reuse water was executed with ‘4.0 - Q\(_R\)’ mL L\(^{-1}\), where ‘Q\(_R\)’ is the residual amount of H\(_2\)O\(_2\) detected after the photochemical treatment [12]. In both cases, the substrate was treated for 30 min at 95 ºC. Then, the bath was cooled to 55 ºC, and the pH was adjusted to 6.5. After 5 min at 55 ºC, 0.5 g L\(^{-1}\) of catalase was added, and the temperature was maintained during the 15 min in order to remove residual of H\(_2\)O\(_2\). The 0.1 mol L\(^{-1}\) (C\(_4\)K\(_2\)O\(_9\)Ti) potassium titanium oxalate solution was used to detect any possible H\(_2\)O\(_2\) residual.

2.2.2. Dyeings. Five colours and their Pantone® numbers were based on the Book of SENAI Mix Design Spring/Summer 2016/2017. The dyeing recipes were obtained by Match Wizard® software (Datacolor 650 SF Plus) and are described in the Table 1.

| Color      | Pantone® |
|------------|----------|
| Black      | -        |
| Cosmic     | 194027   |
| Mystic     | 193323   |
| Refugy     | 191543   |
| Safari     | 180312   |

The Euclidian distance between the colours obtained with normal water versus the colours obtained with treated effluent was calculated by the equation

\[ \Delta E^* = (\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2 \]^{1/2}

where \(a^*\) represents the green-red axis, \(b^*\) represents the yellow-blue axis and \(L^*\) represents the white-black axis.

The amount of salt (NaCl), sodium carbonate (Na\(_2\)CO\(_3\)) and sodium hydroxide (NaOH) used in all the dyeings were obtained using the manufacturer’s recommendations. The only exception was the amount of NaCl that was used in dyeings made with recycled water; in these cases, the recommended amount of NaCl was subtracted from the amount that was already present and determined by conductivimetry (Digimed DM-32). These values were obtained by correlation between the specific conductivity (\(\mu\)S cm\(^{-1}\)) and known concentrations of NaCl. The correlation graphic and the equation are shown in Figure 1.

![Figure 1. Correlation between conductivity and [NaCl]](image-url)
The recipes are described in Table 2, including the amounts of dyestuff and auxiliaries that were utilized in all dyeings.

| Color   | RY145 | RR239 | RB5 | Base RB5 | NaCl | Na₂CO₃ | NaOH 50 °Bé |
|---------|-------|-------|-----|----------|------|--------|-------------|
| Black   | -     | -     | -   | 7.000    | 70.000 | 7.000  | 2.000       |
| Cosmic  | 0.205 | 0.366 | 3.000 | -        | 60.000 | 7.000  | 1.500       |
| Mystic  | 0.284 | 1.040 | 1.420 | -        | 50.000 | 6.000  | 1.500       |
| Refugy  | 0.700 | 1.440 | 0.300 | -        | 50.000 | 6.000  | 1.500       |
| Safari  | 0.950 | 0.800 | 0.680 | -        | 50.000 | 6.000  | 1.500       |

All dyeings were executed by the “All in” process proposed by Salem [13]. The baths of every step were collected, the pH was adjusted to 7.0 (H₂SO₄), and the final effluent was stored to posterior photochemical treatment.

2.2.3. Photocatalysis treatments. The photocatalyses processes were performed in a batch reactor with a capacity of 10 L, using 3 lamps Phillips TL 8 W with irradiation type UV-C in 253.7 nm operating with 50 V, 2 A and independent actuation, setting the potency variation to 8 W, 16 W or 24 W. Circulation of the bath was provided by a 6 W pump, with a circulation capacity equal to 150 L h⁻¹.

Based on the results presented by Rosa et al. [14], the first effluent was diluted in a 4:1 ratio of water and effluent. The water in the next effluent was replaced by the previously treated effluent.

Time was maintained until a minimum of 85% of decolourization efficiency (Dₑ) was reached, as calculated by equation

\[ \% Dₑ = \left[ 1 - \left( \frac{\text{Abs}_0}{\text{Abs}_1} \right) \right] \times 100 \]

In order to use the absorbance decay, aliquots of 12 mL were collected in intervals of 15 min and conditioned in acrylic bucks with 1.0 cm of optical path. The absorbance (Abs) of the aliquots was assessed by spectrophotometry VIS (Konica-Minolta CM 3600d).

