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STUDY OF RASPBERRY EXTRACT APPLICATIONS AS TEXTILE COLORANT ON NATURAL FIBERS

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Abstract: *The present study deals with the biomordant assisted application of natural extracts obtained from red raspberry (Rubus idaeus L.) fruits onto two different cellulosic supports – flax and bamboo. The study relies on the improvement of multifunctionalities such as colour fastness, washing and rubbing fastness, due to the synergism provided by the co-assistance of both a biomordant, and the complex resulted by inclusion of the pigment molecule, in the cavity of MCT-β-CD; it is well known that natural dye molecule have a good selectivity binding to the hydrophobic monochloro-triazynil-cyclodextrin's (MCT-β-CD) cavity to form inclusion complexes. An investigation system provided the characterization of the composites: FT-IR spectroscopy stressed the main chemical bonds created between MCT-β-CD as host molecule and guest molecule represented by natural colorant molecule; Brunauer-Emmett-Teller (BET) Surface Area Analysis completes the analysis, proving the positive contribution of MCT-β-cyclodextrin grafting. Dyeing fastness and colour modifications were conclusive for this research. Samples of bamboo knitting are less colorful than those of the flax fabric in terms of high absorption capacity and stability / durability of natural dye applied by inclusion within cyclodextrin's inner. The results of analysis revealed improvement of washing and rubbing fastness (1-1.5 points). Colour modifications noticed due to the colorant deposition were quantified from up to 3 points.*

Key words: *flax fabrics, bamboo knitted fabric, natural extract, fastness properties, colour difference*

1. INTRODUCTION

Starting from the idea of promoting eco-textiles' innovation and sustainability, new reliable solutions have been searched for textile industry, by using anthocianin extracts, having the main role in dyeing of textile supports. Unlike the production of synthetic dyes application which requires the use of toxic and hazardous materials as well as conditions like strong acids, alkalis, solvents, high temperatures, and heavy metal catalysts, natural dyes do not produce environmental stresses.

Flax fibers supports were dyed with natural anthocyanin-based pigments, being subsequently underlined the synergic effect given by the co-assistance of both a biomordant, and the complex resulted by inclusion of the pigment molecule, in the cavity of MCT-β-CD. Taking into account the previous studies having the same topic, it is assumed that the binding between anthocyanin molecules and host cyclodextrin is barely fixed, being a dynamic equilibrium. Two main elements could contribute to the binding resistance: the compatibility between the host-guest to form a complex, as well as the specific local interactions between surface atoms [1].

As an alternative of natural dyeing by inclusion, the occurence of a biomordant can constitute another reliable and eco-friendly way in the technology of dyeing of natural fibers supports.

Technically, the novelty of this study, compared with the results previously achieved is the addition of a new support made of bamboo fibers, on one side, and a new extract coming from red rasberries. It is well known that these fibers provide excellent performance to textile items, such as: antibacterial, antifungal, UV protection, IR absorbtion and good water absorbion properties [2,3].

These above-mentioned properties can be potentially completed by the natural pigment used for dyeing by enhancing the coloration [4]

Taking into account the the previous researches regarding the anthocyanin extracted from other fruits [5], this present paper refers to utilizing red raspberry extract, although it contains lower anthocyanin contents compared to other similar extracts from blueberry, bilberry, blackberry or red onion skins.

2. EXPERIMENTAL SECTION

Extraction of anthocyanins was done in 70% ethanol solution from selected samples of red raspberry (*Rubus idaeus* L.). The total anthocyanins content spectrophotometrically determined was found of 31.54 mg $100g^{-1}$ FW (fresh weight). Hydroethanolic anthocyanins extract from red raspberry has been used for the dyeing technologies here investigated.

The pretreatment was made by grafting procedure by padding *(impregnation-squeezing)-drying- curing,* according to the previous dyeing receipes with anthocyanin extracts from bilberry, blackberry or amarena cherry [5]. Both flax and bamboo fibers fabrics were immersed in a solution containing 50 g/l of monochlortriazinyl-β-cyclodextrin.

