

Summary of the SCIENTIFIC REPORT
Period of implementation: January 1 – December 31, 2015

All objectives were achieved and all planned results were obtained during the 2015 stage. The obtained scientific results show that anthocyanins extracts from bilberries and blackberries optimized by previously described methodology can be successfully applied for dyeing of textile supports (flax and flax functionalized with MCT- β -CD) by two methodologies - exhaustion and ultrasonication, respectively. The results obtained from characterization of textiles dyed using analytical techniques such as SEM, FT-IR spectroscopy and BET analysis, showed that the ultrasonication technique is useful in optimization of dyeing capacity, expressed through the K/S values, compared to the conventional method through exhaustion. By comparing the color fastness values and the behavior of dyed substrates to abrasion, the results indicate low to satisfactory resistance, for both functionalized samples and dyed samples by the investigated methods of coating. The obtained results show that the natural dyeing procedure with bilberry and blackberry anthocyanin extracts of flax fabrics grafted with a cyclodextrin derivative might be a good alternative for the optimization of the resistance to washing and rubbing.

The visibility of the scientific production of the project team is guaranteed by the publication in 2015 of 2 articles in ISI journals, acceptance for publication of 1 article in ISI journal, 2 articles published in journals indexed BDI, 3 participations at Patent/inventions events and 5 papers presented/published at international conferences in 2015. One undergraduate thesis was developed in the field. International visibility is proved by getting 7 citations of articles already published. Project web page has been updated.

Experimental activity of dyeing textile substrates with anthocyanins extracts

- *Testing the dyeing of textiles substrates with bilberry and blackberry extracts*
- *Pre-treatment of materials*
- *Methodology of dyeing (exhaustion, ultrasonication)*
- *Textile substrates: flax, functionalized flax*

There were extracted and quantitatively determined anthocyanins from bilberry and blackberry fruits, according to the optimized methodology previously set out. The presence of natural extracts in textile fabrics is important, as it contributes to consumer's hygiene and also to clean processes. Application of anthocyanin extracts obtained from fruits on textile substrates could further improve certain properties such as antimicrobial, anti-inflammatory and anticancer.

Conventional dyeing process involves the use of chemical agents and heat. By using ultrasonication, dyeing baths can have lower temperature because of improved dispersion and inclusion of dyes.

In terms of methodology, our experimental studies primarily aimed at preliminary improving the flax substrate by using β -cyclodextrin-monochlorotriazinyl (MCT- β -CD). Secondly, in the experimental protocol, bilberry or blackberry extracts were applied to the material by two methods of the dyeing process: exhaustion and ultrasonication. The motivation of such research is to improve the fastness properties of dyed textile substrates by use of the capacity of the hydrophobic cavity of MCT- β -CD to form inclusion complexes with the pigments based on their selectivity. Moreover, it highlighted the inclusion complex formation between anthocyanin dye and MCT- β -CD.

Characterization of dyed textile substrates (physical chemical resistance, color coordinates, resistance at different factors)

Morphological, structural characterization and strength properties of coated materials was obtained using a SEM investigation, FT-IR, analysis of specific surface area by the BET method and fastness resistance. The results of the analysis of the samples showed homogeneity of samples through dyeing by US procedure. In addition, optimization of resistance to washing and rubbing was quantified by values increased by 0.5-1 points. The morphology of the flax fibers after the grafting and dyeing by the two methods was assessed by SEM. The results showed that the fine structure of

the samples is quite different from the fibers of non-functionalized flax and the absorption properties of the natural extract is probably due to the micro-cavities created after functionalization with the derivative of β -cyclodextrin MCT. By ultrasonication, the fiber morphology becomes very smooth.

