

Natural dyes from lignocellulosic biomass hydrolysates

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Received 16 March 2016; revised received and accepted 3 November 2016

Wheat straw has been hydrolyzed in two different conditions, namely subcritical water and 100 °C boiled water, and the hydrolysates obtained are used to dye wool yarns. The wool samples are pretreated with three types of mordants before dyeing with wheat straw hydrolysates. Irrespective of the metal types used in pretreatment process, subcritical water hydrolysate always results in same color in dyeing process. However, three colors are obtained for each mordant when 100 °C boiled water is used as a dyeing reagent. The effect of the total phenolic contents of the hydrolysates on color development has also been evaluated. The total phenolic and sugar contents of subcritical water hydrolysate are found higher and the dyeing performance of this hydrolysate is better than the 100 °C boiled water hydrolysate. Light and wash fastness of dyed wools are also assessed. Light and wash fastness tests result in 3-4 and 4-5 rating respectively.

Keywords: Fastness test, Mordants, Natural dye, Phenolic compounds, Subcritical water, Wheat straw, Wool

1 Introduction

Natural dyes on textile materials are gaining more attention all over the world due to increased environmental awareness in order to avoid use of some hazardous synthetic dyes. Natural dyes are non-allergic, non-toxic, non-carcinogenic and biodegradable. They do not cause environmental pollution¹. Therefore, in the last few years, an increasing interest has been developed for use of different raw materials to produce natural dyes. The main drawbacks of natural dyes are limitation of their productions and challenging to obtain the same color consistently. A concept to overcome these existing technical barriers is the production of natural dye from plant-based material extracts.

Wheat (*Triticum aestivum*) is a perennial plant, can be grown in any soil conditions with many varieties. For this reason, wheat is grown in almost every part of the world and ranks among the most widely grown plants. Wheat is composed of xanthophylls esters, carotenes, flavones, kriptoksantin and pigments formed from degradation products of chlorophyll^{2,3}. Flavones are yellow compounds in plants. Phenolic substances are usually soluble in water and often associated with a sugar compound such as glycosides. Flavonoids are the important plant pigments with polyphenolic structure as phenolic acids. Simple monocyclic phenols, phenylpropanoids and phenolic quinones are also abundant in wheat. The 5,7,4'-trihydroxy-3',5'-dimet is

the most important flavone in wheat. Wheat straw is primarily composed of cellulose, hemicellulose and lignin⁴. *p*-Coumaric and ferulic acids are the most important phenolic groups in the lignin. Wheat biomass hydrolysates can be a good candidate for natural dye production.

Various methods, such as gamma ray assisted⁵ and microwave-assisted⁶ methods, have been used to extract dyes from plants. However, no study was performed with wheat straw and its subcritical water extracted hydrolysates. Subcritical water (99.97 °C < T < 374.15 °C; 217.76 atm < P) is an alternative way to hydrolyze plant biomass in an environment-friendly manner by using only operating temperature and pressure conditions. The chemical properties of water change significantly at high temperatures and pressures due to the reduction of *hydrogen bonding*, which causes changes in dissociation, solubility, diffusivity, and reactivity. Subcritical water has a lower relative dielectric constant and a higher ionic product than ambient water. At high pressures and temperatures polarity of water decreases and it behaves like a ethanol, acetone, methanol in extraction process. Therefore, it can be used to extract lower polarity components without using an organic solvent. In our previous studies, lignocellulosic biomass was hydrolyzed upto 72% by this method. The hydrolysates were rich in polysaccharides, monosaccharides and phenolics^{7,8}. Based on these studies, the hydrolysates were designed to be used in dyeing also because of their high phenolics and sugar contents.

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Most natural dyes used in textile industry are required to be treated with metal salts (mordants) to increase dyeing properties. Metal salts catalyses attraction of natural colorants towards the fibre surface and increases the efficiency of dyeing by forming a complex compound. Since wool contains both amino and carboxylic groups, it can be dyed in acidic, basic and neutral medium. Dyeing process occurs by formation a salt bridge between wool and natural dye that is provided by a metal salt (Fig.1). Due to existing waste water limits and requirements for eco-textiles, there is a small number of metal salts (iron and aluminum) mordants that can be used for natural dyeing and low concentrations of metal salts should be preferred.

The present study is therefore aimed at preparing natural dyes from lignocellulosic biomass. Wheat straw is used as a representative biomass material. Biomass hydrolysates are prepared by breakdown of wheat straw in subcritical water and in boiling water. The hydrolysates are used along with three different mordants [$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] in low concentrations. The effect of phenolics and total sugar contents of the hydrolysates are evaluated for dyeing performance of wool yarns. Evaluations of dyed wools samples are performed by measuring color and color fastness (light and wash fastness) of the samples.