In this work, 100% flax fiber fabrics and 100% bamboo fiber knitting were dyed with raspberry extract by exhaustion procedure meaning an immersing of the textile supports in dye bath for about 60 minutes at 80°C at 1:30 liquor ratio with 1% solution of anthocianin dye and 1% citric acid (CA).

The descriptions of the studied samples can be specified: F-Reference flax fibres support; F-MCT-ß-CD- Grafted flax support with MCT-ß-CD; sample 1-Non-functionalized flax fiber support dyed by exhaustion procedure with 1% raspberry extract; sample 2- Non-functionalized flax fiber support dyed by exhaustion procedure with 1% raspberry extract and 1% citric acid; sample 3-Functionalized flax fiber support with MCT-β-CD dyed by exhaustion procedure with 1% raspberry extract; sample 4-bamboo knitting support dyed by exhaustion procedure with 1% raspberry extract; sample 5- Bamboo knitting support dyed by exhaustion procedure with 1% raspberry extract and 1% citric acid.

The structure and properties of the raspberry extracted anthocyanin dye-MCT-β-CD-flax and bamboo support composite were studied by nitrogen adsorption-desorption isotherms (BET analysis), FTIR spectroscopy and finally the colorfastness testing measurements completed this study.

For the colour measurement of dyed samples, Datacolor 110 Spectrophotometer, under standard $D65/10^0$ illumination conditions was used. Washing and rubbing strengths were performed according to specific standards, using Crockmaster 760 laboratory equipment.

3. RESULTS AND DISCUTIONS

In **Fig. 1**, the role played by the biomordant is well stressed by the spectrum ascribed to sample dyed with the assistance of citric acid solution. Thus, the stretching band at 1625 cm^{-1} attributed to the C=O in the dissociated carboxylic acid, makes the difference while compared with the non-dissociated species whose stretching occurred at 1730 cm^{-1} [6].

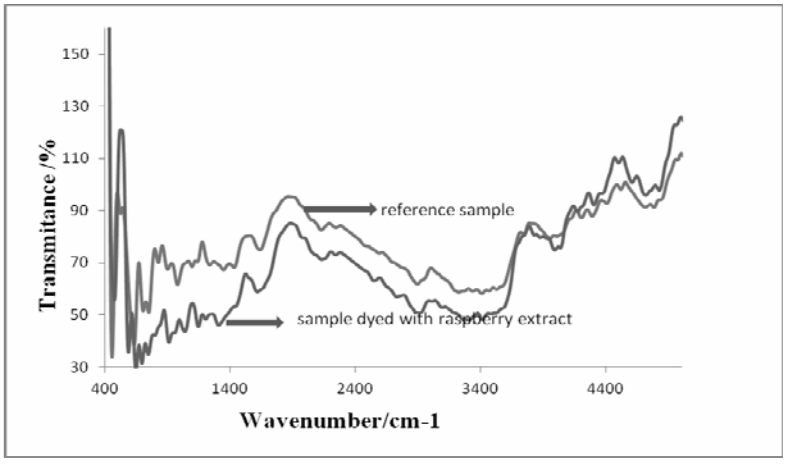

Fig. 1: *FT-IR spectra for flax fiber supports dyed with 1% raspberry natural extract.*

Nitrogen adsorption/desorption isotherms have been used to characterize the textural properties of the studied materials **Fig.2**.