2.2.4. Reuse of treated effluents. The first dyeing effluent treatment was diluted in a 4:1 ratio with water. The second dyeing effluent treatment was diluted in a 4:1 ratio with the first treated effluent instead water; this process continued with the third dyeing and so on, until 15 dyeings were completed.

A white dyeing was performed in order to verify a possible interference in this type of dyeing when executed with treated effluents after treatment with each of the 15 dyeings. In addition, white dyeings were also conducted with water and compared by the whiteness index (Wi), which was determined by the Ganz-Griesser method [15] and calculated by the following equation

\[ \text{Wi} = (1 \cdot Y) + (-1868.322 \cdot x) + (-3695.690 \cdot y) + 1809.441 \]

where Y is the value of Y-tristimulus of the sample; x and y are the values of the chromaticity coordinates assessed by spectrophotometry VIS at 470 nm, under D65 illuminant at 10° (Konica-Minolta CM 3600d).

2.2.5. Colourfastness. The fastness properties of all colours were tested and assessed according to the standards described by the ISO 105-E01 Textiles from the International Organization for Standardization (ISO) [16]. All colour changes and staining were assessed by the grey scale using spectrophotometer software (Konica-Minolta CM 3600d) under illuminant D65. Before the tests, the samples were conditioned for 24 h in a standard atmosphere at 20 ± 2°C and at a relative humidity of 65 ± 2%.

2.2.6. Total organic carbon (TOC). The TOC was determined by the 5310-D/14878 method [17] after the photochemical treatment of the 5th dyeing (proposed process) and in the untreated effluent after 5th dyeings (conventional process).
2.2.7. **Toxicity.** The toxicity test for Daphnia similis was performed according to procedure described by ABNT NBR 12713/2009 norm [18]. The results, expressed in EC₉₀, indicate the median concentration of the effluent that caused toxic effect, or immobility, on the microorganisms exposed to the sample for 48 hours.

3. Results and discussion

3.1. Effluents treatment

All photocatalysis treatments presented D₂₅ values higher than 90%, all of them indicating reactions of first order. The sample values are described in Table 3.

Table 3. Obtained D₂₅ values.

| n  | Color   | Absₐ | Absₙ | D₂₅ | Time (min) | λ_max (nm) |
|----|---------|------|------|-----|------------|------------|
| 1º | Black   | 2.3468 | 0.0003 | 99.99 | 240 | 600 |
| 2º | Cosmic  | 0.7943 | 0.0048 | 99.40 | 240 | 560 |
| 3º | Mystic  | 0.5650 | 0.0013 | 99.77 | 240 | 540 |
| 4º | Refugy  | 0.4669 | 0.0078 | 98.33 | 240 | 540 |
| 5º | Safari  | 0.3394 | 0.0057 | 98.32 | 240 | 550 |

The obtained values allow continuous reuse in the 5-colour dyeings and also in the all-white dyeings.

3.1.1. Reuse of effluent: White dyeings. The Wi values were used as comparisons between white dyeings executed with treated effluent versus white dyeings executed with water, as described in Table 4.

Table 4. Wi values of the white dyeings.

| White dyeing executed after treatment of effluent: | Wi values | Δ (%) |
|--------------------------------------------------|-----------|-------|
| Water                                           | Treated effluent |       |
| 1-Black                                         | 152       | 152   | 0.00 |
| 2-Cosmic                                        | 149       | 148   | 0.67 |
| 3-Mystic                                        | 155       | 148   | 4.52 |
| 4-Refugy                                       | 146       | 144   | 1.37 |
| 5-Safari                                        | 145       | 139   | 4.14 |

Deviation Media 2.14

For the results presented, in which the average deviation was lower than 3%, it is concluded that the difference was not significant between the white dyeings executed with normal water and the treated effluent, which demonstrated that the process can be applied not only for future dyeings of colours but also for washes and other bleaching processes.

3.1.2. Reuse of effluent: Colours. The ΔE* values that were used as comparisons between colours dyeings executed with treated effluent versus colours dyeings executed with water are described in Table 5.