2 Materials and Methods

2.1 Materials

Wool yarns (g/9000 m) and wheat straws were obtained from local commercial suppliers. The 20 cm wool yarn were used in the dyeing process. Wheat straw was grounded (120-140 mesh) before hydrolysis process. The composition⁸ of wheat straw used in the study is given below:

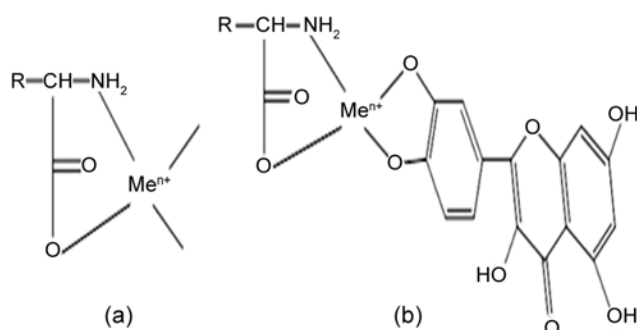


Fig. 1 — Chemical bonding in (a) wool & mordant; and (b) mordanted wool & naturel dye

Components	Value
Moisture	: 8.67 ± 0.40 %
Ash	: 3.08 ± 0.10 %
Cellulose	: 36.0 ± 5.0 %
Hemicellulose	: 27.0 ± 3.0 %
Lignin	: 11.0 ± 2.0 %
Extractives	: 26.0 ± 5.0 %

2.2 Hydrolysis of Wheat Straw

Hydrolysis of wheat straw in subcritical water was performed in a stainless steel reactor at 250°C under 276 bar carbon dioxide pressure for 120 min. The detailed information about hydrolysis experiments has been given in a previous study⁸. The hydrolysate obtained by boiling water extraction was prepared by refluxing 10 g of wheat straw in 350 mL water for 2 h. The hydrolysates were filtered before use.

2.3 Mordanting

The 3g/L potassium aluminum sulfate, copper sulfate and ferrous sulfate were used for mordanting process. The 25 mL of mordant solution was placed in a glass beaker with wool yarn and heated up to 80°C for 1 h. After mordanting, the wool yarn was dried at room temperature (25°C).

2.4 Dyeing

Mordanted wool samples were mixed with 25 mL of wheat straw hydrolysates at 80°C for 1 h. The dyed samples were washed sequentially with hot and cold water and dried at room temperature (25°C). Dyeing process was also performed without using mordant solution for comparison.

2.5 Instrumental Analysis

Total water soluble phenolics contents of hydrolysates were determined by Folin–Ciocalteu assay⁹. Total phenolic acids were expressed as gallic acid equivalents. The 0.5 mL hydrolysate was mixed with 1 mL of 10 times diluted Folin–Ciocalteu reagent and 2 mL of saturated Na_2CO_3 . The mixture was vortexed for 30 s and kept at room temperature (25°C) for 30 min. Absorbance at 765 nm was recorded using a spectrophotometer (Thermo Scientific Genesys 10S UV/Vis).

The color yields (K/S) were measured by a Datacolor 650 spectrophotometer. The measurements were done at 410 nm and transferred to K/S , according to the Kubelka–Munk equation^{10,11}. Fastness tests of dyed samples were performed according to ISO standard methods such as ISO 105 B02 for light and ISO 105 C06 for wash fastness. Colorimetric method (H_2SO_4 -phenol) was used for determination of total sugars in

hydrolysates¹². Quantification was done using a calibration curve prepared with saccharose standard solutions.

The infrared spectra of the samples were recorded on a Thermo Scientific Nicolet iS10 FTIR Spectrometer using ATR (attenuated total reflectance) technique. Total organic carbon content was determined using Tekmar Dohrmann Apollo 9000 instrument.

Wheat straw hydrolysates (100 mL) were extracted with diethyl ether followed by drying through Na_2SO_4 column. The solvent was evaporated from the extract using a rotary evaporator. The compositions of the samples were determined by a Thermo Finnigan Trace Gas Chromatograph and Mass Spectrometer (GC-MS) using Thermo TR-5 MS capillary column (60 m $\times$ 0.25 mm ID $\times$ 0.25 mm film thickness). The oven temperature used was as follows: 5 min at 40 °C; from 40 °C to 280 °C with 2.5 °C/min heating rate and hold at this temperature for 10 min. Inlet temperature was 240 °C. The 70 eV and 240 °C were set as ionization voltage and ion source temperature, respectively. The 1 μL sample was injected in splitless mode. Solvent delay was 6 min. The NIST 2002 mass spectral library was used in identification.