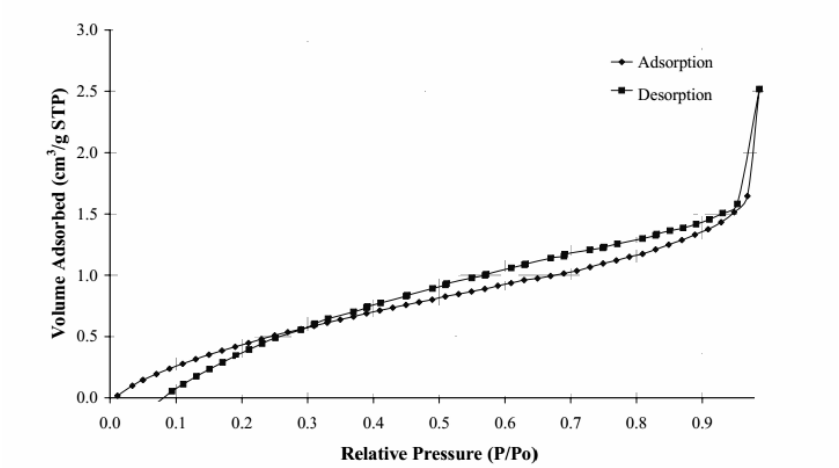

Fig. 2: *The nitrogen adsorption/desorption isotherms of the inclusion compound (MCT-β-cyclodextrin-as host and anthocyanins natural dye as guest molecule).*

BET method requires dehydrating the cellulose fibers at 120°C, under vacuum, having as consequences the elimination of intramolecular water molecules and collapsing of cellulose chains. This explains the small internal surface area of cellulosic fibres, completely inaccessible to the nitrogen molecules. As the result, the adsorption branch overlapses at least one point with the desorption branch. According to the BET isotherm and compared to the previous studies, the inclusion complex is not so well defined.

The colour differences between fruits, flowers and vegetables depend on the nature and concentration of the anthocyanins they contain. The colour changes in case of both flax samples dyed with the assistance of citric acid as biomordant, and for samples dyed by inclusion of the natural extract molecule within the hydrophobic cavity of MCT-β-cyclodextrin, revealed colour differences pretty high, as well as the colour darkening for some of the samples. ΔE* occurs within the acceptable range.

The colour measurements were made having as reference the non-grafted and dyed samples. In the same time, a comparison between flax fabric and bamboo knitting was necessary, in order to set-up the intensity of dyeing with natural pigment, in terms of fibrous composition of the support.

Table 1: *Colour measurements and colour fastness values for flax and bamboo samples dyed with raspberry (Rubus idaeus L) anthocyanin extract*

Textile sample	**ΔL***	**Δa***	**Δb***	**ΔC***	**ΔH***	**ΔE***	**Washing fastness**	**Rubbing fastness**
Reference flax sample, dyed Sample 1	- 0.220	- 0.316	- -0. 517	- 0.371	- -0.479	- 0.645	3	3
Flax sample, dyed with the assistance CA Sample 2	-1.250 -0.803	1.058 1.314	1.889 -1.587	0.967 1.138	1.937 -1.717	2.500 2.211	3-4	4
MCT-β-ciclodextrin grafted flax sample, dyed Sample 3	-3.128	1.477	2.317	2.413	1.313	4.163	4-5	5

Reference bamboo knitting, dyed Sample 4	-	-	-	-	-	-	3	3-4
Bamboo knitting sample, dyed with the assistance CA Sample 5	-0.226	0.060	2.958	0.200	2.952	2.967	4-5	5

Following the colour measurements, average colour changes were noticed:
- the sample dyed with mordant is darker and redder and little bluer compared to the sample dyed without the assistance of biomordant;
- the flax fabric is slightly less red and blue compared to bamboo knitting sample;
- the flax fabrics dyed in presence of the biomordant, are darker and redder and little yellower, than the knittings made of bamboo fibres;
- the samples grafted with MCT-β-cyclodextrin and then dyed have the highest colour intensity, as well as improved washing and rubbing strengths.

4. CONCLUSIONS

The results of the present study show the relevance of using the raspberry anthocyanis extract in the cyclodextrin pretreatment version but with the assistance of citric acid as biomordant. Inclusion of raspberry anthocyanins in the cyclodextrin compound was shown from the FTIR analysis, rather than BET analysis, proving the positive contribution of MCT-β-cyclodextrin grafting. The colour changes as well as the fastness are quantificable (2-3 points) for samples pretreated with cyclodextrin, and the bamboo knitting dyed in the presence of citric acid. It is imperative to continue such researches in this direction in order to demonstrate the potential positive impact for the strategy of textile eco-development and the economic benefit of using natural extracts dyes.

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