CI&CEQ
Chemical Industry & Chemical Engineering Quarterly
Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ
Chem. Ind. Chem. Eng. Q. 27 (1) 1–13 (2021) CI&CEQ

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SCIENTIFIC PAPER

UDC 677.21:667.027.4

CLEAN PRINTING PROCESS OF COTTON WITH NATURAL DYES: EFFECT OF PASTE FORMULATION COMPONENTS ON PRINTING PERFORMANCES

Article Highlights

- *Corchorus olitorius* L. was tested in printing paste formulation as natural dye
- The printing pastes were applied on cotton fabric using screen printing process
- The resulting color shades varied from green to brown
- The effects of various print formulation components on printing quality were investigated

Abstract

A novel natural dye Corchorus olitorius L. was investigated in the preparation of printing pastes for screen printing of cotton fabric. To ensure ecological printing, greener thickeners were used such as: sodium alginate, carboxymethyl cellulose and Ceratonia siliqua L. flour. The nature and concentration of thickener, dyestuff and urea concentrations, mordant type and fixation method were explored. Printed cotton fabric qualities were evaluated by determining different parameters: color strength, penetration percentage, printing fastnesses and mechanical properties, whereas print paste quality was evaluated by measuring its apparent viscosity. The higher dye concentration used in the printing paste led to better apparent viscosity and color strength levels. The increase of urea concentration improved the color strength, but reduced the apparent viscosity of printing paste. Best results of viscosity and color strength parameters were obtained using ferrous sulfate as a mordant and sodium alginate as a thickener, the results being 1346.67 mPa s^{-1} and 4.90, respectively. The resulting color shades varied from green to brown and very good color fastnesses was achieved, but depended mainly on the used experimental conditions.

Keywords: natural dyes, cleaner printing process, cotton fabrics, past formulation components, components effect, printing qualities.

Textile screen printing is a stencil technique of printmaking, in which a design is imposed on a polyester or polyamide screen of fine mesh, with blank areas coated with an impermeable substance. The printing paste is forced into the mesh openings by the pushing operation of a squeegee to reach finally the textile surface [1,2]. For the textile printing industry, the most used dyes include acid, direct, vat, reactive, pigment and disperse dyes [1,2]. These dyes ensure generally acceptable to very good fastness properties but may have hazardous effects on consumers, workers and the environment [3-5]. Such crucial disadvantage is noticeable even at very low concentrations. To deal with the ecological problems associated with coloration processes using synthetic dyes as well as their undesirable auxiliaries, several studies have been directed. Studies proposed the minimization and the optimization of classic auxiliaries and dye consumptions [6,7], the substitution by other less toxic compounds [8,9], the development of novel generations of eco-friendly dyes and auxiliaries [10-15], the use of new greener and recyclable solvents instead of

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Paper received: 4 October, 2019
Paper revised: 27 May, 2020
Paper accepted: 4 June, 2020

https://doi.org/10.2298/CICEQ191004019B

water [16-18], and the creation of innovated processes [19,20].

Many environmental programs have been also established [20-24]. In this context, the application of bio-sourced compounds such as natural dyes in textile coloration processes have been increasingly attracting more attention [25]. The use of natural dyes in the dyeing process was established to be very promising. Many successful applications of bio-sourced pigments and dyes were proposed in the dyeing field [26-32]. Several industrial applications were also noted. However, until now, only few studies have reported the application of natural dyes in printing processes. In fact, compared to the dyeing field, the literature described that only some dyes extracted from known plants, such as madder, curcuma, rhubarb, pomegranate, orange tree leaves, alkanet roots, etc., have been tested for printing processes of natural and synthetic fibers, in the presence of metallic mordants [33-39], chitosan [40-42] and bio-mordants [33,34,37-39,43-44].

In this study, *Corchorus olitorius* L. presented in Figure 1 was chosen as a natural source to develop printing experiments on bleached cotton fabrics. Currently, *C. olitorius* L. belongs to the Tiliaceae family and originates from India and Africa, but nowadays, it is found especially throughout the tropics. It was cultivated to provide bark for the production of fibers (jute) and its mucilaginous leaves are used as a vegetable [45]. The leaves of *C. olitorius* L. are very rich in many components such as vitamins (vitamin A, ascorbic acid, etc.), proteins, lipids, fibers, etc. [46]. In addition, these leaves contain secondary metabolites such as polyphenols, flavonoids, tannins, steroids, etc. [47]. The leaves of this plant were not used previously either in dyeing or printing of textile materials. The color and the mucilaginous characteristic of *C. olitorius* L. leaves inspired us to explore this plant as a green dye in textile printing processes. The presence of the mucilage is the first parameter that allows us to use this dye. This metabolite in some way ensures

Figure 1. Corchorus olitorius L.

the viscosity of the printing paste. So, this natural dye was applied for the first time in this study on bleached cotton fabric by the screen printing process at semi-industrial scale. Two fixation methods were employed, steaming and thermofixation.

The effects of the thickener type, the dyestuff and urea concentrations according to thickener concentration, and the mordant type were investigated. The apparent viscosity of printing paste, the color, fastness and mechanical properties of printed fabric were analyzed and discussed.

EXPERIMENTAL

Textile material and chemicals used

Commercially bleached cotton fabric was supplied from (Ayed Company of Textile Trade, Tunisia). Technical features of the selected fabric were: twill weave; warp count, 16 ends per cm; weft count, 32 picks per cm; area density, 385.2 g m^{-1}; tensile strength through warp direction, 494.09 N m^{-2}; tensile strength through weft direction, 213.06 N m^{-2}.

Commercial grade *Corchorus olitorius* L. powder was used in this work as a natural dye for cotton printing. It was purchased from a local market in Tunisia.

Alum ([$KAl(SO_4)_2$], Fluka), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, Fluka), urea (CH_4N_2O, MOPCO, Egypt) and sodium bicarbonate ($NaHCO_3$, Fluka) were laboratory grade reagents and were used as received.

