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VEGETABLE FOOD WASTE FOR COTTON DYEING-NEW DIRECTIONS FOR ENVIRONMENTAL SUSTAINABILITY

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Abstract

The present paper presents the results obtained in the attempt of valorisation of the natural pigments obtained from vegetable wastes by considering the principles of the circular economy. For this purpose, was used the waste from different technological steps of food preparation (outer leaves, spine with seeds).

The extracted pigments were used for the dyeing of cotton fabric that firstly was bioscoured and bleached.

The results showed that the treated cotton fabric presents good properties (weight loss, hydrophilicity, whiteness and colour intensity K/S, etc.).

This paper also addressed to the monitoring of the parameters for the wastewater resulted after the treatment of cotton fabrics with the studied pigments.

The results showed that the wastewater from the dyeing proved to comply with the imposed limits for the wastewater according to the environmental standards.

Keywords: *eco-friendly cotton treatments, natural dyeing, wastewater analysis*

Introduction

Nowadays, industrial technologies should be designed in a manner that ensures their sustainability and also to have a lower impact on the environment. In this context also, the fabrics processing and dyeing need to be adapted to these new demands.

One of the first steps in the textile processing of cotton fabrics is scouring. The treatment is imposed by the specific composition of those natural fibres (more than 95% cellulose) and by the need to remove all present organic (various acids, wax, colorants, pectin) and inorganic impurities (dust, salts) (Sheikh & Bramhecha 2019). Traditionally, the operation consists of an alkaline treatment at high temperature. As an eco-friendly alternative, the bioscouring based on an enzymatic treatment at low temperature can be applied.

The enzymatic treatment in our study is based on a commercial product containing a mixture of pectinases. This type of enzyme total or partially hydrolyses the pectin present in the primary cell wall of the cotton, in aqueous solutions. As a result of the pectic matrix distortion, removal of other impurities is facilitated. The data presented in the literature underline the efficiency of the bioscouring treatments

related to technological characteristics of treated fabrics obtain from natural fibres (wettability, whiteness degree) as well as the economic and ecological aspects (energy and chemical lower consumption) (Abdel-Halim et al 2008).

Various data presented in the literature suggest the potential of natural dyes as eco-friendly alternatives in the dyeing process. One possible difficulty is raised by the specific chemical structure of the cotton, which is a predominant cellulosic fibre and therefore has low affinity to many natural dyes. This situation imposes the use of additional compounds, which will lead to reactive carboxylic and amino groups that will be able to link to the dye molecule.

To improve the colour strength, are currently used salts of the transitional metals (mordants) (Özlenen & Yıldırım 2019).

Cotton fabrics have been dyed with natural pigments obtained from plants since ancient times. They are generally easy to obtain as they are soluble in polar solvents. The pH of the dyeing solution has a big influence on the obtained colour. The changes in this parameter could lead to various colour results, varying from brown to green and blue (Vankar 2017).

In respect to the tinctorial characteristics of the red cabbage, it has been proven that a blue-green colour is obtained in alkaline media using mordant pre-treatment (Ticha et al 2016). To activate the cellulose's carboxylic and amino groups, whey proteins could be used as mordant. In this case, the best colour strength for *Xylocarpusgranatum* pigments is obtained at the acidic pH value of 5 (Pisitsak et al 2016).

Four major directions could be considered for the valorisation of food waste, such as use as raw materials for obtaining biofuels, different valuable bio components, biomaterials, or absorbents for wastewater treatment (Gupta et al 2019, Nayak & Bhushan 2019). Previous studies of other researchers showed promising results obtained in the case of using orange tree leaves, pomegranate peels, alkanet roots or nutshell, products which are normally considered to be vegetable waste (Benli & Bahtiyari 2015).

The proposed alternatives are related to the use of natural pigments obtained from vegetable wastes. The natural pigments have a lower impact on the environment due to their integration in a circular process, ensuring the sustainability of the dyeing process. Adopting these strategies could be reduced the use of the synthetic dyes used in the textile finishing sector. The use of the pigments extracted from vegetable waste brings a number of advantages (biodegradability, renewability, low environmental influence), but some disadvantages should also be considered (high production cost, a less variety of colours and shades and lower intensity compared to the synthetic ones, possible difficulties of supplying and sustainability, or toxic effects following the skin contact) (Vankar & Shukla 2019).

