Laser Induced Dyeing (LID) with Reactive Blue 21 on Hemp Fibers

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Abstract. Effects of 532 nm and 320 mJ laser beam on aqueous solution of Reactive Blue 21 (RB21), a copper based on reactive dye, have been studied in both presence and absence of garnet gemstone with the aim to receive a proper coating of the hemp fibers contained in the yarns of a woven texture while reducing the dyeing time compared to the classic exhaustion dyeing method. Results show that both laser beam and garnet influenced the dyeing process with RB21, enhancing the absorption and reaction of RB21 with the composite structured hemp fibers, effect observed in the color intensities for all samples measured with the grayscale. The best results are noticed for laser effects in presence of garnet gemstone when highest coating is achieved among all samples, and the process is 11 times shorter than the classical exhausting method. Compared FTIR and UV-VIS spectra of initial dyestuff and residual dyestuff isolated from the wastewaters offered information about dyestuff exhaustion process under garnet and/or laser influence. Laser Induced Fluorescence completed the study with the information about RB21 behavior under UV laser beam of 362 nm.

1. Introduction

The dyeing with reactive dyes of cellulose fibers included either in yarns or in fabrics is a technological process that can last between 60 minutes and 110 minutes, at high temperatures (over 60 degrees Celsius) and with the use of auxiliaries according to the manufacturers' recommendations. Most of the time, dyeing is followed by various fixing processes, from those with specific chemical compounds to thermal ones. Also, because reactive dyes have affinity for both the OH group in the cellulosic structure and the OH group in the water, some of the dye will hydrolyze, becoming inactive for reaction with the cellulosic fiber. The hydrolyzed dye is deposited on the cellulosic fiber, without fixing and will have to be removed by washing following dyeing [1, 2]. This produces wastewater both in the dyeing process itself and in the next stages of post-dyeing treatments that involve water. This shortcoming has led to numerous studies on wastewater treatment, which have led to observations on the stability of dyes reactive to various physical and chemical exposures [3- 8]. Some of the wastewater treatments resulting from reactive dyeing have even focused on their reuse in the technological dyeing process [9- 12].

The present study aims to investigate a new method of dyeing using the reactive dye contained in the Color Index (C.I.) with the code Reactive Blue 21. The proposed method is an absolutely new one, namely laser induced painting (LID). Both the dyeing effect on the hemp fabric (cellulose fiber) and the changes occurred on the dye structure during the process are studied. The method aims at reducing...
the dyeing process time, the energy consumption, and the consumption of chemical auxiliaries commonly used in dyeing processes with reactive dyes.

2. Method and materials used for laser induced dyeing (LID)

The laser induced dyeing (LID) with C.I. Reactive Blue 21 (RB21) was tested on 100% hemp fabric (noted herein as HMP). The procedure consists in irradiating the dyeing system in free atmosphere with pulsed laser beam of 532 nm wavelength, 10 ns pulse width, 10 Hz repetition rate and 320 mJ energy, using YG 981E/IR-10 laser system. A dye bath using 5 ml Reactive Blue 21 aqueous solution 1g/l was used for the first sample P1 (RB21+HMP+LSR) and for the second sample P2(RB21+GRNT+HMP+LSR) a garnet gemstone granule was added. The dye baths were used for 0.131 g hemp fabric (HMP) each. The dyeing process was conducted in test tubes and laser irradiated through the walls of the glass tubes. Irradiation time was of 10 minutes for each sample.

3. Results, spectroscopy analyses and discussions

3.1. Gray Scale dyeing results evaluation

The dyeing results are evaluated in dyeing intensity on the 10 tones gray scale and a difference from 8 for classical dyeing (CLSS) to 6 for sample P1 and 7 for sample P2, as seen in Figure 1, is noticed. As 1 tone on the 10 tones gray scale is the equivalent of ½ tones in the 5 tone gray scale used in textile finishing, it turns out that the dyeing intensity is higher by ½ tone on the textile gray scale as it follows: P1 (RB21+HMP+LSR) < P2 (RB21+GRNT+HMP+LSR) < CLSS. It turns out that the garnet stone produces an intensification of the laser-induced dyeing (LID) process. Also, the two dyes obtained by the LID method are very close in intensity to the dyeing by the classical process.