Sodium alginate (Bezema, Switzerland), carboxymethyl cellulose (CMC) (Jeniuschem, Italy) and commercial local *Ceratonia siliqua* L. flour were used as green thickeners. Tubicide TDM (Bezema, Switzerland) was used as an antifungal agent free of formaldehyde for printing pastes.

Preparation of printing paste

The stock paste of each thickener was prepared by slow sprinkling of 7% of natural thickener powder with distilled water under continuous stirring during 2 h in order to prevent lump formation.

For the preparation of the printing paste, 357.1 g of the thickening paste prepared previously was taken to add 20 g of the natural dye, 30 g of the mordant, 50 g of urea and 25 g of sodium bicarbonate with 4 g of the antifungal agent. Distilled water was added to this mixture until a total amount of 1 kg was reached. The preparation of the paste was carried out by an electric stirrer in a uniform manner. The paste was kept next to it and was ready for printing.

Apparent viscosity measurements

Apparent viscosity measurements of the printing pastes were carried out at 25 °C using a rheometer

(Rheotec RC30, France) equipped with the coaxial cylinder system CC14 DIN. This parameter is one of the key factors that can extremely affect the printing quality. Each experiment was performed in triplicate and results were given in terms of the mean value.

Cotton printing process

The prepared printing paste was applied to cotton fabric by using a semi-industrial scale table for screen printing processes (SILKB 480 Mathis AG, Switzerland). Then, after drying, two fixation methods were tested. In fact, the printed samples were treated either at 130 °C for 5 min by thermofixation method or at 102 °C for 30 min by steaming method. Next, the printed samples were washed with cold water at 40 °C for 10 min and then hot water at 60 °C for 5 min in order to remove the residual unfixed paste. Finally, they were rinsed well and air-dried at room temperature.

Color evaluation

Color evaluations of printed samples were based on the following colorimetric parameters: color strength (K/S), parameter $Integ(K/S)$ and the penetration percentage PP (%).

Color measurements of printed samples were carried out by a SpectraFlash SF300 colorimeter equipped with a DataMaster 2.3 software (Datacolor International, USA), using D65 light source and a viewing angle of 10°.

The color strength (K/S) values were calculated using the Kubelka-Munk equation [48,49]:

$$K / S = \frac{(1-R)^2}{2R} \tag{1}$$

where: R is decimal fraction of a reflectance of printed fabric; K is absorption coefficient; S is scattering coefficient.

$Integ(K/S)$ can provide an efficient colorimetric evaluation when the shades of printed fabrics vary according to experimental parameters. $Integ(K/S)$ is given by the following equation [50]:

$$Integ(K / S) = \sum E_\lambda \left(\frac{K}{S}\right)_\lambda \left(\overline{x_\lambda} + \overline{y_\lambda} + \overline{z_\lambda}\right) \tag{2}$$

where E_λ is the spectral energy distribution of the light source (D65/10°); $(K/S)_\lambda$ is the color strength of the printed fabric; $\overline{x_\lambda}, \overline{y_\lambda}, \overline{z_\lambda}$ are the CIE standard observer color matching functions.

The penetration percentage PP (%) was used to evaluate the depth of the dye across the textile surface. The penetration percentage value PP (%) of the printing paste was determined by using the following equation [51-53]:

$$PP(\%) = 100\frac{Integ(K / S)_b}{0.5(Integ(K / S)_f + Integ(K / S)_b)} \tag{3}$$

Where $(K/S)_f$ and $(K/S)_b$ are the color strength values of the front and back side of the printed fabric, respectively.

For all color measurements, each experiment was performed in triplicate and results were given in terms of the mean value.

Fastness testing

Fastness properties of printed fabrics were controlled with ISO standard methods. The specific tests concern colorfastness to washing (ISO 105-C02, 2010), colorfastness to light (ISO 105-B01, 2015) and colorfastness to rubbing (ISO 105-X12, 2016). In order to verify the reproducibility of results, each experiment related to fastnesses testing was performed in triplicate.

For washing fastness, the results were evaluated using the relation between the CIELAB color difference ΔE^*_{ab} and the gray scale fastness grade GS_C (Table 1), reported in ISO 105-A05 (1996) [54]. ΔE^*_{ab} was calculated between the washed and unwashed samples using the following CIELAB color difference equation [55]:

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{4}$$

Table 1. Relation between CIELAB color difference ΔE^*_{ab} and the grey scale fastness grade GS_C (ISO105-A05 (1996))

CIELAB color difference ΔE^*_{ab}	Grey scale fastness grade GS_C
ΔE^*_{ab} <0.40	5
0.40 ≤ ΔE^*_{ab} < 1.25	4.5
1.25 ≤ ΔE^*_{ab} < 2.10	4
2.10≤ ΔE^*_{ab} < 2.95	3.5
2.95 ≤ ΔE^*_{ab} < 4.10	3
4.10 ≤ ΔE^*_{ab} < 5.80	2.5
5.80 ≤ ΔE^*_{ab} < 8.20	2
8.20 ≤ ΔE^*_{ab} < 11.60	1.5
ΔE^*_{ab} ≥ 11.60	1

Mechanical properties evaluation

Mechanical properties of printed cotton fabrics were appreciated through the determination of the maximum force using the grab method. Before proceeding to mechanical evaluation, samples were stored under standard relative atmospheric conditions T = 20±2 °C, Hr = 65±4% for 24 h after washing.

Thus, the tensile strength levels of printed samples were measured according to ISO 13934-2, 1999(F), using tensile testing machine (LR5K, USA), with a crosshead speed of 100 mm min^{-1} and a load of 2.00 N. All experiments were performed in triplicate. The presented results were the mean values of the three experiments for each weft and warp direction.