In our present study, cotton fabrics were dyed using vegetable pigments with and without mordants. The treatment without mordants is an eco-friendly one, and it is recommended even if the colour strength obtained is less intense.

We believe that these results are a good example of the application of a circular economic model. As the food wastes are not always possible to be minimised, these approaches should be considered for further advanced processes.

Materials and Methods

The dyeing treatments were made on 100% cotton woven fabric with the following characteristics: width (150 ± 3 cm), weight (200 ± 10 g/m²), and warp of 100% cotton yarn with Nm 25/2 and weft of 100% cotton yarn with Nm 25/1.

For the bioscouring, the pectinolytic product Beisol PRO, a mixture of pectinases and Denimcol Wash RGN as surfactant supplied by CHT Bezema Company were used.

The sodium hydroxide, sodium silicate, hydrogen peroxide, tannic acid, acetic acid, Felosan RG-N, sodium citrate and the iron sulphate were purchased from Sigma-Aldrich. All reagents used had purity between 97-99%.

The dyeing pigments were obtained from red cabbage outer leaves, red and yellow onions peel, and red pepper spine with seeds.

Preliminary washing

The cotton samples were washed with hot water (100°C) in an AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company-USA. Subsequent, were dried, conditioned and weighing as specified by the international standards.

Bioscouring treatment

The bioscouring was made in the same AATCC standardized Lander-Ömeter, model M228-AA with a commercial enzymatic product. The enzyme concentration was 2% (o.w.f-concentration over fibre), 2 g/L sodium citrate and 0.5% Denimcol Wash RG-N. The reaction was developed at 55°C for 35 minutes in liquor to fabric ratio of 1:20. After applying the above treatment, the cotton samples were washed with hot (70°C) and cold water and dried at room temperature.

Bleaching treatment

The bioscoured cotton samples were treated with an aqueous solution containing 3 mL/L hydrogen peroxide, 4.5 mL/L sodium silicate and 1 g/L sodium hydroxide. The bleaching process was performed at a material to liquor ratio of 1:20 and temperature of 95°C for 60 min with stirring in AATCC standardized Lander-Ömeter. The bleached samples have been neutralized with a solution of 10% acetic acid and washed several times with hot water then with cold water and finally dried at ambient conditions.

Dyeing solution

To obtain the dyeing solutions red cabbage outer leaves, red and yellow onions peel and red pepper purchased from a local store were used. The outer leaves of cabbage, onions peel and spine with seeds of the red pepper were used. 40 gr. of each vegetable material was mixed with 500 mL of distilled water and boiled for 1 hour. The cooled extract was filtered and used for dyeing the cotton fabrics.

Mordanting

To form the reactive carboxylic and amino groups on the cotton samples surface, the fabrics were treated with 3% tannic acid for 2 h followed by the treatment with 35 g/L iron sulphate. Both treatments were made in the Lander-Ömeter with constant agitation at 80°C.

Dyeing treatment

The dyeing treatments were carried out on various pre-treated cotton samples with and without mordanting. 1:20 material to dyeing solution ratio was used at a temperature of 95°C for 60 min. After that, the dyeing bath temperature was reduced to 70°C and the dyeing treatment was continued for 15 min. Dyed cotton samples were washed at 80°C for 10 min with 1 g/L Felosan RG-N and then successively rinsed with hot and cold water, squeezed and air dried (Chirila et al 2018).

Analysis of the material properties after preliminary treatments

After drying and conditioning of the bioscoured samples till constant weight, the hydrophilicity and weight loss were determined. The weight loss was determined by gravimetric method. The samples were dried at 105 °C in an oven from Caloris Group, Romania till constant weight. The weight loss was calculated using the following equation:

$$\% \text{ weight loss} = (W1 - W2) \times 100 / W1 \quad (1)$$

where W1 and W2 are the weights of dried samples fabric before and after the treatment.