3 Results and Discussion

3.1 Colors and Color Measurements

Wheat straw has been hydrolyzed separately in subcritical water and 100°C boiled water and the two different hydrolysates thus obtained are then used as dye solutions. Hydrolysis percentages, calculated based on residue leftover after hydrolysis process, are found to be $25.5 \pm 5.6\%$ and $76.2 \pm 1.4\%$ for 100°C boiled water and subcritical water processes respectively. The total organic carbon contents of the hydrolysates obtained are 1572.4 ± 35.0 and 4811.8 ± 123.4 ppm C respectively. In subcritical water hydrolysis, pressurization of the reactor is provided by CO_2 . The CO_2 causes formation of carbonic acid in reaction media that enhances the solubilization of wheat straw. The effect of carbonic acid is clearly visible on hydrolysis yield and total organic carbon contents of hydrolysates. Lignin fraction of biomass, a source of phenolic compounds, is important in dyeing process. When lignin fraction is broken down, it releases phenolic components into hydrolysates.

The colors obtained after dyeing the mordant treated wool yarns with wheat straw hydrolysates are presented in Table 1. Since water absorption capacity of wool yarn is high, it is selected as a testing material. Irrespective of metal types used in pretreatment process, subcritical water hydrolysate always results in same color in dyeing process. However, three colors (light green, bronze and

beige) are obtained for each mordant when 100 °C boiled water is used as a dyeing reagent (Table 1). Dyeing the wool without mordant does not show any color on the wool material.

The color yield (K/S) and the CIELab coordinates of the dyed wools are shown in Table 2. The color yield is significantly increased when dyeing process is performed with subcritical water hydrolysate (Table 2). Highest color yield (K/S) is obtained when $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ mordant and subcritical water hydrolysate are used in dyeing process. The color yields obtained with 100°C boiled water hydrolysate decrease in the order: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} > \text{CuSO}_4 \cdot 5\text{H}_2\text{O} > \text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

The wool shows darkest color when dyed with subcritical water hydrolysate. This hydrolysate exhibits the highest color yield with copper sulfate mordant ($L^* 16.78$). On the other hand, boiled water hydrolysate with potassium aluminum sulfate mordant shows lowest color yield. Although aluminum is able to make strong bonds in its coordination complexes, these aluminum complexes are not capable to form strong bonds with textile materials. The lightest color is observed when wool sample is mordanted with $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and dyed with boiling water hydrolysate ($L^* 71.63$).

The (+) values for a^* indicates redish color, while negative a^* value shows compliance with greenish. The copper sulfate shows negative a^* value (-3.03) when it is used as mordant for dyeing with boiled water hydrolysate. This indicates that the color obtained is more greenish as compared to others. Positive values of b^* show that all wool yarns are yellowish in color. Since copper complexes are stronger than iron ones, the higher K/S values are observed when copper metal is used in mordanting process.

Table 1 — Colors obtained from wheat straw hydrolysates

Mordant	Color	
	Boiling water	Subcritical water
No mordant	No color	No color
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Light green	Dark brown
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Beige	Dark brown
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Bronze	Dark brown

Table 2 — Color measurements results of wool samples

Sample	K/S	L^*	a^*	b^*
Subcritical water (No mordant)	21.85	28.63	9.04	16.93
Boiling water (No mordant)	1.83	59.68	1.25	16.60
Subcritical water+Cu	31.24	16.78	4.39	6.00
Subcritical water+Al	19.62	28.58	8.09	14.85
Subcritical water+Fe	30.16	19.31	4.40	8.61
Boiling water+Cu	5.19	53.88	-3.03	22.07
Boiling water+Al	1.51	71.63	2.36	27.28
Boiling water+Fe	8.55	50.06	9.50	27.94

3.2 Effect of Total Phenolic and Sugar Contents of Hydrolysates on Color Development

The effects of phenolic and sugar contents on color development are investigated by spectrometric measurements. FTIR spectra of non-treated wheat straw shows aromatic C–O stretching band for guaiacyl ring of lignin at $1507\text{--}1515\text{ cm}^{-1}$ (ref.13) (Fig. 2). The small sharp bands at 1113 cm^{-1} and 910 cm^{-1} are related to C–O vibrations of crystalline and amorphous celluloses respectively. The bands at $3345\text{--}3352\text{ cm}^{-1}$ belong to O–H stretching and the absorption at $2904\text{--}2916\text{ cm}^{-1}$ is due to C–H stretching. The C–C stretch from cellulose gives peak at 1375 cm^{-1} (refs 14,15). There are significant changes in wheat straw structure after subcritical hydrolysis process. The changes are condensed between 1750 and 1000 cm^{-1} , indicating C–O bond cleavages in wheat straw structure because of solubilization. Solubilization of wheat straw in