RESULTS AND DISCUSSION

The nature and concentration of thickener, dyestuff and urea concentrations, the mordant type as well as the type of fixation method are the main operating conditions influencing the screen printing process. First, the effects of these parameters were studied on the print paste quality by measuring its apparent viscosity, then on the printed cotton fabrics performances by evaluating their color, fastness and mechanical properties.

Effect of the nature of thickener on printing quality

Effect on the apparent viscosity of print pastes

The main purpose of the thickener is to increase the viscosity of the printing paste. Consequently, the printing paste could be applied on the textile surface without bleeding or spreading and be capable of maintaining the design outlines. In this work, sodium alginate, carboxymethyl cellulose and *Ceratonia siliqua* L. flour were mixed with *Corchorus olitorius* L. powder as a natural dye, in the presence of alum or ferrous sulfate as mordants. First, the apparent viscosity of the printing pastes was measured. Results are mentioned in Figure 2.

In Figure 2, it was found that sodium alginate is the thickener that offers the most important values of apparent viscosity. In addition, apparent viscosity becomes more important, especially in the case of ferrous sulfate as a mordant (1346.67 mPa s^{-1}). However, *C. siliqua* L. flour gave poor values of apparent viscosity for both cases of mordant. In terms of thickening quality, the studied thickeners could be classified in the following order: sodium alginate > carboxymethyl cellulose > *C. siliqua* L. flour.

The obtained result can be explained by the important ability of sodium alginate to absorb a great amount of water and swell significantly in comparison to other thickening agents. However, *Ceratonia siliqua* L. flour is the thickener that presents the lowest swelling capacity.

Effect on the color and fastness properties of printed fabrics

In the screen printing process, the thickener may also improve the color strength and fastness properties of printed fabrics. So, the effect of thickener type on color properties and printing fastnesses were also investigated in this work. Likewise, using natural dyes, the mordant often fixes the dye and prevents discoloration of the surface of the textile material. In fact, mordant has the power to improve the fastness properties of printed samples. Besides, using different kinds of mordants with natural dyes, a variety of colors can be obtained [35]. In this study, color properties were appreciated by determining both the color strength and penetration percentage, whereas printing fastnesses were measured according to washing, rubbing and light. All the obtained results are summarized in Table 2 for both the steaming and thermofixation methods.

Table 2 shows that the color strength values obtained with sodium alginate are clearly higher for the two fixation methods. Moreover, the combination of sodium alginate with ferrous sulfate gave the highest color strength value compared to other results

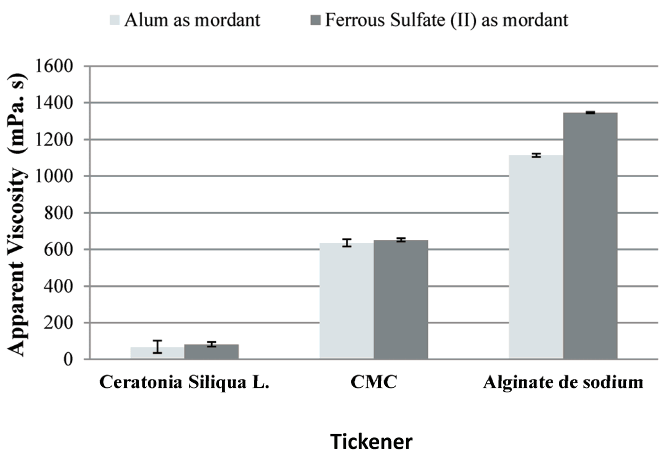


Figure 2. Effect of the type of thickener on apparent viscosity.

Table 2. Effect of thickener type on Integ color strength, penetration percentage and fastness properties of printed cotton fabrics

Fixation method	Thickener	Mordant type	Integ. color strength	Penetration %	Washing fastness (ISO 105-C02)	Rubbing fastness (ISO 105-X12)		Light fastness (ISO 105-B01)
						Dry	Wet	
Steaming	CMC	Without mordant	0.43±0.07	14.61±0.083	1.5	2-3	2	4
		Alum	0.89 ±0.065	28±0.8	2.5	4-5	4-5	5
		Ferrous sulfate (II)	4.08±0.167	13±0.4	3.5	4-5	4	7
	Sodium alginate	Without Mordant	0.29 ±0.064	39.93±0.34	1	2-3	2	4
		Alum	0.97±0.045	27±0.3	1.5	4-5	3-4	3
		Ferrous sulfate (II)	4.90±0.104	11±0.07	1	4-5	3	6
	Ceratonia siliqua L.	Without mordant	0.59 ±0.059	21.64±0.09	1.5	3	2	2
		Alum	0.81±0.030	36±0.5	1	4-5	3-4	2
		Ferrous sulfate (II)	1.79±0.025	23±0.1	2.5	4-5	4	5
Thermofixation	CMC	Without mordant	0.20±0.11	34.94±0.37	1	2	2	3
		Alum	0.87±0.031	20±0.2	2	4-5	4	4
		Ferrous sulfate (II)	3.78±0.118	11±0.2	2	3-4	3	6
	Sodium alginate	Without mordant	0.26 ±0.037	67.83±0.134	1	2	1-2	3
		Alum	0.64±0.043	29±0.7	1	4	3-4	3
		Ferrous sulfate (II)	4.37±0.126	10±0.2	2	3-4	2-3	5
	Ceratonia siliqua L.	Without mordant	0.62±0.04	24.87±0.34	1	2-3	2	2
		Alum	0.81±0.030	35±0.6	1	4	3	4
		Ferrous sulfate (II)	2.27±0.203	15±1.2	1.5	4	3-4	6

obtained with alum. All samples treated with alum underlined color strength values less than 1. It causes this mordant to be poorly suited using *C. olitorius* L., whatever the thickener studied.