The hydrophilicity of the bioscoured samples was determined according to AATCC Test Method 79-2007. Whiteness and yellowness index were determined after the bleaching treatment of cotton material on a Datacolor 500 spectrophotometer. For an opaque view each sample was folded twice to give four plies and the whiteness was measured four times at different points. The reflectance (R %) at 420 nm was measured in comparison with a standard of barium sulphate for absolute white. The Hunter Whiteness Index and DIN 6170 Yellowness Index were calculated automatically by Datacolor Tools 2.0 software.

Colour measurements

Colour measurements were performed according to AATCC Evaluation Procedure 6-2008 by using Datacolor 500 spectrophotometer. The data obtained for colour difference represent the average of three determinations made in different areas on dyed samples. To evaluate the colour strength of dyed samples the K/S value was calculated at dominant wavelength (420 nm) based on Kubelka-Munk theory:

$$K/S = (1 - R) / 2R \quad (2)$$

where K is the absorption coefficient, S is the scatter coefficient and R is the sample reflectance value at the dominant wavelength.

Wastewater analysis after dyeing

The wastewater resulted after the dyeing treatments was collected and analysed with a WTW multi-parameter inoLab Multi 740. pH, salinity, TDS (total dissolved solids), conductivity and total dissolved oxygen were determined. For the determination of the turbidity a HI 88713 HANNA Instruments Turbidimeter was used.

Results and Discussion

In order to obtain efficient and uniform dyeing of the material, a good preparation is required. The cotton fabric undergoes different chemical pre-treatments such as scouring and bleaching to withdraw impurities which negatively influence the subsequent technological operations and to improve fibre whiteness and dyes

affinity. Table 1 presents the characteristics of cotton fabric after bioscouring and bleaching treatments.

Table 1. The parameters obtained for cotton fabric after bioscouring and bleaching treatments

No.	Weight loss [%]	Hydrophilicity [s]	Whiteness index	Yellowness index
1	1.65	0.78	73.07	12.20
2	1.80	0.79	74.45	11.32
3	1.93	0.80	74.67	11.27
4	1.97	0.77	74.00	11.60
5	1.77	0.86	73.52	12.30
6	1.80	0.87	73.85	12.47
Row cotton fabric	-	>500	45.79	27.35

The weight loss values of bioscoured samples show the effectiveness of bioscouring treatment by removing non-cellulosic attendants, which is also confirmed by the values of hydrophilicity. For all treatments, the weight loss is in agreement with the data from the literature which mention values below 5% for enzymatically treatments (Bashar et al. 2015). Also a hydrophilicity lower than 1 second is considered to be optimum.

A good whitening of the material was obtained after bleaching with hydrogen peroxide (~75) compared to the raw cotton fabric (~46). The whiteness index was increased with ~61% and the yellowness index was decreased with ~41%.

Evaluation of the chromatic parameters, using the spectrophotometric measurement allowed establishing the colour intensity K/S and colour differences of naturally dyed samples with pre-mordanting with those without mordanting. Colour difference was determined considering as reference the bleached undyed cotton fabric. The K/S values recorded at dominant wavelength ($\lambda_{\text{dominant}}=574$ nm) and total colour difference DE between all dyed samples and the reference are shown in figure 1.

To highlight the influence of pre-mordanting treatment on colour intensity, the samples were analysed by comparing the K/S and total colour difference (DE) values obtained for pre-mordanted samples and those obtained for un-mordanted and dyed samples.

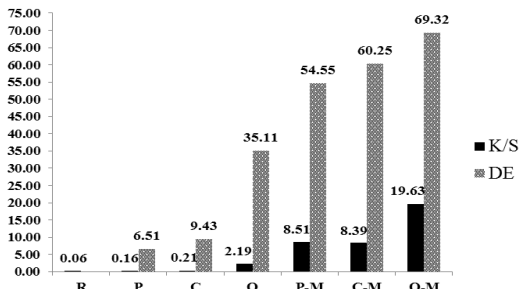


Figure 1. K/S and total colour differences (DE) between the naturally dyed and pre-mordanted naturally dyed cotton samples

Note: R-reference; P-red pepper; C-red cabbage; O-onions peel; P-M-pre-mordanted red pepper; C-M-pre-mordanted red cabbage; O-M-pre-mordanted onions peel

From the data presented in Figure1 it can be observed that the best results were obtained for samples pre-mordanted and dyed, this is positively influencing the adsorption capacity of the natural dye in the cotton fibres, leading to darker colours. The behaviour is given by the specific chemical structure of the cotton, this being a predominant cellulosic fibre it has low affinity to many of the natural dyes, so a mordanting treatment being necessary. In the both cases, with mordanting and without mordanting, more saturated colours were obtained for the samples dyed with onions peel followed by samples dyed with red cabbage and red pepper.