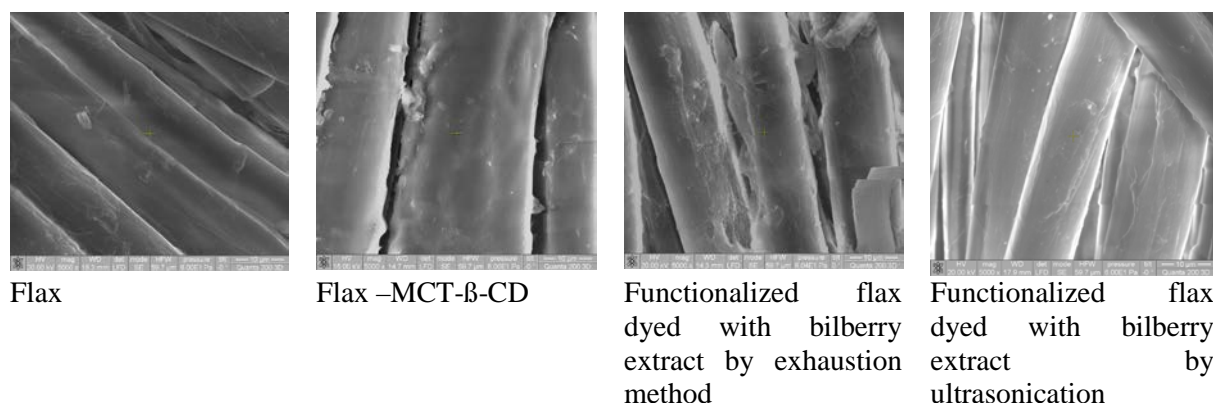


Fig. 1: SEM images of flax functionalized substrates dyed by exhaustion and ultrasonication methods with 2% bilberry extract (*Vaccinium myrtillus*) at $\times 5000$ magnification

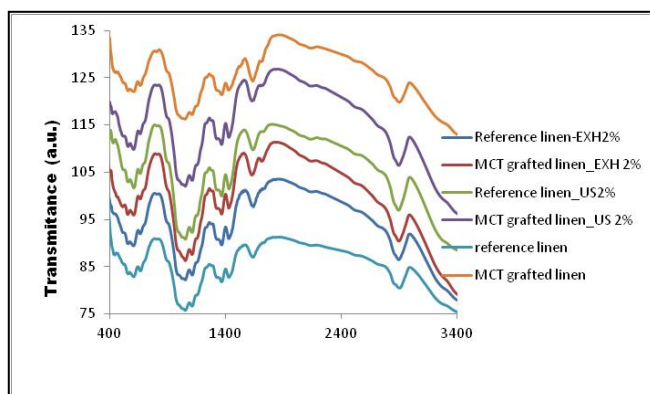


Fig. 2: FT-IR spectra of flax substrates dyed by exhaustion and ultrasonication methods with 2% bilberry extract.

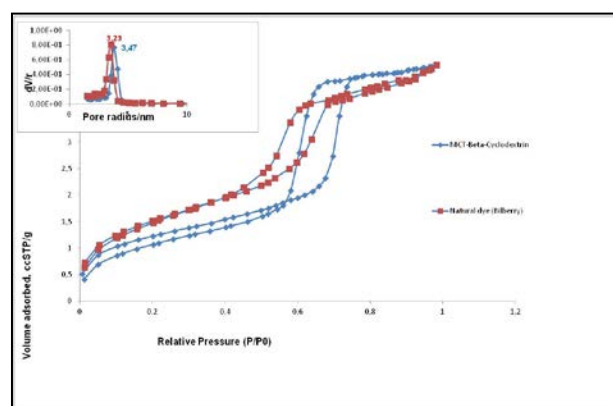


Fig. 3: Nitrogen adsorption/desorption isotherm of inclusion compound (MCT- β -cyclodextrin and pigments)

Spectroscopic investigations demonstrate the formation of the inclusion compound. In addition, there are changes in IR spectra, which can be noticed at 1634, 1180, 1127, and 900 cm^{-1} , due to binding of β -CD MCT. This is well supported by BET analysis, revealing entrapping of dye molecule inside the MCT- β -cyclodextrin.

Evaluation of dyed materials with extracts relevant for dyeing technology was completed by determination of color fastness and color attributes of the treated supports. The fastness intensities, respectively the K/S values of dyed lignocellulosic substrates were measured using the spectrophotometer Datacolor 110 LAV. Abrasion testing was performed using the instrument NU-Martindale for abrasion and pilling. The friction test was performed using the Crockmaster instrument.