Color strength also shows a big dependency on the used fixation method. Printed fabrics fixed by steaming showed a slight improvement of color strength. Indeed, steaming of natural dye prints is a process involving dyestuff penetration [56]. The condensed water vapor accelerates the penetration of the dye molecules into the textile surface, from where an increase in the color strength of the printed fabrics fixed by the steaming is observed, compared to those fixed by the thermofixation method [33]. As can be shown in Figure 3, the steaming process introduces hot vapor to the cellulosic micro-vacuums leading to a swelling phenomenon. Swelled cellulose allows better interactions with the paste. By swelling, the cellulose conformation becomes more regular and leading to a better deposition of the paste. In this study, the penetration percentage evolution in function of thickener type or mordant type shows a reversed behavior since this parameter decreases for higher color strength.

Besides, results indicate that washing fastness depends directly on the type of thickener and mordant, but the influence of the fixation method is more remarkable. In fact, washing fastness results are closely related to the interactions that could be created after printing. These interactions are ensured by mordant which may act as mediator between natural dye and hydroxyl groups of the cellulosic material. The selected fixation method is also crucial in this case. For all experiments, the fixation by steaming showed better washing fastness results. As presented in Figure 3, this may be attributed to the easier penetration of natural dyestuff into cotton vacuums, which became more accessible after swelling by steaming treatment [33].

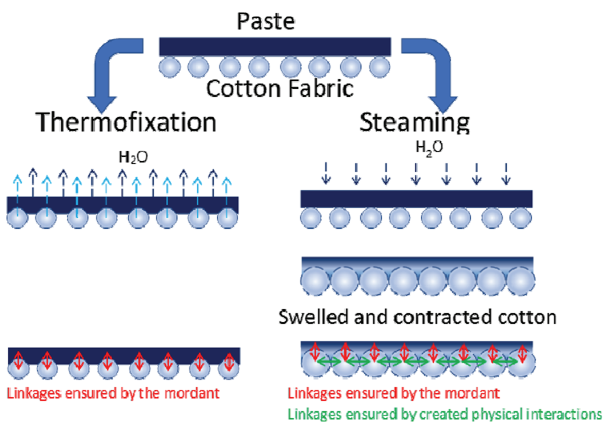


Figure 3. Influence of the fixation process (steaming or thermofixation) on the behavior of paste fixation.

Carboxymethyl cellulose demonstrated the highest washing fastness compared to the other two thickeners studied. These results are acceptable. Likewise, the sample treated with ferrous sulfate and steaming possessed the most interesting washing fastness which is of the order of 3.5. From these results, it can be concluded that the selection of suitable thickener depends on the type of mordant used in the printing paste and the selected fixation method.

Although sodium alginate is widely used in the industry, results obtained with carboxymethyl cellulose as thickener allow a slight improvement in rubbing and light fastness as presented in Table 2. Results indicate also that dry rubbing fastness could be as high as grade 4, while wet rubbing fastness is in the range of 3 to 4-5 for alum regardless of method of fixation used. For ferrous sulfate experiments, the results show that dry rubbing fastness could be as high as grade 3-4, while wet rubbing fastness is in the range of grade 2-3 to 4. This implies that the type of thickener and mordant have a slight effect on rubbing fastness. For light fastness, the obtained grades are given in Table 2 which should be considered with great importance because natural dyes are well known by their insufficient light fastness levels [57]. This presents one of the most important limitations of natural dyes in dyeing processes. Surprisingly, in our case, printing with *C. olitorius* L. gives good results. This may be attributed to the synergistic effect of paste components. In fact, the interactions between the components of the printing paste and the interactions between these components and cotton cellulose may create a printed surface which is more stable towards light than the natural dye when the latter is applied alone on textile fabric.

Taking into account the evolution of the color strength and the fastness properties, the results presented in Table 2 show that the depth of the printing paste on the textile material is related to the type of the thickening agent in terms of chemical composition, rheological properties and molecular weight [58]. It can also be noted that fastness results could be considered as sufficient if only washing and rubbing fastness values are higher than 3-4. For light fastness, the value should be higher than 5. All these interpretations were deduced from printing factories and they are appropriate only for the clothing sector.

Effect on the tensile strength of printed fabrics

Following the determination of color strength and fastness properties, the tensile strength through the weft and warp directions of printed cotton fabrics was also studied. The obtained values are reported in Figure 4a and b, respectively.

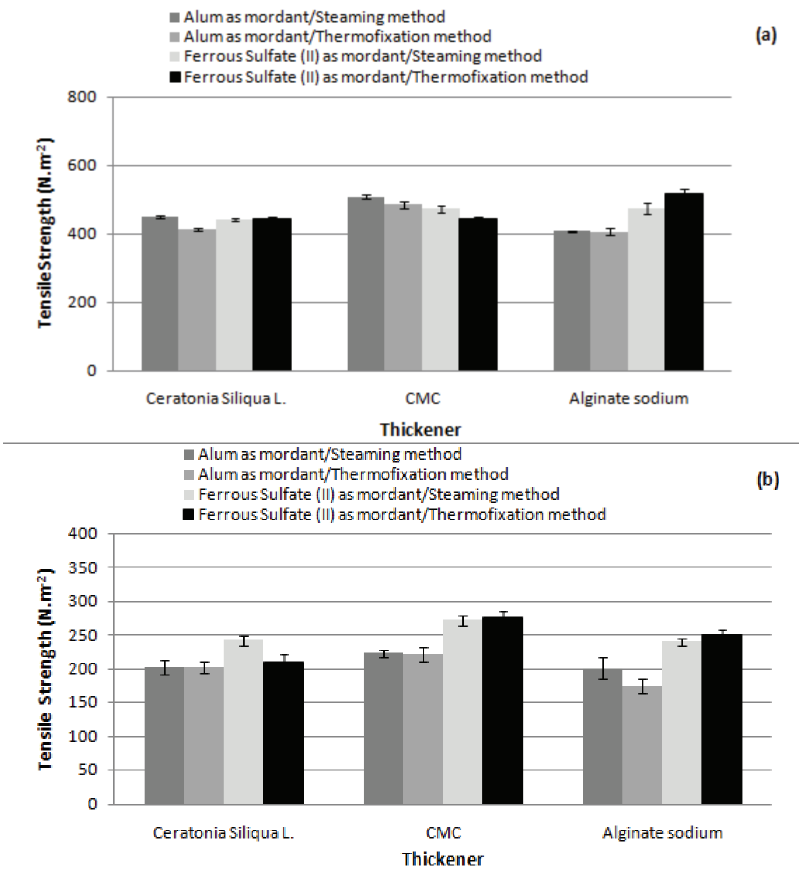


Figure 4. Effect of the type of thickener on fabric tensile strength: a) warp direction; b) weft direction.