![Figure 1. Dyeing intensity compared evaluation of dyed samples P1 (RB21+HMP+LSR), P2 (RB21+GRNT+HMP+LSR) and P3 (RB21+AUX+HMP+LSR) with classical procedure (a,b) based on the 10 tones gray scale (c).](image)

Note: (The classical dyeing involved the same concentration of 1g/l RB21 in the dye bath, 10g/l Na₂CO₃, 50g/l NaCl, 80°C temperature and 110 minutes was the time for the dyeing process).
3.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR compared spectra (Figure 2) of the residual dyestuff obtained after drying out the exhausted baths of the two dyeing processes (P1: RB21+HMP+LSR and P2: RB21+GRNT+HMP+LSR) show changes in the chemical structure of the dyestuff during the pulsed laser induced dyeing (LID) process. Specific functional groups in accordance with the chemical structure of the C.I. Reactive Blue 21 are identified in Table 1 and their changes during LID process are noticed.

![Figure 2. FTIR compared analysis of Reactive Blue 21 (RB21) and residual dye extracted from exhausted dye baths P1ex (RB21+ HMP+LSR); P2ex: RB21+GRNT+HMP+LSR.](image)

In FTIR spectra (Figure 2) and Table 1, most of the vibrations of the specific functional groups of C.I. Reactive Blue 21 dyestuff are also identified for the exhausted dye baths resulted from the laser induced dyeing (LID) process, exception those related to the side chain. The groups in the main chromogen structure (the chromofore and auxochromes) are proved to be stable during the two processes P1(ex) and P2(ex). That is evidenced by the vibrational bands of 3422 cm⁻¹ (N–H and O–H stretching), 3216 cm⁻¹ (chelates and N–H stretching), 3053 cm⁻¹ (aromatic C–H stretching), 1632 cm⁻¹ (C = C aromatic stretching, C–N stretching; N–H deformation), 1589 cm⁻¹ (C–C aromatic stretching, N–H deformation and ring skeleton in aromatics and heteroaromatics), 1496 cm⁻¹ (Cu–N complexation, C–C ring modes), 1453 cm⁻¹ (O–H deformation), 1390 cm⁻¹ and 1326 cm⁻¹ (-SO₂ asymmetric stretching), 1241 cm⁻¹ (C–N stretching), 1134 cm⁻¹ (-SO₂ symmetric stretching), 1028 cm⁻¹ and 985 cm⁻¹ (aromatic C – H deformation), 872 cm⁻¹ (S – O stretching, = C – H deformation), 736 cm⁻¹ (o-di-substitution in 6-membered aromatic rings, = C – H deformation), 622 cm⁻¹ (C – S stretching). Thus, the very weak intensity of the 907 cm⁻¹ band of S – N vibrations in the P2(ex) sample and missing in the P1(ex) sample denotes formation of the components CHR (chromogen) in Figure 3 b and SCH (side chain) in Figure 3 c, after S – N bond is broken. The missing 829 cm⁻¹ band in the P1(ex) spectrum, assessed to p-di-substitution in 6-membered aromatic rings, indicates an advanced decomposition of SCH. The component SCH (Figure 3 c) may decompose into amino-
benzene (phenylamine or aniline), vinyl sulfone or into amino-benzene sulfonic acid and sulfur dioxide. Formation of aniline could explain the more greenish color received on the P1(ex) and P2(ex) samples, the green shift being more advanced for the P1(ex) sample. That is in accordance with the FTIR spectra of P1(ex) where the 907 cm\(^{-1}\) and 829 cm\(^{-1}\) bands are missing. As 907 cm\(^{-1}\) is assessed to S – N group, it means that in a first decomposition of the dyestuff, the component SCH in Figure 3(c) was formed when the S – N bond was broken. Also, as the 829 cm\(^{-1}\) band is assessed to p-disubstitution in 6-membered aromatic rings, it means that a second decomposition of the SCH component into alanine, vinyl sulfone and sulfur dioxide followed the first one.