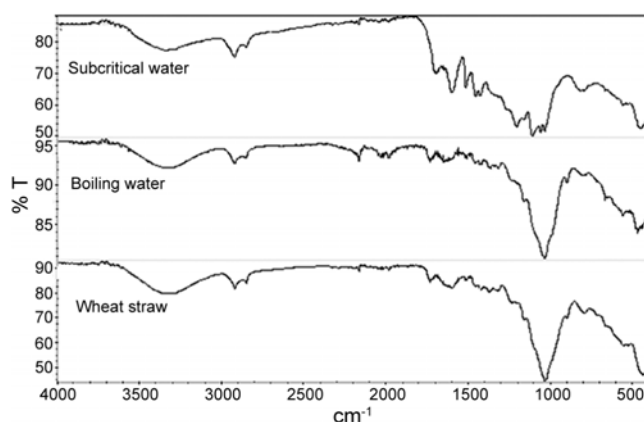


Fig. 2 — FTIR spectra of wheat straw before and after hydrolysis

subcritical water causes release of phenolic compounds into solution. Total phenolic contents of hydrolysates are determined by colorimetric measurements and are found to be $1733.69 \pm 2.34\text{ mg.L}^{-1}$ and $213.83 \pm 1.44\text{ mg.L}^{-1}$ for subcritical water and boiled water hydrolysates respectively. Since the break down process is more effective in subcritical water, total phenolic content of subcritical water hydrolysate is significantly higher than boiling water one. It is observed that when total phenolic content of the hydrolysate is higher the color yield values calculated after dyeing process is also higher.

Total phenolic data give total content of phenolic acids, flavonoids and often volatile and small molecule compounds. Flavonoid groups are mostly responsible for color development and stability¹⁶. Sugar moieties in the structures affect the color intensity¹⁷. For instance, monoglucosidic anthocyanins tend to possess deeper color than their diglucosidic forms; however, diglucosidic anthocyanins seem to be more stable than their monoglucosidic counterparts¹⁸. The results show that high content of total phenolics in subcritical water hydrolysate results in darker colors compared to boiled water one (Tables 1 and 2). On the other hand, total sugars contents of subcritical water hydrolysate are two times more than that of boiled water hydrolysate, $1938 \pm 5.78\text{ mg.L}^{-1}$ and $1083 \pm 3.45\text{ mg.L}^{-1}$ respectively; this also has significant contribution on color development.

Wheat straw hydrolysates from subcritical water and boiling water treatments are also analyzed for organic compounds by GC-MS and determined using NIST spectral library (Fig. 3). The compounds found

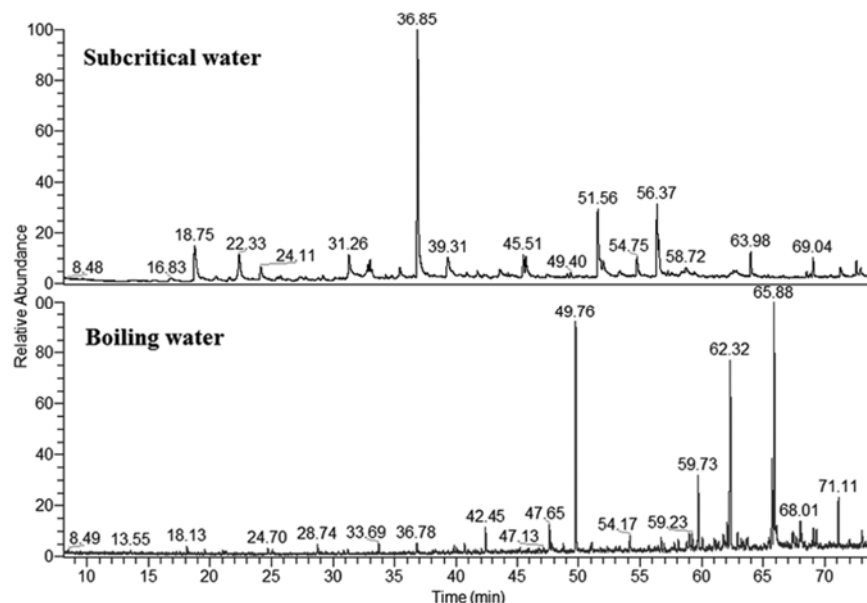
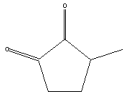
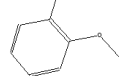
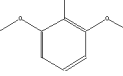
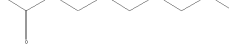
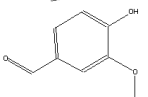
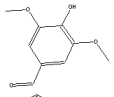
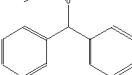
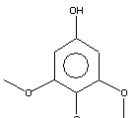
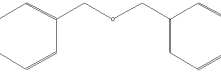
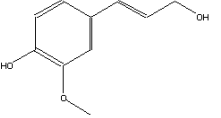