From these figures, it can be observed that printed fabrics with sodium alginate and CMC emphasize generally remarkable tensile strength values compared to those of *C. siliqua* L. flour. Taking into account that the initial tensile strength through the warp direction is equal to 494.09 N m^{-2} and the initial tensile strength through the weft direction is equal to 213.6 N m^{-2}, the tensile strength decreases generally for many fabrics printed with *C. olitorius* L. according to the tensile strength of unprinted fabric. For example, in the warp direction, and in the presence of alum, sodium alginate showed a decrease of about 17% for both fixation methods. Similarly, for the weft direction, sodium alginate (alum, thermofixation method) and CMC (alum, steaming method) caused fabric degradations of 17 and 16%, respectively.

However, an increase of the tensile strength is observed in some cases, especially with sodium alginate, irrespective of the fixation method (ferrous sulfate, weft direction).

Related to all printing qualities investigated until now, results with CMC and ferrous sulfate were the most encouraging which will be considered for the next printing experiments.

Effect of dye concentration on printing quality

The amount of natural dye was varied from 0, 5, 10, 20, 30 and 40 g Kg^{-1} in the tested printing pastes. The apparent viscosity, color strength, penetration factor, fastness properties and mechanical properties (tensile strength) were the evaluation parameters of printing quality.

Effect on the apparent viscosity of print pastes

The results of apparent viscosity are plotted in Figure 5. This figure shows that as the dye amount increases, the apparent viscosity decreases for all tested mordants. This result seems obvious since the amount of dye was varied according to the amount of thickener, *i.e.*, when the amount of dye increases, the amount of thickener decreases. Consequently, the apparent viscosity decreases too. On the other hand, the values of the apparent viscosity of the printing pastes containing ferrous sulfate are slightly higher than those of alum. The results described elsewhere, showed also that the use of ferrous sulfate allows more stable conditions [59].

Effect on the color and fastness properties of printed fabrics

Table 3 shows the effect of dye concentration on the color strength, penetration percentage and fastness properties of printed cotton fabrics for both steaming and thermofixation methods. The *Integ*(*K*/*S*) values presented in Table 3 note that as the dye concentration increases in the printing paste, the amount of dye entering into the fiber increases and consequently, the color strength increases too. Generally, the increase of dye concentration is related to the increase of the availability of dye molecules in the printing paste. Thus, the fixed dye on the surface of textile support rises and the color strength becomes more important [60]. The *Integ*(*K*/*S*) values increase rapidly as the concentration of natural dyestuff increases from 0 to 20 g kg^{-1} of the weight of printing paste regardless of the type of mordant or the fixation method. For dye concentrations higher than 20 g kg^{-1}, the *Integ*(*K*/*S*) values decrease, because there was an significant loss of dye during washing of the printed samples.

Results of washing fastness are also given in Table 3 which show that generally higher dye concentrations made washing fastness lower. This is probably because of the lack of accessible sites on the surface of textile support. In addition, and as found before, the steaming fixation method allowed better fastness results. The same observation is noted for rubbing fastness. However, light fastness results

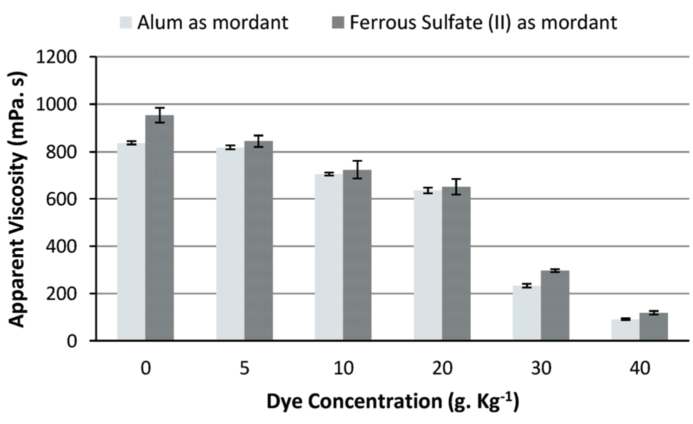


Figure 5. Effect of the dye concentration on apparent viscosity.

