

## SONICATION AND CONVENTIONAL DYEING PROCEDURES OF FLAX FIBRES WITH *ALLIUM CEPA* ANTHOCYANIN EXTRACT

DIANA COMAN,\* SIMONA OANCEA,\* NARCISA VRÎNCEANU\*<sup>\*\*</sup> and MIHAELA STOIA\*

\*“Lucian Blaga” University of Sibiu, 10 Victoriei Bd., 550024 Sibiu, Romania

\*\*“Alexandru I. Cuza” University of Iași, 11 Carol I Street, 700506, Iași, Romania

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The aim of this paper was to improve the dyeability of flax fibre substrates by a previous modification *via* their grafting and explore the mechanism of such an improvement.

The comparative results of the dyeing efficiency of grafted flax fabrics, using both ultrasound and conventional dyeing methods, are presented. The dyeing process involved the use of a natural red dye extracted from red onion (*Allium cepa*). Morphological, structural and chemical properties of the obtained samples were examined, in terms of a co-assisted investigation system: scanning electron microscopy (SEM) images for the morphology and energy-dispersive X-ray spectroscopy (EDX) analysis for surface composition.

The obtained results showed the superiority of sonication dyeing over the conventional dyeing procedure. Moreover, the research emphasizes the idea of the mesoporosity of the inclusion complex formed by encapsulating dye molecules inside the cavity of monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD).

**Keywords:** flax textile support, anthocyanin extract, morphology, natural dye, ultrasonication, colour fastness

### INTRODUCTION

In view of the increasing awareness of health and environment safety, naturally dyed textile products are gaining more popularity, leading to the improvement of their competitiveness on commercial markets.<sup>1,2</sup>

As the uniformity of dyed materials mainly depends on the efficiency of fabric preparatory processes, different studies regarding solvent dyeing with various dyes used on several textile substrates have been carried out. Having inherent limitations, these methods are not commercially viable.<sup>3</sup>

The poor dyeability of flax fibre by natural dyes has been reported.<sup>4</sup> The main reason of the dyeing difficulty was the higher crystallinity and orientation index of flax fibre and the lower rate of dye-uptake resulting from the poor permeation of the dye molecules into the fibre. To surpass this problem, a number of studies regarding different modifications have been carried out in order to improve the levels of dye exhaustion.<sup>5-7</sup> In addition, a lot of studies reported that modifying the flax fibre *via* the inclusion of quaternary ammonium groups, epoxy quaternary ammonium salt, or grafting with acrylonitrile, *N*-hydroxymethyl acrylamide amide, could remar-

kably enhance the dyeability of the flax fibre.<sup>8,9</sup> Our study is an attempt to combine the advantages of surface modification of textile supports by grafting and of their dyeing with a red onion anthocyanin extract, by using a non-conventional method, such as ultrasounds.

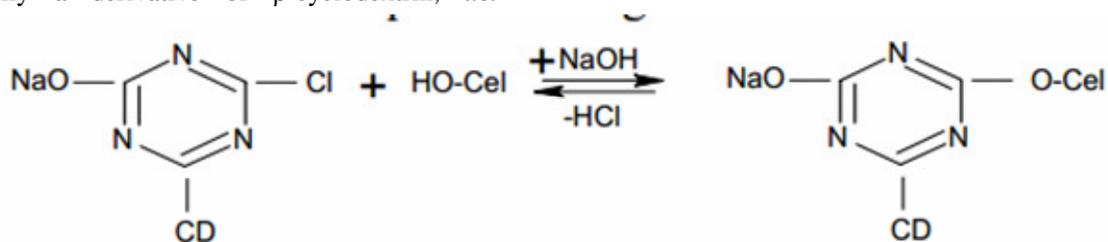
The present work focused on a new approach to dyeing as a natural alternative method that was proven to be environmentally friendly.

Today, given the decreasing prices of electronic components, one can reasonably consider the industrial application of ultrasounds in dyeing processes. The use of ultrasounds in textile dyeing is based on the absorption of the ultrasound waves by the liquid system and on the cavitation phenomenon that takes place.<sup>10</sup>

In the case of water soluble dyes, ultrasound constitutes an effective means of mechanical agitation and the frequency of the ultrasound affects the dyeing results. The most effective proved to be frequencies ranging between 22 and 175 KHz, the latter being preferable for silk, wool and nylon. According to the literature, ultrasounds of 40 kHz frequency determine the highest colour intensity. Furthermore, dyeing carried out at a low temperature in the ultrasonic

field showed an adsorption equivalent to that achieved in dyeing without ultrasound at a higher temperature.<sup>10-19</sup>

At this point, monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD) has been used due to its properties to react with the hydroxyl groups of cellulose through its anchor group – monochlorotriazinyl. Consequently, MCT- $\beta$ -CD becomes covalently bound onto the fibre surface. Some researchers reported the ability of hydrophobic MCT- $\beta$ -CD's cavity to form inclusion complexes with dyes based on their selectivity.<sup>12-18</sup> In order to simplify the graphs, the notation MCT- $\beta$ -CD has been used, which is actually a derivative of  $\beta$ -cyclodextrin, *i.e.*



In the present investigation, we have selected red onions as a good source of anthocyanin pigments for textile dyeing. The first objective of our work was to explore the mechanism of improving the dyeability of flax *via* a previous grafting treatment by using MCT- $\beta$ -CD. The methods of bath and ultrasound-dyeing were used to dye the lignocellulosic supports.

The possibility of formation of an inclusion complex (composite) between red onion anthocyanin dye and MCT- $\beta$ -CD, and the effect of the inclusion complex on the colour fastness of MCT- $\beta$ -CD textile support dyed with the natural extract, have been studied.