Table 1 shows the results of measurements of resistance to washing and rubbing of flax fabrics dyed with bilberry extract, compared to reference samples (flax or flax grafted with MCT- β -cyclodextrin), together with the values attributed to nanocavities of MCT- β -cyclodextrin and of the dye molecule.

Table 1: Fastness values and ratio radius cyclodextrin/pigment of flax fabrics dyed with bilberry extract.

Sample	Dry rubbing fastness	Wet rubbing fastness	Washing fastness	Ratio CD ray /dye ray, nm
Flax	2	1-2	2-3	
Flax / MCT- β -cyclodextrin	3-4	2	4-5	
Flax dyed with bilberry extract by exhaustion method	3	3	2-3	-
Functionalized flax dyed with bilberry extract by exhaustion method	4-5	3-4	4-5	2.17 / 2.76
Flax dyed with bilberry extract by ultrasonication	3-4	3	4	-
Functionalized flax dyed with bilberry extract by ultrasonication	5	4	4-5	3.23 / 3.47

During the experiments, the color fastness values of the samples dyed with anthocyanins extracts from bilberries and blackberries reveals moderate to good washing and rubbing fastness for most samples, in particular for those of functionalized flax and dyed using the ultrasonication procedure. Color attributes of naturally dyed samples show the sustainability through superior resistance to washing, friction and abrasion due to the encapsulation process. These experiments are relevant for the use of (micro)encapsulation technology of a natural dye directly on the fabric treated with MCT- β -CD *versus* conventional technique of dyeing by assisted mordants. This process has the potential to substitute the classic treatment, favoring future applications, in order to obtain new ecological textiles.

The resistances of the color of samples dyed with the blackberry anthocyanins extract have shown that the washing and rubbing fastness, in great majority of samples, are moderate to good, in particular for functionalized and dyed textile substrates.

Table 2: Values of color changes after the abrasion test of flax fabrics dyed with blackberry anthocyanins extract.

Sample	Resistance to abrasion			Ratio CD radius /dye radius, nm	
	ΔE		K/S		
	Reference	Abrading	Control	Abrading	Control
Flax	-	-	2.74	-	
Flax / MCT- β -cyclodextrin	-	-	2.53	-	
Flax dyed with blackberry extract by exhaustion method	5.20	3.14	6.52	5.42	8.34
Functionalized flax dyed with blackberry extract by exhaustion method	8.74	6.34	7.89	6.47	7.15
Flax dyed with blackberry extract by ultrasonication	3.57	2.26	4.30	3.60	6.8
Functionalized flax dyed with blackberry extract by ultrasonication	3.78	2.11	4.60	3.59	4.7

Cumulative results of analytical techniques of SEM, FTIR and BET analysis showed that ultrasonication technique is useful for optimization of the dyeing capacity, expressed by K/S values compared with the conventional method of dyeing by exhaustion. By comparing the values of color fastness and the behavior to abrasion, the results indicate low to satisfactory resistance, both for functionalized samples, as for the dyed samples using both methods of coating. The results show that

the natural dyeing with bilberries and blackberries of flax fabric grafted with cyclodextrin derivative might be a good alternative for the optimization of the washing and rubbing fastness.

Dissemination and evaluation of research results by publication of articles, participation at scientific conferences

Published/in press scientific papers 2015:

- 2 articles *published* in ISI journals with total impact factor = 1.137 and relative influence score = 0.581
- 1 article *accepted* in ISI journal
- 2 articles *published* in journals indexed BDI
- 5 scientific papers *published and presented* at international conferences/congresses
- 3 participations at Patent international events

Training young researchers:

- 1 undergraduate thesis was developed in the field
- 2 oral presentations of scientific papers by students at Student's Symposia, Textile Technology section, ULBS)

7 ISI citations according to ISI Web of Science of the published articles

In the coming period, in order to complete all the project objectives, activities regarding applications of natural extracts in textile dyeings will be planned by testing the optimal conditions for dyeing with natural extracts rich in anthocyanins. Also, dissemination and evaluation of research will be conducted.

Project director,
Professor OANCEA Simona, PhD