Table 3. Effect of dye concentration on Integ color strength, penetration percentage and fastness properties of printed cotton fabrics

Fixation method	Dye concentration g kg^{-1}	Mordant type	Integ. color strength	Penetration %	Washing fastness (ISO 105-C02)	Rubbing fastness (ISO 105-X12)		Light fastness (ISO 105-B01)
						Dry	Wet	
Steaming	0	Alum	0.51±0.049	31±3.9	4.5	4-5	4	2
		Ferrous sulfate (II)	2.35±0.282	26±3.7	3	4-5	4	3
	5	Alum	0.54±0.053	30±2.9	2.5	4-5	4-5	3
		Ferrous sulfate (II)	2.64±0.109	18±0.8	3	4-5	4	6
	10	Alum	0.57± 0.069	28±2.9	2	5	5	3
		Ferrous sulfate (II)	3.66±0.243	17±0.3	2.5	4-5	4	4
	20	Alum	0.89±0.065	28±0.8	2.5	4-5	4-5	5
		Ferrous sulfate (II)	4.08± 0.167	13±0.4	3.5	4-5	4	7
	30	Alum	0.84±0.049	25±2.6	2	4-5	4	5
		Ferrous sulfate (II)	3.98±0.129	13±0.4	3.5	4	3	7
	40	Alum	0.65±0.076	28±3.1	1.5	4	3	2
		Ferrous sulfate (II)	3.12±0.279	14±1.3	3.5	3-4	3	6
Thermofixation	0	Alum	0.21±0.043	60±8.9	1.5	5	5	2
		Ferrous sulfate (II)	1.19±0.123	28±2.5	1	4	3	3
	5	Alum	0.23±0.017	50±3	1.5	4-5	4	2
		Ferrous sulfate (II)	1.65±0.055	25±1.3	2.5	4	3-4	5
	10	Alum	0.46±0.041	33 ±3	2	4-5	4	2
		Ferrous sulfate (II)	3.18±0.266	15±1.3	2	4-5	4	3
	20	Alum	0.87± 0.031	20±0.2	2	4-5	4	4
		Ferrous sulfate (II)	3.78± 0.118	11±0.2	2	3-4	3	6
	30	Alum	0.81±0.039	23±1.4	2	4-5	4	3
		Ferrous sulfate (II)	3.50±0.095	13±0.6	2	4	3	6
	40	Alum	0.53±0.019	38±3.2	1	4	3	3
		Ferrous sulfate (II)	2.73±0.118	13±0.5	1.5	3	2-3	5

reach 7 for high dye concentrations (20 and 30 g kg^{-1}) and with ferrous sulfate. As noted above, the samples printed in the presence of ferrous sulfate, showed significant fastness properties compared to those printed with alum. This may be explained by iron, which is able to form a rigid complex with both cellulose cotton fiber and natural dye. It seems that this complex is more stable towards light than that of aluminum.

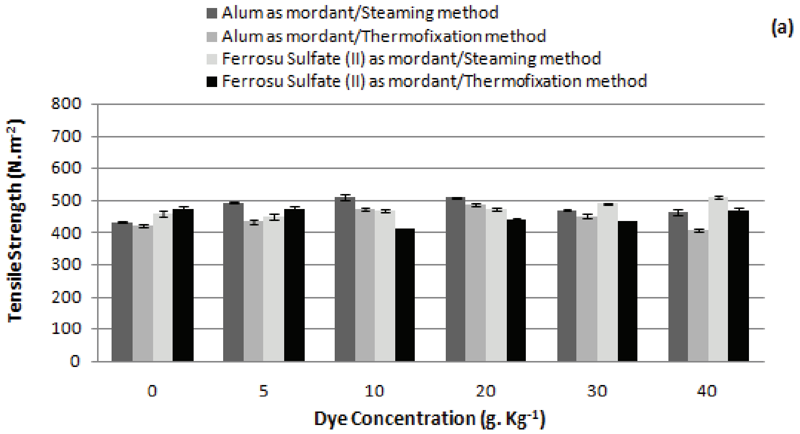
Effect on the tensile strength of printed fabrics

Otherwise, the tensile strength of printed samples was performed in order to evaluate the effect of variation of dye amount through the thermofixation and steaming methods on the fabric structure. The results obtained for this parameter are presented in Figure 6.

From Figure 6, it can be seen that the tensile strength values of different printing samples are around 409 and 511 N m^{-2} in the warp direction, whatever the fixation method used. In this direction, the dye amount of 40 g kg^{-1} presents the most important fabric degradation in the case of alum and with the thermofixation method. This fabric degradation is of the order of 17%. Likewise, the tensile strength studied in the weft direction showed slight decrease, with the exception of the dye amounts of 20 and 40 g kg^{-1}. In fact, the fabric degradation is of the order of 16% for 20 g kg^{-1} for alum using the thermofixation method. The amount of dye of 40 g kg^{-1} underlines fabric degradations of the order of 23% in the steaming method and a second one of the order of 36% in the heat setting.

Effect of the urea amount on printing quality

Urea is an essential auxiliary in the printing paste formulations. It can increase the dye solubility in water and so enhance the color brightness and color intensity [34]. Indeed, the fibers will swell, thanks to the action of this auxiliary, making easier the capillarity penetration of pastes [34]. For these reasons, the effect of the urea amount was also studied by varying its concentration from 0 to 150 g kg^{-1} of the weight of printing paste.



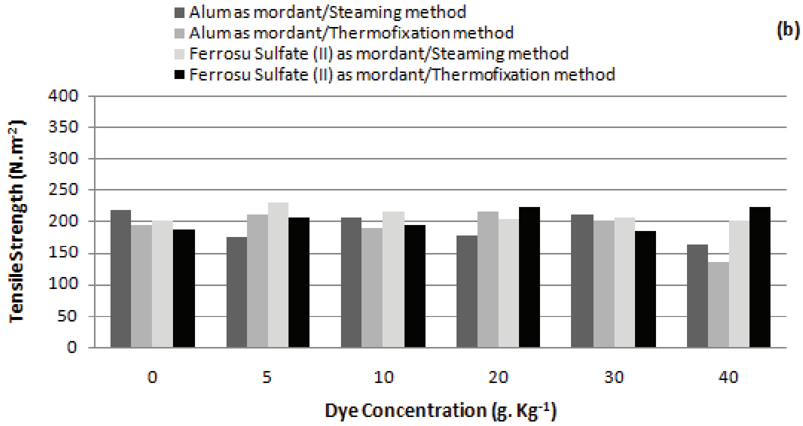


Figure 6. Effect of the dye concentration on fabric tensile strength: (a) warp direction; (b) weft direction.