The originality of the research relies on the coupling of both effects: of the inclusion complex (composite) between red onion anthocyanin dye and MCT- $\beta$ -CD, and of applying the sonication dyeing procedure.

Techniques, such as scanning electron microscopy coupled with an energy-dispersive X-ray spectroscopy (EDX analysis) and X-ray diffraction (XRD), were applied here to evaluate the composite (onion anthocyanin dye – MCT- $\beta$ -CD – textile support).

The present paper continues an initial study by the same authors on natural dyeing with anthocyanin extracts by both standard and sonication procedures onto lignocellulosic supports.<sup>23</sup>

monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD). They have a toroidal shape with a hydrophobic central cavity and a hydrophilic outer surface, where the hydroxyl groups are located.<sup>20</sup> Besides, the inclusion compound of MCT- $\beta$ -CD helps the penetration of the natural dye and also affects the depth to which the penetration takes place in the fabric.<sup>17-21</sup> The host-guest interactions of MCT- $\beta$ -CD have been demonstrated with significant applications in the textile field.<sup>22</sup>

The grafting of MCT- $\beta$ -CD on the cellulosic support takes place according to the reaction below:

## EXPERIMENTAL

### Materials and methods

Twill 100% flax supports, each sized 3 cm  $\times$  3 cm, with a yarn count of 40/2 tex and specific mass of 200 g/m<sup>2</sup> and MCT- $\beta$ -CD (CAVAMAX<sup>®</sup>, Wacker Chemie AG) were used. Ethanol (from Chemical Company) of purity grade was also used in this experiment.

The dyeing colour coordinates (L\*, a\*, b\* values) of the dyed lignocellulosic fabrics were obtained using a Flash SF300 Spectrophotometer from DataColor company with a D65 illuminant used to make software guided measurements.

FT-IR spectroscopy measurement was performed on an FTIR JASCO 660+ spectrometer. The XPS analysis was carried out using an XPS PHI 5000 VersaProbe ( $\Phi$  ULVAC-PHI, INC., Thermo Fisher Scientific Co. Ltd).

The ultrasound device (CREST 575D, LG Electronics Tianjin Appliances Co. Ltd, China) was used for dyeing the lignocellulosic fabrics.

### Extraction and assay of red onion anthocyanins

Red onion (*Allium cepa*) samples grown in Sibiu, Romania, were purchased and used in the present investigation.

The extraction of anthocyanins from selected samples was conducted in 70% ethanol solution (v/v) for 2 hours at 4 °C, followed by centrifugation at 8000 rpm, at 4 °C. The content of total anthocyanins was determined by the spectrophotometrical pH differential method.<sup>24</sup> The NF800R refrigerated centrifuge (HT) and the T80 UV-Visible spectrophotometer (PG Instruments Ltd.) were used. Total anthocyanins were

expressed as cyanidin-3-O-glucoside in milligrams  $100 \text{ g}^{-1}$  fresh weight ( $\text{mg } 100 \text{ g}^{-1} \text{ FW}$ ). The content of total anthocyanins in red onions was determined as  $38 \text{ mg } 100^{-1} \text{ g FW}$ .

#### Fabric treatment procedure

##### *Grafting of flax fibre support (Procedure of MCT- $\beta$ -CD pretreatment of flax fibres)*

The grafting treatment was carried out at a liquor ratio of 1:10 with MCT- $\beta$ -CD and  $\text{Na}_2\text{CO}_3$

The treatment consisted in the following phases:

- impregnating the fabric with MCT- $\beta$ -CD ( $100 \text{ g/L}$ ) and  $\text{Na}_2\text{CO}_3$  ( $25 \text{ g/L}$ ) solution ( $x/4$ ,  $x$  is the amount of MCT- $\beta$ -CD) for 2 minutes, followed by a padding stage at a squeezing ratio of 135%; the impregnations was performed on a Benninger (Switzerland) type padder, at a speed of 50 m/min, hydro-extraction pressure of 0.5 bars, level of liquid extraction of 150%, temperature of  $20 \text{ }^\circ\text{C}$ , width of 1200 mm;
- drying for 10 minutes at  $80 \text{ }^\circ\text{C}$  (on Mesdan Lab Dryer);
- curing (using a Mesdan Lab Dryer) at  $160 \text{ }^\circ\text{C}$  for 7 minutes;
- repeated hot ( $90 \text{ }^\circ\text{C}$ ) and cold washing up to  $\text{pH} = 6.5\text{-}7$  to remove the reaction products;
- drying at room temperature ( $22 \text{ }^\circ\text{C}$ ) for 72 hours.<sup>25,26</sup>

The samples were thoroughly rinsed with water and dried.

#### Dyeing procedures

##### *Bath-dyeing procedure (standard)*

Bath-dyeing was done with an *Allium cepa* anthocyanin extract. The liquor ratio was 1:30 and 10 g

of flax fabrics was used as a textile material for all dyeing experiments. The dye bath concentrations were 1 and 2%. The lignocellulosic fibre support was dyed at  $80 \text{ }^\circ\text{C}$  for about 30 min in the dye bath. Higher temperatures may affect the stability of the natural pigments.

The dyed flax supports were washed with a soap solution for several minutes and air-dried at room temperature.

##### *Ultrasound-dyeing procedure*

An Elmasonic E Ultrasonic bench top cleaner bath, model S10H, with a capacity of 0.8 L and internal dimensions of  $190 \times 85 \times 60 \text{ mm}$ , was used. The experimental setup used was composed of an electrical generator at a frequency of 38.5 kHz and power of 50 W. Ultrasonic dyeing was carried out in 100 ml water, using a concentration of the anthocyanin dye from *Allium cepa* at a liquor ratio of 1:30, for about 15 min, at  $30 \text{ }^\circ\text{C}$ . The dye concentration was 1 and 2%.