Fig. 3 — GC-MS chromatograms of subcritical water and boiling water treated wheat straw hydrolysates

Table 3 — The Mass spectral data and the compounds identified in wheat straw hydrolysates^{1,2}

Retention time, min	Compound	Fragments ions (m/z)	Molecular structure
18.75 (SW)	Corylon (2-hydroxy-3-methyl-2-cyclopenten-1-one)	112 (M ⁺), 97, 83, 69, 55	
22.33 (SW)	2-methoxyphenol	124 (M ⁺), 109, 95, 81, 53	
31.26 (SW)	Cryptone	138 (M ⁺), 96, 95, 67, 53	
36.85 (SW)	2-6-dimethoxyphenol (Syringol)	154 (M ⁺), 139, 96, 65, 51	
42.45 (BW)	Nonoic acid	158 (M ⁺), 129, 115, 73, 60	
47.65 (BW)	p-hydroxybenzaldehyde	122 (M ⁺), 121, 94, 93, 65	
49.76 (BW)	Vanillin	152 (M ⁺), 123, 93, 81, 65	
51.56 (SW)	4-hydroxy-3,5-dimethoxybenzaldehyde (syringyl aldehyde)	182 (M ⁺), 181, 111, 93, 65	
56.37 (SW)	Benzylhydrylvinyether	210 (M ⁺), 167, 123, 106, 78	
59.73 (BW)	3,5,7-trimethoxyphenol	184 (M ⁺), 169, 141, 126, 111	
62.32 (BW)	Benzyl ether	182, 119, 91, 65, 56	
5.88 (BW)	Coniferyl alcohol	180 (M ⁺), 137, 124, 119, 91	

SW—Subcritical water, BW—Boiling water.

in the hydrolysates are listed in Table 3. The main compound in subcritical water treated wheat straw hydrolysate is 2-6-dimethoxyphenol (Syringol). However, coniferyl alcohol, vanillin and benzyl ether are the main composition products in boiling water treated wheat straw hydrolysates. The mass data indicate that the organic compounds in these hydrolysates are solubilized from lignin fraction; however, since solubilization degrees are different in both treatments, the compounds released into solutions are not same in subcritical water and boiling water treated hydrolysates.

3.3 Fastness Tests of Wool Yarns

The fastness tests results are evaluated according to blue and gray scale for light fastness. Light fastness test results in mostly 3-4 rating; subcritical water + Fe shows 4-5 light fastness. The high values of fastness tests indicate dye quality for natural coloring. Ferrous sulfate gives the best results as a mordant when the dyeing is performed with subcritical water hydrolysate. Subcritical and boiled water hydrolysates exhibit same behaviour in terms of wash fastness (4-5). These results are in accordance with the findings reported for natural dyes¹⁹⁻²².

4 Conclusion

In the present study, possible natural dye production from non-edible biomass material has been investigated. Dyeing process of wool yarn is performed by using the hydrolysates obtained from solubilization of wheat straw in environment-friendly mediums; subcritical water and 100 °C boiled water. The total phenolic and sugar contents of those two types of hydrolysates differ from each other and subcritical water treated one has higher amount of those components. When dyeing process is performed with higher total phenolics and sugars containing hydrolysate, darker color is obtained although same mordants are used. The hydrolysates show promising results as sources of natural, non-toxic and ecofriendly dyes. The results indicate that the hydrolysate from subcritical water has better color yields (K/S). Four colors such as light green, bronze and beige are obtained for 100 °C boiled water and dark brown for subcritical water using different mordants. Fastness values of the hydrolysates are found almost the same. As the hydrolysates have the medium and quite good fastness values, they increase the kenaf biomass natural dyeing availability for industrial application. The results of this study could lead to new opportunities for development of new plant-based natural dyes. The compositions of various biomass hydrolysates may be adjusted by hydrolysis process to enhance the dyeing performance of hydrolysates to be obtained.

Acknowledgement

The authors would like to thank Eksoy Dyes and Chemicals Company (Adana, Turkey) for the support on fastness tests.

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