Effect on the apparent viscosity of print pastes

Figure 7 shows the effect of the urea concentration on apparent viscosity. It was observed that the apparent viscosity values increase rapidly as the urea amount in the printing paste increases from 0 to 150 g kg^{-1} of the weight of printing paste. This result is also expected since the amount of urea was varied according to the amount of water.

Effect on the color and fastness properties of printed fabrics

From Table 4, it can be seen that for both mordants, ferrous sulfate and alum, when the urea amount increases from 0 to 50 g kg^{-1}, the color strength and wash fastness increase, but the penetration percentage decreases. This behavior becomes much more important in the case of experiments done with ferrous sulfate and fixed by steaming. This result may be attributed to the role of urea, which is a

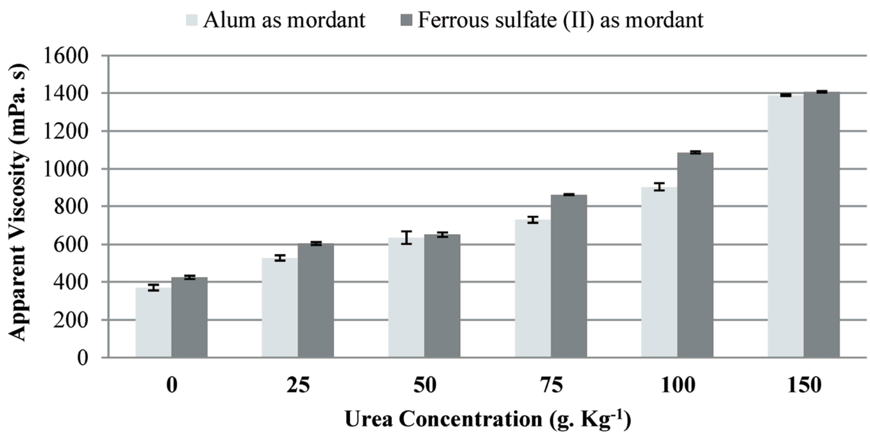


Figure 7. Effect of the urea concentration on apparent viscosity.

Table 4. Effect of urea concentration on Integ color strength, penetration percentage and fastness properties of printed cotton fabrics

Fixation method	Urea concentration g kg^{-1}	Mordant type	Integ. color strength	Penetration %	Washing fastness (ISO 105-C02)	Rubbing fastness (ISO 105-X12)		Light fastness (ISO 105-B01)
						Dry	Wet	
Steaming	0	Alum	0.44±0.041	43±1.9	2	4	3-4	3
		Ferrous sulfate (II)	0.98±0.040	21±0.7	3	4	3-4	5
	25	Alum	0.76±0.037	28±5.6	1	4	4	2
		Ferrous sulfate (II)	1.493±0.144	13±1.3	2.5	4-5	4	6
	50	Alum	0.89±0.065	28.5±0.8	2.5	4-5	4-5	5
		Ferrous sulfate (II)	4.08± 0.167	13±0.4	3.5	4-5	4	7
	75	Alum	0.99±0.065	15±0.5	3	4	4	2
		Ferrous sulfate (II)	1.74±0.055	19±0.6	3	4-5	3-4	7
	100	Alum	0.80±0.039	19±0.8	1.5	4	4	3
		Ferrous sulfate (II)	0.71±0.051	23±2.2	2	4-5	4	7
	150	Alum	0.70±0.034	21±1.1	1.5	4	3-4	4
		Ferrous sulfate (II)	0.67±0.065	22±1.9	2	4	3	6
Thermofixation	0	Alum	0.44±0.010	43±2	1	3-4	3	2
		Ferrous sulfate (II)	0.84±0.051	43±1.4	2.5	4	3	4
	25	Alum	0.62±0.013	14±2	1.5	4-5	4-5	2
		Ferrous sulfate (II)	1.42±0.082	34±0.7	1.5	4	3	5
	50	Alum	0.87± 0.031	0.20±0.002	2	4-5	4	4
		Ferrous sulfate (II)	3.78± 0.118	11± 0.2	2	3-4	3	6
	75	Alum	0.62±0.060	12±2	2.5	4	4	3
		Ferrous sulfate (II)	1.50±0.035	23±0.3	2.5	4	3-4	5
	100	Alum	0.44 ±0.050	27±3	1	4-5	3	2
		Ferrous sulfate (II)	0.59±0.050	31±2	1.5	4	3-4	6
	150	Alum	0.31±0.021	35±2.3	1.5	3-4	3	2
		Ferrous sulfate (II)	0.39±0.035	42±3.2	2	3-4	3-4	5

humectant agent. Indeed, urea can create a eutectic mixture with water. The increase of the urea amount enhanced the swelling of cotton fibers, especially during steaming fixation and so increased the dye solubility. Moreover, using a urea concentration between 50 and 75 g kg^{-1}, the highest color strength and consequently the lowest penetration percentage values are reached with both ferrous sulfate and alum, for the two methods of fixation. After that, a decline of color yield can be observed for higher urea concentrations. This can be attributed to the difficult spreading of paste due to the hygroscopic behavior of urea, making slower the solubility of the whole paste. So, this may make the diffusion of dye molecules more difficult.

Best washing fastness results (Table 4) are also noted for this interval of urea concentration regardless of the fixation process or the mordant type used. However, the influence of these parameters on rubbing fastness is not clear. For light fastness results, an significant influence of mordants can be noticed. With ferrous sulfate, light fastness reached higher performances.