The description of the obtained specimens is presented in Table 1.

In order to characterize the surface morphology and chemical consistency of the treated/dyed supports, the system of instrumental methods described below has been utilized. Moreover, appropriate analytical techniques were used, the results revealing coherent and specific characteristics of the obtained eco-textiles, in terms of morphology, molecular and surface structure, porosity, as well as colour strength and fastness.

Table 1  
Specifications and description of prepared samples

Sample name and code	Description
	Flax fibre supports
F	Reference flax fibers – non-functionalized flax fibre support (without MCT- $\beta$ -cyclodextrin)
F-MCT- $\beta$ -cyclodextrin	Flax fiber support functionalized/grafted with MCT- $\beta$ -cyclodextrin
Sample 1	Flax fiber support functionalized with MCT- $\beta$ -cyclodextrin and dyed by the exhaustion method with 1% solution of <i>Allium cepa</i> natural extract
Sample 2	Non-functionalized flax fiber support, dyed by the exhaustion method with 1% solution of <i>Allium cepa</i> natural extract
Sample 3	Flax fiber support functionalized with MCT- $\beta$ -cyclodextrin and dyed by the exhaustion method with 2% solution of <i>Allium cepa</i> natural extract
Sample 4	Non-functionalized flax fiber support, dyed by the exhaustion method with 2% solution of <i>Allium cepa</i> natural extract
Sample 5	Non-functionalized flax fiber support, dyed by the ultrasonication method with 1% solution of <i>Allium cepa</i> natural extract
Sample 6	Flax fiber support functionalized with MCT- $\beta$ -cyclodextrin and dyed by sonication with 1% solution of <i>Allium cepa</i> natural extract
Sample 7	Non-functionalized flax fiber support, dyed by the ultrasonication method with 2% solution of <i>Allium cepa</i> natural extract
Sample 8	Flax fiber support functionalized with MCT- $\beta$ -cyclodextrin and dyed by the ultrasonication method with 2% solution of <i>Allium cepa</i> natural extract

**SEM analysis**

Grafted samples were qualitatively analyzed as to their morphological structure, using scanning electron microscopy–energy-dispersive X-ray spectroscopy. Scanning electron microscopy (SEM) images were acquired with a Quanta 200 3D Dual Beam type microscope, FEI Holland, coupled with an energy-dispersive X-ray spectroscopy (EDX) analysis system, manufactured by AMETEK Holland, equipped with an SDD type detector (silicon drift detector).

**FT-IR spectroscopy analysis**

FT-IR was used to examine changes in the molecular structures of the samples. Infrared spectra were recorded on an FTIR JASCO 660+ spectrometer, operating in the 4000–400  $\text{cm}^{-1}$  range.

**X-ray diffraction (XRD)**

Diffractionograms were recorded using a PW1710 diffractometer, using a Cu-K $\alpha$  radiation ( $k = 1.54 \text{ \AA}$ ) source (applied voltage – 40 kV, current – 40 mA). Scattered radiation was detected in the  $2\theta = 10\text{--}80^\circ$  range at the speed of  $1.5^\circ \text{ min}^{-1}$ .

**BET analysis**

Porosity and surface area studies were performed on a NOVA 2200e system, using nitrogen as an adsorbate at liquid nitrogen temperature ( $-196^\circ\text{C}$ ). All the samples were out gassed under vacuum, for 6 hours at  $25^\circ\text{C}$  before adsorption measurements. The surface area was calculated using the BET method in the relative pressure range of 0.05–0.35. Pore volume was calculated at the relative pressure of 0.95. Pore size distributions were calculated from the desorption branches of the  $\text{N}_2$  adsorption isotherms, using the Barrett-Joyner-Halenda (BJH) model.

**Colour strength and colour fastness testing**

The washing fastness was determined at  $40^\circ\text{C}$ , according to EN ISO 105-C10:2007 specific conditions. Colour fastness to dry and wet rubbing has been tested, according to SR EN ISO 105- X12:2003, using a 760 Crockmaster equipment. The shifts have been quantified with respect to a standard grey scale.

**RESULTS AND DISCUSSION****SEM investigation**

Scanning electron microscopy (SEM) permitted to visualize separate flax fibers in much more detail. Figure 1 reveals the difference between the untreated fiber (F) and the fiber grafted with MCT- $\beta$ -CD (F-MCT- $\beta$ -CD), at magnifications of X5000 and X12000. Using the SEM analysis, little bolls were observed on the surface, which were not observed in the reference material. Grafted samples were considerably

stiffer than untreated samples. A significant change of surface morphology was observed.

As shown in Figure 2, sample 2 has the typical convolutions of flax, and still possesses the main morphological characteristics of flax, but the natural dye is distributed non-uniformly. An evenly distributed MCT- $\beta$ -CD film is visible on the fiber surface of sample 3. At larger magnifications, *i.e.* X12000, the differences between the dyed untreated and dyed grafted support become even more obvious and the change in the morphology of the fiber surface can be clearly observed, as shown in Figure 3.

As observed in Figure 3, a more uniform distribution of the natural dye on the fibre surface is obtained in sample 7 (non-functionalized support dyed with 2% natural extract), compared to sample 5 (non-functionalized support dyed with 1% natural extract), which has a rough distribution.

Figure 4 presents comparatively the grafted samples dyed with two different concentrations of the anthocyanin extract. It clearly reveals that the higher the dye concentration, the more uniform the coating achieved. The explanation relies in the fact that the higher the concentration of the grafting agent, the higher the possibility of chromophores or groups to covalently bind/attach to the active groups belonging to grafted fiber, conducting to a proportional distribution of the dye molecules.

Binding strength depends on how well the host and guest fit together in the complex and on specific local interactions between surface atoms.