![Figure 3. Chemical structure of the C.I. Reactive Blue 21 (RB21): a) RB21 derivatives resulted after the pulsed laser induced dyeing (LID); b) process on hemp CHR; c) the SCH component.](image)

It is important to notice that the component denoted as CHR (chromogen) in Figure 3 (b) represents a copper phthalocyanine structure with sulfone groups linked to the benzene groups of the molecule. Such structure is very similar to the C.I. Direct Blue 86 and it will be still able to dye the cellulosic fibers, but following a mechanism specific to direct dyestuffs, different from the dyeing mechanism specific to reactive dyestuffs. Also, the FTIR analysis shows the effect induced in P2 sample by the garnet gemstone during laser induced dyeing (LID) process, in the way of preserving the dyestuff structure compared to the P1 process.

| IR bands (cm\(^{-1}\)) | Functional groups [13, 14, 15] | RB21 (HMP+RB21+LSR) | P1 (HMP+RB21+GRNT+LSR) | P2 (HMP+RB21+GRNT+LSR) |
|------------------------|---------------------------------|----------------------|--------------------------|--------------------------|
| 3422                   | \(-NH\) stretching free; \(-O - H\) stretching H-bonded | Strong and broad     | Stronger and broad       | Strong and broad         |
| 3216                   | Chelates: \(-N - H\) stretching H-bonded | Overlaps with 3422 – 3216 broad band | Overlaps with 3422 – 3216 broad band | Overlaps with 3422 – 3216 broad band |
| IR bands (cm\(^{-1}\)) | Functional groups [13, 14, 15] | P1 (HMP+RB21+LSR) | P2 (HMP+RB21+GRNT+LSR) |
|------------------------|-------------------------------|------------------|-------------------|
| 3053                   | Aromatic – C – H stretching  | Very weak        | Very weak         |
| 2925                   | Aliphatic – C – H stretching; −O – H stretching, H – bonded | Weak             | Very weak         |
| 2854                   | Aliphatic – C – H stretching | Weak             | Very weak         |
| 1830 – 1728 comb       | Substitution in 6-membered aromatic rings | Very weak | Very weak |
|                        | −C = C – aromatic;           |                  |                  |
|                        | −C = N –;                    |                  |                  |
|                        | −N – H deformation           |                  |                  |
| 1632                   | −C – C – aromatic stretching; −N – H deformation; Ring skeleton in heteroaromatics Complexation Cu ← N; −C − C – ring modes | Medium          | Weaker            |
|                        |                               | Weak             | Medium           |
| 1496                   | −O – H in plane deformation  | Weak             | Weak, overlaps on 1390 band, denoting H-bonding and Van der Waals interactions |
| 1390                   | O = S = O stretching asymmetric in R – SO\(_2\) – OR | Medium           | Weak, broad, denoting H-bonding and Van der Waals interactions |
|                        |                               |                  | Weak, broader and overlapped on 1390 band, denoting H-bonding and Van der Waals interactions |
| 1326                   | O = S = O stretching asymmetric in R – SO\(_2\) – OH and R – SO\(_2\) – N | Medium           | Very weak        |
| 1241                   | −C – N stretching; O = S = O stretching symmetric in R – SO\(_2\) – OH, R – SO\(_2\) – OR and R – SO\(_2\) – N | Strong           | Very weak        |
|                        |                               |                  | Weak              |
| 1134                   | Aromatic – C – H in plane deformation | Strong    | Weak broad to strong |
| 1028                   | Aromatic – C – H in plane deformation | Strong    | Weak              |
| 985                    | Aromatic – C – H in plane deformation | Medium    | Weak              |
| 907                    | −S – N stretching;           | Medium           | Missing           |
|                        |                               |                  | Very weak         |
| IR bands (cm⁻¹) | Functional groups [13, 14, 15] | RB21 (HMP+RB21+LSR) | P1 (HMP+RB21+GRNT+LSR) |
|-----------------|--------------------------------|----------------------|------------------------|
| 872             | $S - O$ stretching; Aromatic $C - H$ out of plane deformation; $C - H$ out of plane deformation; Mono-substitution in 6-membered aromatic rings | Missing | Weak | Weak |
| 829             | p-di-substitution in 6-membered aromatic rings | Weak | Missing | Very weak |
| 736             | o-di-substitution in 6-membered aromatic rings; $C - H$ out of plane deformation | Strong | Very weak | Weak |
| 622             | $C - S$ stretching vibrations | Weak | Weak | Very weak |