Effect on the tensile strength of printed fabrics

A comparison of the tensile strength values of fabrics printed with *C. olitorius* L. in both warp and weft directions according to the variation of the urea amount is shown in Figure 8. The fabric degradation through the warp direction is not important, except for the urea quantity of 150 g kg^{-1}. This urea amount underlines fabric degradation in the case of alum with a percentage of 17% for the steaming method and 24% for the thermofixation method. However, the fabric degradation through the weft direction is extremely important. For 75 g kg^{-1} of urea, the tensile strength of cotton fabric printed with ferrous sulfate and using the steaming method decreased by a percentage of 35%. Using an amount of urea equal to 100 g kg^{-1} and in the presence of alum as a mordant, the fabric degradation reached 38 and 22% for the steaming and thermofixation methods, respectively. It also reached 17% for ferrous sulfate in the case of the thermofixation method.

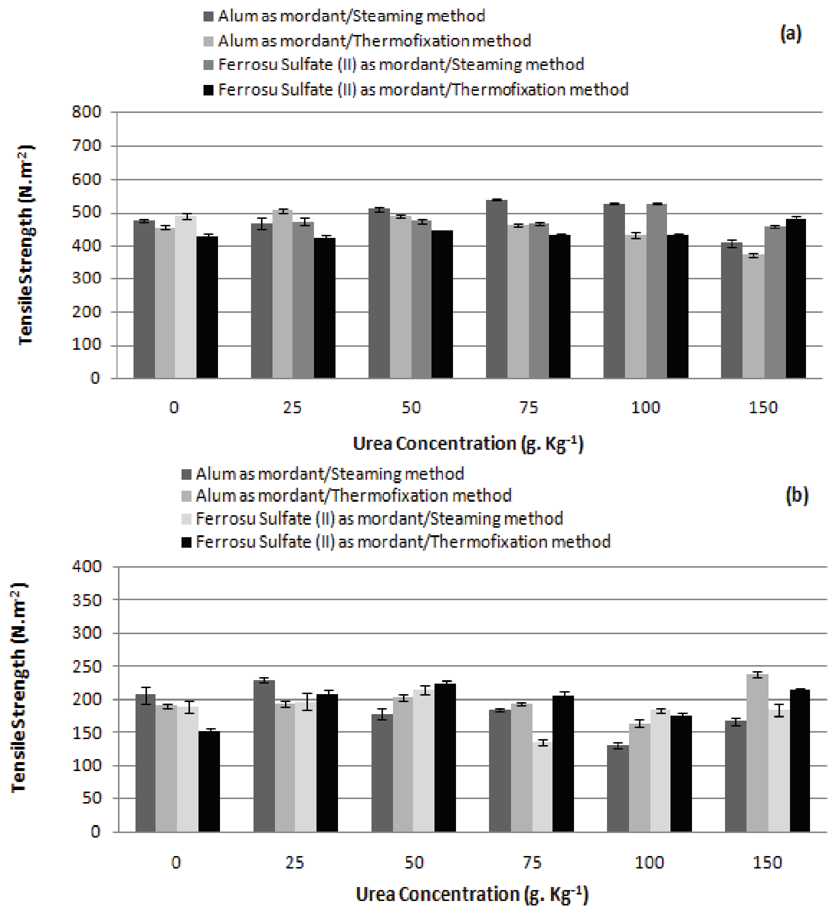


Figure 8. Effect of the urea concentration on fabric tensile strength: (a) warp direction; (b) weft direction.

CONCLUSION

In this study, the potential application of a new natural dye *Corchorus olitorius* L. leaves in the screen printing process of cotton fabrics was investigated in order to solve ecological and toxicological problems related to some of synthetic dyestuffs. For this aim, thickener type, dye and urea concentration, mordant type and fixation method were varied and studied.

Printing results showed a big dependency on the thickener type, the dye and urea concentrations. Among all the tested greener thickeners, carboxymethyl cellulose exhibited generally better results in terms of color strength, penetration percentage, fastness properties and mechanical properties.

The most stable prepared printing paste leading to the best apparent viscosity was obtained with sodium alginate. According to the obtained color strength values, 20 g kg^{-1} of dye and 50 g kg^{-1} of urea was selected as the optimum concentration of printing paste.

Results also showed that the samples printed and fixed by steaming method gave higher color strength. Fastness properties of samples printed have been good. A remarkable light fastness can reach the order of 7 for some conditions, especially with ferrous sulfate.

All theses discussed, using the new proposed natural dye, were confirmed on a semi-industrial scale.

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NAUČNI RAD

ČIST PROCES ŠTAMPANJA PAMUKA PRIRODNIM BOJIMA: UTICAJ KOMPONENTA PASTE NA PERFORMANSE ŠTAMPE

Nova prirodna boja dobijena iz Corchorus olitorius L. korišćena je u pripremi štamparskih pasta za sitoštampu pamučnih tkanina. Da bi se obezbedilo ekološko štampanje, korišćena su" zelenija" sredstva za zgušnjavanje, kao što su: natrijum-alginat, karboksimetil celuloza i brašno Ceratonia silikua L. Istražena je priroda i koncentracija zgušnjivača, koncentracije bojila i uree, tip močila i način fiksiranja. Kvalitet štampanog pamučnog platna ocenjen je određivanjem različitih parametara: jačine boje, procenta prodiranja, brzine štampe i mehaničkih svojstava, dok je kvalitet paste za štampu ocenjen merenjem njene prividne viskoznosti. Veća koncentracija boje koja se koristi u štamparskoj pasti dovela je do bolje prividne viskoznosti i jačine boje. Povećanje koncentracije uree poboljšalo je jačinu boje, ali smanjilo prividnu viskoznost štamparske paste. Najbolji rezultati viskoznosti (1347 mPa s) i čvrstoće boje (4,90) dobijeni su upotrebom gvožđe(II)-sulfata kao močila i natrijum-alginata kao zgušnjivača. Dobijene nijanse boja varirale su od zelene do smeđe. Postignuta je dobra postojanost boja, ali je to zavisilo od primenjenih eksperimentalnih uslova.

Ključne reči: prirodne boje, čistiji postupak štampe, pamučne tkanine, komponente paste, efekat komponenata, kvalitet štampe.