With respect to the samples dyed by ultrasonication, the uniform distribution is much more notable than in the previously grafted sample and dyed by the same procedure, as presented in Figures 3 and 4. In the case of the grafted flax fibre, the dye did not cover the entire surface of the sample. On the contrary, some small balls can be observed.

The images reveal that the natural anthocyanin extract is more uniformly deposited on the fibre surface, in the case of the previously grafted sample, as compared to the specimen dyed with the same extract, but in the absence of MCT- $\beta$ -CD, where the dye has been scarcely diffused on the fibre. This result is very well supported by the colour measurements: the grafted samples present a good dye distribution, with pale, but wash resistant colours.

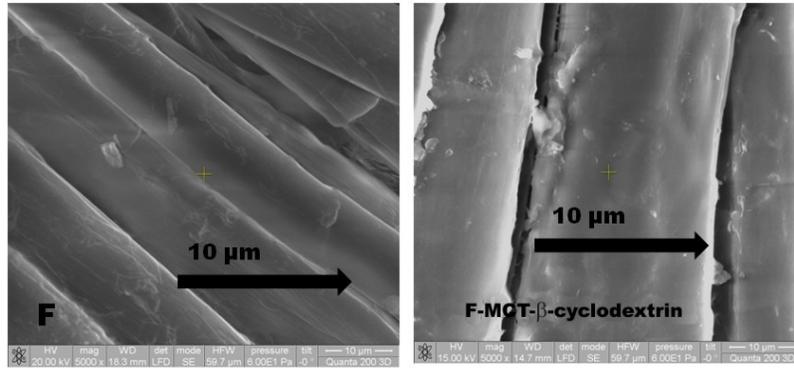


Figure 1: SEM images at X5000 magnification for samples F and F-MCT-β-CD

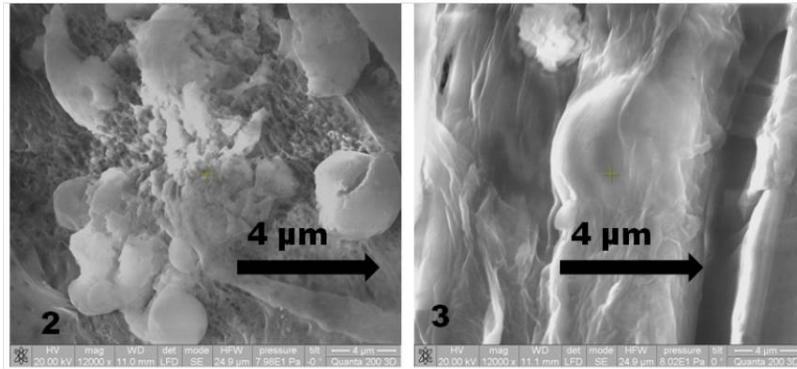


Figure 2: SEM images at X12000 magnification for samples 2 and 3

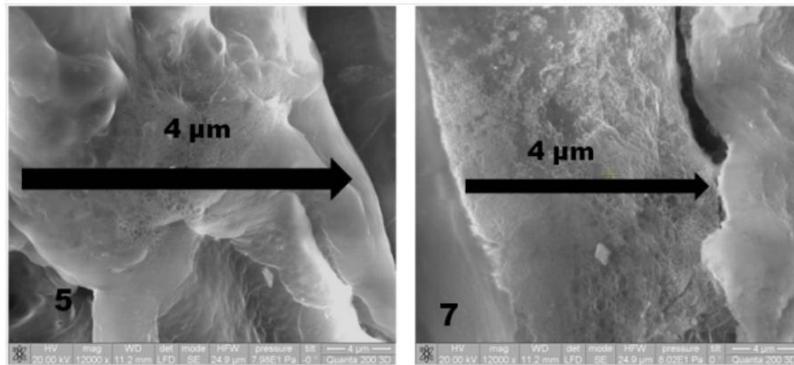


Figure 3: SEM images at X12000 magnification for samples 5 and 7

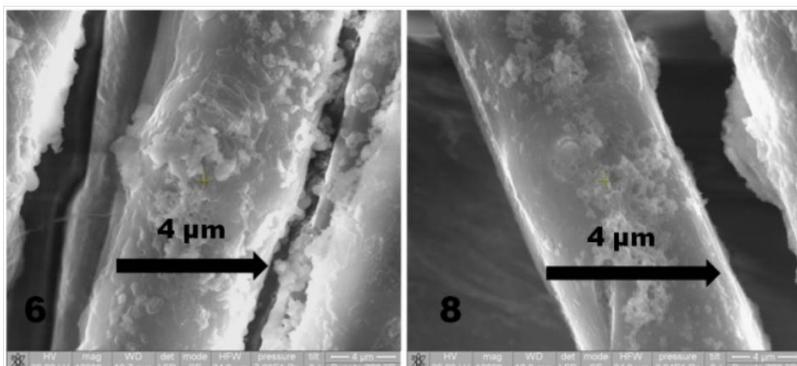


Figure 4: SEM images at X12000 magnification for samples 6 and 8

The control samples have vivid colours, but are not resistant in terms of washing and rubbing fastness.

The changes are homogeneous, as the free radical grafting is initiated over the entire fiber simultaneously.

**EDX - elemental analysis**

EDX analysis revealed a proportionally decreased content of nitrogen and chlorine – as

the main chemical elements coming from the triazinyl group – with the modification of dyeing conditions. In the case of samples 1 and 4, nitrogen showed the highest content. The decrease of the nitrogen content can be explained by the fact that the triazinyl group is involved quantitatively in the reaction with the dye molecule, which is supported by the FT-IR spectroscopy.