### 3.3. UV-Vis spectroscopy

In UV-Vis spectroscopy, the analysis was conducted on the waste waters (exhausted dye baths P1ex, resulted in RB21+HMP+LSR procedure and P2ex, resulted in RB21+GRNT+HMP+LSR procedure) and compared with RB21 aqueous spectrum. In UV-Vis spectroscopy, the solutions were analyzed in quartz tubes. UV-Vis absorption spectroscopy completes the information about the Reactive Blue 21 aqueous solution (RB21aq) during P1 and P2 processes, namely laser induced dyeing (LID) without and with garnet gemstone.

![Figure 4](image-url). UV-Vis compared spectra of Reactive Blue 21 aqueous solution and exhausted dye baths resulted in laser induced dyeing (LID), namely P1(ex): RB21aq+HMP+LSR and P2(ex): RB21aq+GRNT+HMP+LSR.
The band at 337 in the UV-Vis spectra denotes Cu$^{2+}$ ions complexation assessed to copper phthalocyanines and on visible spectra, copper complexation with phthalocyanine group is noticed in the peak at 668 nm for RB21aq and 656 nm for the samples P1(ex) and P2(ex). Absorption spectra in visible denote hypsochromic shift from 628 nm and 668 nm in the RB21 aqueous solution to 620 nm and 665 nm, respectively, in the exhausted dye baths of the P1 and P2 samples (Figure 4). That indicates changes in the functional groups playing the role of auxochromes. It is thus evidenced that some of the auxochromes have been removed from the dyestuff molecule under the laser irradiation. The auxochrome groups influence the dyeing color, exerting its bathochrome or hypsochrome effect. The auxochromes in p-$\pi$ conjugation with the chromophore increase the wavelength at which the light is absorbed and the intensity of absorption. Once such groups are removed, the opposite effect of shifting light absorption to lower wavelengths and decreasing the intensity of absorption occurs. This is the case in the present study when the wavelength of the absorbed light decreases compared to the initial dye (blue shift), by losing one or more auxochromes which are situated in the side chain. Literature reports absorbance wavelength in the same range for copper binding with proteins and other organic compounds as ligands [16, 17].

However, the large chromogene (phthalocyanine with sulfone groups) involved in a complexation with copper ions remains stable during laser irradiation, and despite there are changes in the side chain which is a vinyl sulfone structure that is responsible for binding with the cellulose and in the bridging aniline structure, there is still possible that the component CHR (Figure 3b) binds with the cellulose through the sulfonic groups attached to the chromofore benzenic groups, under a mechanism specific to the direct dyestuffs, as iterated before.

3.4. Laser induced fluorescence (LIF)

Laser induced fluorescence spectroscopy (LIF) analysis performed on Reactive Blue 21 aqueous solution (RB21aq) and on the exhausted dye baths P1(ex): RB21+ HMP+LSR and P2(ex): HMP+RB21+GRNT+ HMP+LSR, in quartz tubes, at 30 ns, 40 ns and 50 ns delay using the same YG 981E/IR-10 laser system as for the laser induced dyeing, this time with 355 nm beam wavelength, 10 ns pulse width, 10 Hz repetition and 150 mJ energy.