Table 5. Values of ΔE*.

| Color | Water | Treated effluent | ΔE* |
|-------|-------|------------------|-----|
|       | Δa*  | Δb*  | ΔL*  | Δa*  | Δb*  | ΔL*  |     |
| Black | 23.81 | -2.14 | -12.04 | 24.21 | -2.29 | -12.17 | 0.45 |
| Cosmic| 30.75 | 6.35  | -10.72 | 30.68 | 6.31  | -10.82 | 0.13 |
| Mystic| 36.83 | 15.94 | 1.06  | 37.95 | 15.81 | 1.09  | 1.13 |
| Refugy| 32.82 | 2.53  | 3.36  | 32.09 | 3.20  | 3.36  | 0.99 |
| Safari| 49.07 | 14.34 | 18.96 | 48.19 | 15.00 | 18.95 | 1.10 |
The presented $\Delta E^*$ values for all developed colours are below 1.5, which are accepted values in the Brazilian market.

3.1.3. **Colourfastness.** The values of the colourfastness test are described in Table 6.

| Color | Water | Treated effluent |
|-------|-------|------------------|
|       | C     | S                |
|       | C     | S                |
| Black | 4     | 3/4              |
| Cosmic| 4     | 3/4              |
| Mystic| 4/5   | 4/5              |
| Refugy| 4/5   | 4/5              |
| Safari| 5     | 5                |

*Obs: C = Color change; S = Staining*

The difference between the colours executed with water and the colours executed with the treated effluent is not significant. The difference between the values was not higher than $\frac{1}{2}$ point.

3.1.4. **TOC.** Table 7 shows the values obtained after 5 dyeings with water and with treated effluents.

| Total Organic Carbon | % Remotion |
|----------------------|------------|
| Proposed process (*)  | 34         | 92.89      |
| Conventional process (**) | 435       |            |

(* = after last treatment; (**) = effluent of 5 dyeings)

The amount of TOC after treatment with the 5th dyeing was 34 mg L$^{-1}$ compared with 435 g L$^{-1}$ presented after 5 dyeings that were executed with no treatment. The treatment promoted 93% of TOC reduction.

3.1.5. **Salinity.** The amount of NaCl present after the last treatment was 2.34 g L$^{-1}$ compared with 25.0 g L$^{-1}$ after fifteen dyeings executed by the conventional process, which is a decrease of approximately 95%. This difference is due mainly to the amount that is already present in the treated effluent for implementing the following dyeing, which was subtracted from the amount of NaCl recommended by the supplier of the original recipe.

3.1.6. **Toxicity.** The EC$_{50}$ presented values, with 95% confidence interval, were 10.15 for the effluent after 5 dyeing against <6.25 for the treated effluent. The effluent treated cause 100% mortality of the microorganisms, which means that the treated effluent sample was more toxic than the effluent after five dyeings done by conventional methods.

4. **Conclusion**

Based on the results in this study, which present 5 colours achieved with the studied dyestuffs, we found that the proposed treatment and process can be applied for the purpose of reusing the treated effluent not only in the new colours dyeings but also in other process such as bleaching, washing off and white dyeings. However, the treated effluent presented more toxicity, increasing the mortality to *D. Similis*. The results suggest an evaluation with more than one class of test organism.

The colourfastness of the dyeings achieved with treated effluents did not present a significant difference compared with the dyeings achieved with water. The difference between the $\Delta E^*$ values in the studied colours were lower than 1.5 points. Moreover, the white dyeings achieved with treated effluent showed Wi values similar to white dyeings made with water. The median of the deviations did not exceed 3%. In some cases, white dyeings achieved with treated effluent showed a higher Wi value than the white dyeings achieved with water.
The average water consumption for dyeing a kilogram of cotton was 24 L after fifteen dyeings achieved by the proposed process using the colours and dyestuffs studied, which is less compared with the 70 L that were consumed by the same dyeings achieved by the conventional process. Theoretically, in the dyeing of 1000 kg executed by the proposed process leads to eventual replenishment of water about 10%, indicate that the economy would conserve approximately 66.5 m$^3$ of water when compared to conventional process.

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