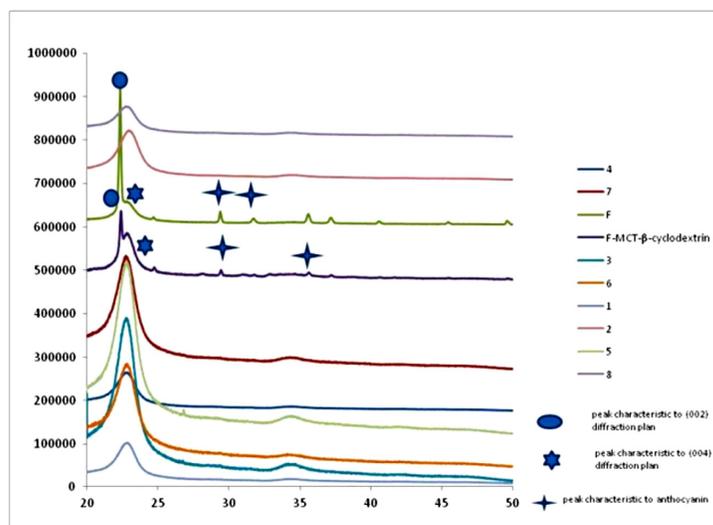


Figure 5: XRD patterns for flax fiber supports dyed with *Allium cepa* anthocyanin extract

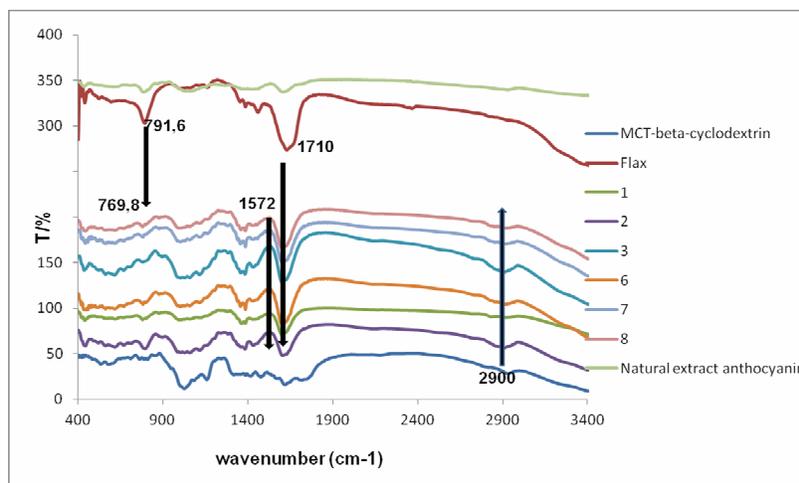


Figure 6: FT-IR spectra for flax fiber supports dyed with *Allium cepa* anthocyanin extract

### XRD pattern interpretation

The XRD patterns presented in Figure 5 exhibit two main specific peaks for flax fibres, as follows: four well-defined peaks at  $22.0^\circ$  and  $34.4^\circ$ , corresponding to the 002 and 004 planes, which is in accordance with the literature.<sup>27,28</sup> In the case of the functionalized lignocellulosic support, two peaks appeared around  $22.0^\circ$  and  $34.4^\circ$ , corresponding to the 002 and 004 planes, respectively. This is due to the large amount of amorphous regions present in cellulose, and also to the presence of amorphous lignin and hemicelluloses, which agrees with the results of other authors.<sup>29</sup>

The immobilization of anthocyanin in the complex induced the appearance of new small peaks that may be ascribed to anthocyanins.

The most relevant aspect is that, in the case of flax supports (reference and grafted with MCT- $\beta$ -CD), a certain level of crystallinity should be noticed, which is due to the small peaks that appeared.

On the contrary, the XRD patterns characteristic of the dyed samples show less pronounced peaks, meaning that the content of amorphous regions tended to increase in most cases.

### FT-IR spectroscopy analysis

The FT-IR analysis results of the reference flax supports and those treated with the MCT- $\beta$ -CD solution of 10 g/L are shown in Figure 6.

The obtained FT-IR spectra of the reference flax supports showed peaks with very low intensity around  $1646.7\text{ cm}^{-1}$  and with higher intensity around  $3555.6$ ,  $2900\text{ cm}^{-1}$ , corresponding to  $\text{NH}_2$ ,  $\text{OH}$  and  $\text{CH}_2$  stretching vibration, respectively. The absorption band that occurred in all spectra at  $3450\text{ cm}^{-1}$  corresponds to the  $\text{OH}$  bond (intermolecular hydrogen bond). The maximum absorption at  $1710\text{ cm}^{-1}$  is assigned to the carbonyl group.<sup>30</sup>

The occurrence of some bands characteristic of both host and guest species in the spectrum, which are usually shifted, compared to pure component bands, can be considered as evidence of the formation of an inclusion compound.

In the case of MCT- $\beta$ -CD treated flax support, the significant difference from the reference flax fibre was that the characteristic band of triazinyl appeared with significantly higher intensity. This was attributed to the triazinyl nucleus  $\nu(\text{C}=\text{N})$ , namely at  $1572$  and  $1455\text{ cm}^{-1}$ , which was successfully introduced and attached to the flax

fibre. The triazinyl group ( $\text{C}=\text{N}$ ) could react with the dye molecule more actively than the hydroxyl group ( $\text{OH}$ ). The obtained FT-IR spectra also confirmed the grafting, from a qualitative point of view. The absorption peak at  $1728\text{ cm}^{-1}$  is attributable to the stretching vibrations of the carbonyl group. The band at  $1636\text{ cm}^{-1}$  can be attributed to the  $\text{C}=\text{N}$  valence vibration (or, possibly  $\text{C}=\text{O}$  in aldehydes and carboxylic groups). The  $\text{C}=\text{C}$  valence vibration is weak and often not visible. The  $1335\text{-}1316\text{ cm}^{-1}$  doublet is assigned to the cellulose component. There is an absorption band present at  $1200\text{ cm}^{-1}$ , which is assigned to the vibration of  $\text{C}-\text{O}$ . The deformation beyond the double bond plan from the lateral catena is highlighted by the bands at  $780\text{-}790\text{ cm}^{-1}$ .