In the LIF spectra (Figures 5, 6), the copper fluorescence is indicated by the peak contouring towards 699 nm and that could go up to 750 nm [18]. Sulfur dioxide generation due to UV laser beam interaction with sulfone groups is indicated by the spectra curves going up towards 400 nm and that could form a peak in the 300 nm wavelength region [19, 20]. The radicals formation, mainly ·OH radicals, is indicated by the tower shaped bands in the 481 nm – 508 nm and 588 nm – 627 nm as noticed before in the literature [21, 22–25]. The two emission lines at 514 nm and 550 nm may be assessed to a mirrorless laser phenomena induced during the interaction of UV laser beam and the copper phthalocyanine structure in the dyestuff. The RB21aq presents a strong 30 ns delay emission in the green region (524 nm – 550 nm) which mitigates for the exhausted dye baths P1(ex) and P2(ex), indicating that the emission is related to the initial chemical structure of the dyestuff.

![Figure 5. LIF spectra of RB21aq: Reactive Blue 21 aqueous solution and exhausted dye baths P1(ex): RB21+ HMP+LSR and P2(ex): HMP+RB21+GRNT+ HMP+LSR at: (a) 30 ns; (b) 40 ns; (c) 50 ns delay.](image-url)
Figure 6. LIF compared spectra at: (a) 30 ns, (b) 40 ns and (c) 50 ns delay of the RB21aq: Reactive Blue 21 aqueous solution versus exhausted dye baths resulted in laser induced dyeing (LID) of P1ex: RB21+HMP+LSR and P2ex: HMP+RB21+GRNT+ HMP+LSR samples.

Table 2. LIF spectra emission intensities (x10^5).

| Sample     | RB21  | P1(ex) | P2(ex) |
|------------|-------|--------|--------|
| Wavelength |       |        |        |
| (nm)       | 30    | 40     | 50     |
| 481        | 0.3   | 0.8    | 0.4    |
| 508        | 0.3   | 0.8    | 0.4    |
| 514        | 1.3   | 2      | 0.6    |
| 515        | 0.4   | 3.5    | 7.9    |
| 524        | 0.2   | 0.7    | 0.4    |
| 538        | 0.2   | 0.7    | 0.4    |
| 550        | 1     | 1.6    | 0.5    |
| 561        | 0.1   | 0.5    | 1      |
| 562        | 0.16  | 0.3    | 1.5    |
| 588        | 0.18  | 8      | 0.45   |
| 602        | 0.4   | 1      | 0.5    |
| 608        | 0.2   | 1.9    | 4.3    |
| 615        | 0.4   | 1.2    | 0.7    |
| 626        | 0.4   | 1.2    | 0.7    |
| 627        | 0.2   | 1.6    | 3.3    |

Compared spectra in Figure 6 show a longer fluorescent time life of the exhausted dye baths P1(ex) and P2(ex) compared to the Reactive Blue 21 aqueous solution (RB21aq). That indicates intermolecular interactions during UV laser irradiation, as well as different chemical structures of the three analyzed solutions. The level of copper complexation with the phthalocyanine may influence the variation in emission intensity because of the energy transfer from the excited state of the ligand to the metal ions causing decrease in intensity [17]. Table 2 includes the emission intensities in the three fluorescence spectra.

4. Conclusion and perspectives
The laser induced dyeing method proposed and studied herein proves to be suitable, with very good results regarding fiber coating when compared with the classical dyeing. Considering the substantial reduction of the dyeing process time, namely 11 times compared to classical process, the fact that no
auxiliary substances were used, as well as the very good dyeing/coloring results, the method proves useful and deserves further investigation and possibly improved.

It is not clear yet how the garnet gemstone influenced the physico – chemical process induced by laser interaction with the dyeing system, but the results of the FTIR analysis proved that the structure of the RB21 dyestuff was preserved in P2(ex) when the garnet gemstone was used, compared with the P1(ex) when decomposition at bridging group level (S – N) and furthermore is clearly evidenced. Further investigation is needed to explain the phenomena.

It is very important that the LID method can be applied for dyeing small amounts of textile materials. Currently, the dyeing of small amounts of textile material is a problem primarily in terms of optimizing energy consumption, as well as materials and chemicals. Applications of the laser induced dyeing (LID) method could be used especially for dyeing materials with special destination (medical, cosmetics, etc.).

5. References
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