For a better characterization of the proposed dyeing treatments, the evaluation of the wastewater parameters was done. For comparison, all values used as a reference represent the minimum admissible values reported in the literature in the case of cotton dyeing wastewaters. pH, conductivity, total solids dissolved, salinity, total dissolved oxygen and turbidity were analysed. Figure 2 and figure 3 present the wastewater parameters resulted from all variants of natural dyeing treatments.

Conductivity and total solids dissolved are two complementary parameters used frequently for wastewaters characterisation. From figure 2 it can be seen that in all studied cases the values registered are 10 times lower compared with the results obtained after the dyeing of the cotton with synthetic dyes. Mordant utilisation does not have a significant influence on the two parameters. Another important parameter of wastewater is the turbidity. This is given by the soluble coloured products, organic and inorganic compounds in suspension. In the case of onion and cabbage dyeing solution with mordants, this indicator has values 10 times higher compared with the one reported in the literature for dyed cotton. In the case of the cotton dyed with cabbage without any mordants in the bath, was registered the lowest turbidity value, 15.5 NTU.

The pH values registered are in the acidic domain, around 3.4. Higher values can be observed for the cases with cabbage and pepper cotton dyeing wastewater.

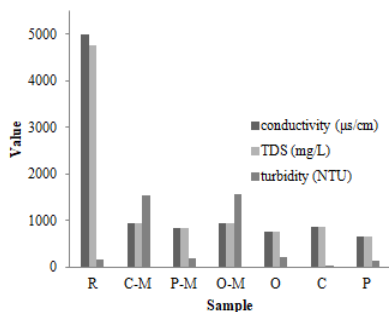


Figure 2. Waste water conductivity, total solids dissolved and turbidity for all variants of natural dyeings

Note: R-reference; P-red pepper; C-red cabbage; O-onions peel; P-M-pre-mordanted red pepper; C-M-pre-mordanted red cabbage; O-M-pre-mordanted onions peel.

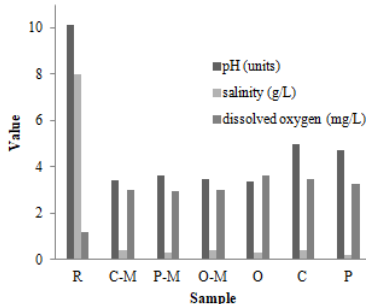


Figure 3. Waste water pH, salinity and dissolved oxygen for all variants of natural dyeings

The salinity data recorded vary between 0.2 g/L (pepper) to 0.4 g/L (cabbage with and without mordant and onion with mordant). The ions types which determine this parameter could determine the appearance of different toxic phenomena on plants or problems in water absorption if the wastewater is not well treated before reaching the environment. In all of the discussed cases, the recorded values for the total dissolved oxygen are higher (2.5-3 times) compared with the reference one. There are almost the same values in all 6 cases presented (2.95-3.6 mg/L). Increase quantity of dissolved oxygen inhibits the development of anaerobic microorganism, but it is a growth factor for the aerobic one.

Conclusions

The obtained results revealed that the natural pigments obtained from vegetables waste, in some cases, might be an alternative for synthetic dyestuffs for cotton fabrics dyeing.

The preliminary treatments like bioscouring and bleaching have provided adequate hydrophilicity and whiteness degree of the cotton fabric, leading to an even dyeing. Pre-mordanting has positively influenced the adsorption capacity of natural dye in cellulosic fibres and darker colours were obtained compared with the un-mordanted samples. Good results for colour intensity were obtained for all pre-mordanted and naturally dyed samples. A high increase of the colour strength was observed for samples dyed with onions peel in both cases.

The wastewater resulted from all dyeing variants is less polluting compared to the parameters of the wastewater reported for dyeing with synthetic dyes, but some corrections are needed before disposal on water bodies or in the environment in order to assure less pollution and an eco-friendly environment.

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