The use of the FT-IR technique allows the detection of complex formations in the solid phase. It also makes it possible to point out the implication of the different functional groups of guest and host molecules in the inclusion process by analyzing the significant changes in the shape and position of the absorbance bands of the natural dye, MCT- $\beta$ -CD, physical mixture and inclusion complexes.

The MCT- $\beta$ -CD exhibited a significant FT-IR peak at wavenumbers  $942$ ,  $1094$ ,  $1166$ ,  $1337$ ,  $2929$  and  $3467\text{ cm}^{-1}$ , while the natural dye showed FT-IR peaks at wavenumbers  $1059$ ,  $1102$ ,  $1161$ ,  $3362$ ,  $3434$  and  $3464\text{ cm}^{-1}$ .

### BET results

As to their structure, natural fibers like flax can be considered as non-porous solids, and therefore, one should expect, according to Brunauer *et al.*<sup>31</sup> an adsorption isotherm of type II (for non-porous solids) out of the 5 classes. Nevertheless, regarding the studied samples, the performed BET measurements highlighted only the sorption-desorption behaviour of both MCT- $\beta$ -CD and dye molecules. Thus, Figure 7 shows the nitrogen adsorption-desorption isotherms for the dye-molecule inclusion complex, considered as a mesoporous material. The studied sample displays a typical type IV isotherm with a hysteresis loop, which is characteristic of mesoporous materials, according to the IUPAC classification.<sup>32</sup> The hysteresis loops have sharp adsorption and desorption branches, indicating a narrow mesopore size distribution and a good quality of the sample.

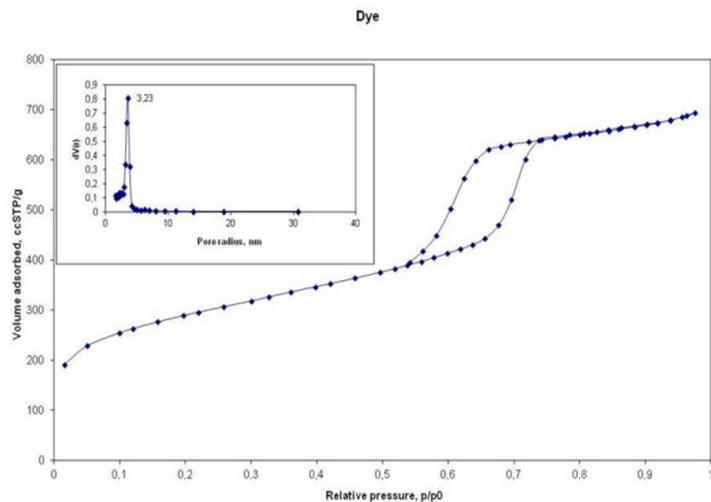


Figure 7: Nitrogen adsorption/desorption isotherm and pore size distribution (inset picture) of the MCT-β-CD sample

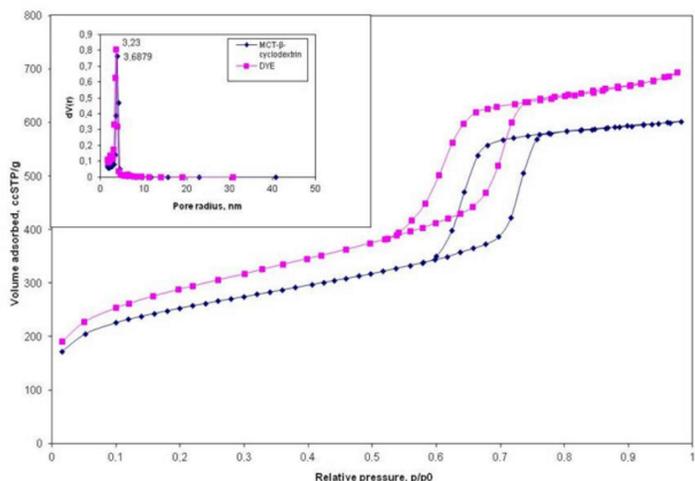


Figure 8: Nitrogen adsorption/desorption isotherm and pore size distribution (inset picture) of the dye molecule and the cavity of MCT-β-CD

The observed decrease in surface area, pore diameter and pore volume is a proof that the dye molecules are located inside the pores/cavity of MCT-β-CD.

According to Table 2, the decreases in surface area, from 749.5 to 644.37, in pore diameter, from 7.15 nm to 5.3 nm, and in pore volume, from 1.42 to 0.88 cm<sup>3</sup>/g, are due to loading/incorporation of pigment molecules within the pores of the MCT-β-CD host support, which causes contraction of the nanopores by bridge-bonding of dye species, involving different functional groups of guest and host molecules in the inclusion process.<sup>17</sup>

### Colour fastness analysis

The best coloring results, in terms of fastness properties, were obtained by inclusion of the natural dye inside the MCT-β-CD (Table 3). In other words, colour fastness improved after flax fabrics were grafted. The reason for this is that MCT-β-CD has a toroidal shape with a hydrophobic central cavity and a hydrophilic outer surface, where the hydroxyl groups are located.<sup>19</sup> Thus, the dye molecules are bound to the MCT-β-CD, which explains the good stability in terms of colour fastness.

Table 2  
Values of surface area, pore diameter and pore volume for the studied samples

Sample	Pore diameter (nm)	Surface area, BET (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
MCT-β-cyclodextrin cavity	7.15	749.5	1.42
Dye	5.3	644.37	0.88

Table 3  
Colour measurements and colour fastness values for samples dyed with the *Allium cepa* anthocyanin extract

Textile sample	Dry and wet rubbing fastness		Washing fastness	L*	a*	b*	C*	H*	ΔC*	ΔH*	ΔE*
Flax untreated	3	2	3	92.57	-0.45	4.12	4.14	96.29	-	-	-
Flax/MCT-β- cyclodextrin	3-4	2-3	3-4	88.08	0.03	6.55	6.55	89.77	2.41	-0.59	5.13
1	5	3	5	56.88	15.42	13.17	20.28	40.48	8.85	-3.72	3.86
2	4-5	3-4	3-4	40.78	21.51	11.09	24.20	27.28	20.05	-11.34	56.69
3	3-4	3	4-5	62.84	13.27	15.41	20.34	49.28	8.91	-1.39	18.19
4	3-4	3	3-4	56.29	15.88	13.04	20.55	39.39	16.41	-8.79	40.78
5	3	2-3	3	64.66	16.59	5.79	17.57	19.23	13.43	-10.63	32.75
6	3-4	3	4	67.22	17.57	7.95	19.28	19.28	7.86	-7.73	15.87
7	3-4	3	3	55.15	22.58	7.31	23.73	17.94	19.59	-12.53	44.06
8	4-5	4	4-5	50.76	26.12	8.66	27.51	18.35	16.09	-11.01	34.02

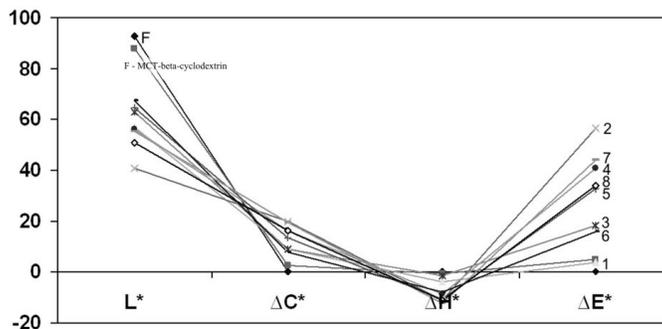


Figure 9: Changes in colour, saturation and hue for the samples dyed with anthocyanin extract, using standard and sonication dyeing procedures

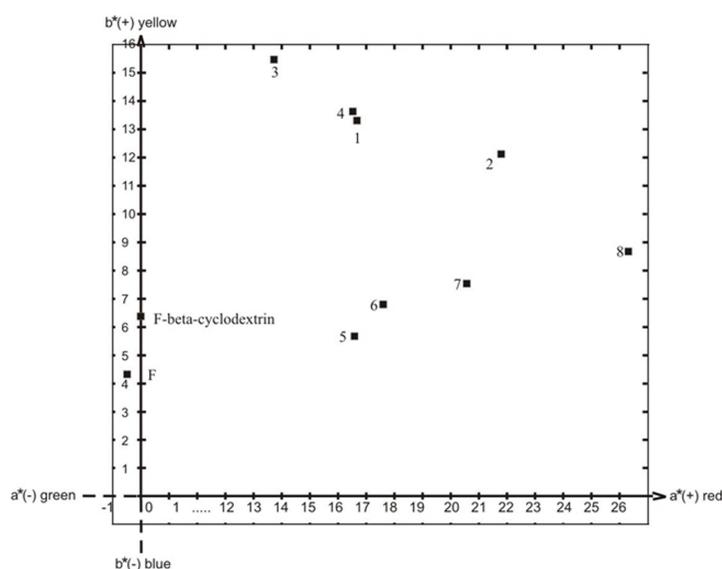


Figure 10: The  $a^*b^*$  diagram for the investigated specimens non-functionalized and functionalized with MCT- $\beta$ -CD and dyed by standard and sonication procedures with the natural extract (samples 1, 2, 3, 4, 5, 6, 7, 8)

The colours of the dyed specimens are slightly modified. The dyeing fastness is obviously improved. Colour measurements were performed using a Flash SF300 Spectrophotometer Datacolour. The results acquired were processed using the Micromatch 2000 software. D65 was the illuminant used to make the measurements.

According to Figures 9 and 10, a decrease of brightness is noticed. This is probably due to the formation of a polymer–natural dye complex. An increase in the saturation and darkening of the samples, in particular, of those non-grafted and dyed, as well as shifts of shades to the red-yellow colour with respect to the reference samples, is observed.

After the thermal dyeing treatments that the samples were subjected to, the colour changes in the samples treated with MCT- $\beta$ -CD were

considerably lower than in the untreated samples dyed with the same natural dye. For the non-grafted and dyed samples, the colour changes were major, probably due to a superficial deposition of the anthocyanin extract onto the fabric surface. In the case of the grafted samples, one can appreciate that by the embedding of anthocyanins in MCT- $\beta$ -CD, colour differences became less noticeable.<sup>33</sup>

The results clearly show that dyeing is, to a certain extent, more resistant when the anthocyanin extract is applied onto grafted specimens, especially at higher concentrations. It is well known that poor wash fastness has been one of the main inconvenience of natural dyes. This aspect could be a weak point of the present research. In our investigation, the conjunction of the anthocyanin-based dye to the monochloro-

triazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD) used as inclusion compound, was found to be efficient in increasing and stabilizing the colour fastness.

Regarding dyeing of samples by ultrasounds, the deviation of an intense hue is noticeable, as well as an even distribution of dye, in comparison to the standard dyeing procedure.

The red shade of the dyeing becomes more visible through the increasing of the  $a^*$  coordinate from the CIELAB system for the functionalized and ultrasonically dyed samples (samples 6 and 8), as compared to the reference ones (samples 5 and 7), being a proof of the dyeing intensity augmentation with the natural colorant, along with the increase of concentration. The decrease in the  $L^*$  luminosity for the functionalized and ultrasonically dyed samples at a high concentration and also the augmentation of the  $C^*$  saturation represent an enhancement of the dyeing, compared to the standard protocol.<sup>34</sup>

It can be concluded that, following the experiments, for a brief time and normal dyeing temperature (15 min, 30 °C), an intense colour was achieved by the sonication procedure, compared to the standard dyeing method (30 min, 80 °C).

This idea is emphasized by the present research, by using a natural dye applied on a lignocellulosic support functionalized with monochlorotriazinyl- $\beta$ -cyclodextrin (MCT- $\beta$ -CD). Thus, one can identify a potential industrial application, by decreasing the thermal energy and dyeing duration, involving a reduction in process costs.

Dyeing performance for the samples dyed with coloured matter was characterized in terms of colour fastness to washing, wet and dry rubbing, and with respect to the colour value of the CIELAB system with the 10° standard observer and illuminant D65. The specimens used as references are indexed as “non-treated flax” for all the measurements of non-functionalized and standard dyed samples and flax/(MCT- $\beta$ -CD) for functionalized and dyed by the two procedures. Thus, the  $\Delta E^*$  colour differences are very substantial for the reference samples (samples 2, 4, 5, 7) by quantifying the un-dyed samples, leading to the idea that the fibres are easy to dye, they gather the natural colorant, but lose it through washing and rubbing, providing average fastness. The natural dye deposited by complexation onto grafted samples is more stable, with smaller colour

differences (samples 1, 3, 6, 8), but superior fastness values. Meanwhile, the ultrasonically dyed specimens have enhanced/improved chromatic features, meaning the darkening of the shade and augmentation of saturation (samples 5, 7 and 6, 8), as compared to the standard dyed samples (samples 1, 3 and 2, 4).

The good values for dry rubbing and washing fastness (0.5-1) for functionalized and dyed samples (samples 1, 3, 6, 8) are well supported by the fact that a dye-cyclodextrin complexing agent was formed; in this way, the dye molecule was stabilized inside the cyclodextrin cavity. This positive finding of the study has already been reported in the literature, with respect to direct and azo disperse dyes forming inclusion complexes with cyclodextrins.<sup>35</sup>

An improvement in the dyeability of the flax fibre supports, due to higher activity of the triazine group, compared to that of the hydroxyl group (-OH) of raw flax fibre, resulting in an increased reaction probability between the dye molecules and the lignocellulosic fibres. The modification technique could be adapted to industrial scale flax dyeing, with satisfactory levels of exhaustion and fixation.

Besides, by this research the assisting effect of the ultrasonic power on the dyeability of flax fabrics dyed with a natural extract is emphasized once more and can be explained by facilitating the dye-fibre contact and accelerating the interaction or chemical reaction between dye and fibre.<sup>5</sup> The proposed alternative dyeing method, provided more intense shades, under conditions of short dyeing times and reduced temperatures (30 °C).

In addition to the specified references, the current study promotes the innovative character of the dyeing process with the natural red onion extract by ultrasonication, in order to develop novel solutions that are both more ecologically and economically sustainable.

By this study, an outline of the MCT- $\beta$ -CD-dye complex formation on the functionalized textile has been made. The research has not excluded the possibility of the attachment of dye molecules around the MCT- $\beta$ -CD cavity, based on the core-shell association principle. Further studies will reveal the stabilization mechanism of the natural dye. Subsequently, future research will be oriented towards “blocking” the dye molecule inside the MCT- $\beta$ -CD cavity, or, on the contrary, the deposition of colorant onto the MCT- $\beta$ -CD shell.

**CONCLUSION**

The following conclusions can be drawn from the present investigation:

- A sustainable eco-dyeing method was achieved, which can combine the non-conventional energy type, such as sonication, on the one hand, and the interaction between the complex effect of monochlorotriazinyl- $\beta$ -cyclodextrin and the anthocyanin extract, on the other hand, in order to obtain coloured textile materials.
- Flax fabrics were successfully dyed with red onion anthocyanin extract in conjugation with MCT- $\beta$ -CD, which is a very useful non-toxic polymer and granted remarkable colour fastness properties to the textile supports.
- The co-assisted investigations involved in this research envisaged a novel natural dyeing method, with and without the use of the MCT- $\beta$ -CD agent. After grafting with MCT- $\beta$ -CD, the subsequent dyeing with the natural extract generated a decrease in the crystallinity of flax fabrics, but enhanced the fastness properties of the modified lignocellulosic supports.
- Although natural fibers like flax are considered as non-porous solids, the research emphasizes the idea of the mesoporosity of the inclusion complex obtained by encapsulating the dye molecules in the MCT- $\beta$ -CD cavity. The observed decrease in the surface area, pore diameter and pore volume is a proof that dye molecules are located inside the pores/cavity of  $\beta$ -CD.
- The improvement in the dyeing methodology using the anthocyanin extract of *Allium cepa* has been attributed to the presence of MCT- $\beta$ -CD, which acts as a functionalization agent of the flax substrate.
- As a perspective approach to our research in the field of textile dyeing, the superficial grafting of MCT- $\beta$ -CD on textile supports as pretreatment (inclusion complex), realized for other natural dyes, will assure health-promoting benefits and environmentally protective effects.
- Thus, the use of MCT- $\beta$ -CD–natural dye extract complexes is fostered by both ecologic (a decreased pollutant charge) and economic reasons (a more efficient exhaustion of the dyeing bath).

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