Red Dyeing Silk in Room Temperature Using Fermented Rice (*Oryza Sativa*) and Yam Tuber (*Pachyrhizus erosus*) by *Monascus purpureus* as an Alternatives of an Eco-friendly Textile Dyes

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Abstract. Potential dyes to be developed derived from fermentation by *Monascus purpureus*. As a staple food, rice can be replace to the yam tuber lees as a substrates. The purpose of this study was to compare the dyeability between fermented rice and yam tuber by *Monascus purpureus* on silk fabrics at the room temperature in any different pH of dyebath. *Monascus purpureus* first cultured on Potato Dextrose Agar for 7 days. Yam tuber peeled, grated and squeezed. The material is taken from yam tuber lees, then inoculated with *Monascus purpureus* for 14 days until an uniform red color obtained. The substrate is dried and then characterized by UV-Vis spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR). Dyes obtained from fermented rice and yam tuber then extracted and used for dyeing silk at room temperature with various pH of the dyebath. Results showed that dyeing silk with fermented yam tuber having the same color characteristics as fermented rice. The optimum color absorption at a wavelength of 520 nm for both, except on the results of dyeing using fermented yam tuber extract with pH 6 and pH 7. The maximum absorption is achieved at pH 3 with values dyeing K/S 5.840. Color fastness to rubbing are excellent (5 point) in dry rub, while the wet rub still good at the range of 4 to 4/5.
Keywords—*Monascus*; rice; yam tuber; fermentation; dyeing; silk

1. Introduction

Red is one of the primary colors that are rarely obtained from the dye derived from natural materials. There are 32 natural red dyes listed in Colour Index, they are extracted from the roots or bark of plants, or stands in the bodies of insects such as cochineal. However, the sources of these dyes are limited. Natural red dyes have been of significant and importance [1]. This resources are difficult to cultivate in large quantities. The difficulties arise mainly in terms of area planted, harvesting time, and degree of uniformity both of these natural ingredients when it grown in different environments [2].

IOP Conf. Series: Materials Science and Engineering **105** (2016) 012035 doi:10.1088/1757-899X/105/1/012035

One of the challenges in the production of natural dyes is the quantity of dye produced, especially during the extraction process. *Monascus purpureus* is one of biological source which has the ability to produce a red color during metabolism. Its small size and easily cultivated make this fungal has the potential to improve pigment production yields [3]. Fungi have the potential for use in production processes that are themselves less polluting than traditional chemical processes [4]. During this time, the use of dye from fermented by *Monascus purpureus* dominated for food coloration. *Monascus purpureus* able to produce a red color when grown on media which has a wide range of carbon sources, not only in the form of starch, but may include glucose, fructose, cellulose and others. The red color is generated not only from carbon but nitrogen is needed as a source of food.

Media that already in place to the growth of industrialization *Monascus purpureus* is rice. This reality is not in accordance with the main function of rice in human life. The function of rice as a staple food is the limiting factor is significant in industrialization *Monascus* dye. Therefore, we have to find another media that can be used as a growing medium of *Monascus purpureus*. Criteria required as a growing medium *Monascus* which have carbon and nitrogen sources are sufficient.

Almost all natural dyes have low affinity at room temperature, but in the case of natural dyes used in this study it does not apply. Therefore, the purpose of this study was to compare the dyeability between fermented rice and yam tuber by *Monascus purpureus* on silk fabrics at the room temperature in any different pH of dyebath.

2. Literary Review

2.1. Monascus purpureus

Monascus species produce orange, water-insoluble pigments such as monascorubrin and rubropunctatin. These well-characterized compounds can be converted to high-purity red, water-soluble pigments by reaction with amino acids, yielding monascorubramine and rubropunctamine. This red pigments commonly use as food colorants [4].

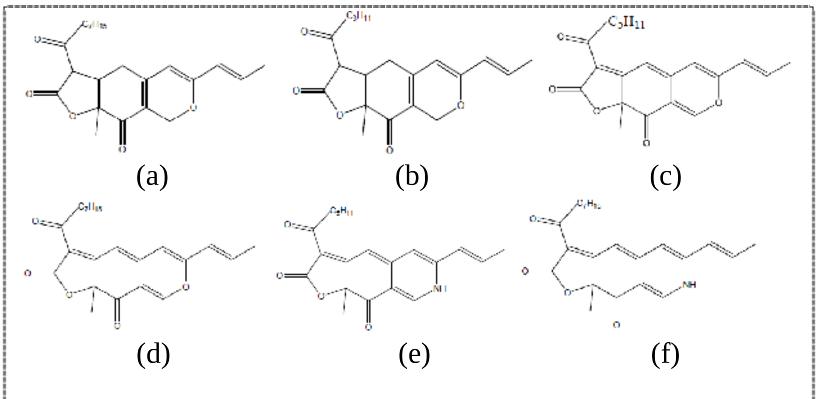

Figure 1. Chemical Structure of *Monascus* pigments, (a,b) yellow pigments, (c,d) orange pigments, (e,f) red pigments

Parameters that play a role in the production of the dye is nutrient content, pH, inoculum size, temperature, and moisture content [5]. Substrates that have the potential to produce pigment during fermentation, especially that contain starch (amylose and amylopectin), dextrin, glucose, maltose, galactose, fructose as a carbon source, and a protein as a source of nitrogen. The use of rice as a fermentation medium becomes significant constraints when it is connected to human consumption. Therefore, some of the research that has been developed is the search substrate capable of producing fermentation product quality without having to use a staple food. Media substrate selected in the present study is the yam tuber lees. Yam tuber lees provide as a substrate because it is not a staple food, but has a carbon content and nitrogen.

Production of dyes by fungi is very advantageous because it can grow quickly, so productivity is high. In addition, fermentation methods which can be performed on solid media or better known as solid state fermentation will produce a dye with a large amount but the cost of relatively lower than in the submerged media [5].

2.2. Dyeing silk with natural dyes

There are many types of fibers and substrates used in the textile industry. The dyeability of a substrate varies according to the material properties, such as surface properties, ionic character, roughness, structure, penetration and swelling properties [2].

Textile coloration using red dye from Monascus has been studied previously in cotton and wool fibers. Coloration on cotton fiber yield a pale red color [6,7,8]. The kinetics and thermodynamics of monascus red dyeing on wool fiber also has been studied [9].

Silk is a protein-based fiber produced as a continuous filament by the larva from a variety of insects and spiders. Silk produced in the form of two filaments consisting fibroin and glued together by sericin. Fibroin consists of many amino acids linked together [10]. Under acid conditions amino groups in the protein fibers are protonated to form NH3+ groups. In this form, they are able to attract dyes containing acid anions. Natural dyes from many sources have good affinity for protein fibers and often in conjunction with mordants [11].The existence of both these functional groups result the ability of silk to hold an ionic bond with the dye. Fastness tests are important tools for assessing the quality and the stability of dyeing.

3. Materials and Methods

The material used was Monascus purpureus obtained from the Laboratory of Microbiology, Chemical Engineering, ITB. Rice and yam obtained from traditional markets in East Bandung area. Research took place in the laboratory of chemical analysis and laboratory of textile physical chemistry, Politeknik STTT, Bandung.

1.1 Monascus Purpureus

Monascus purpureus cultures obtained from the microbiology laboratory of Chemical Engineering, Institut Teknologi Bandung. Culture of *Monascus purpureus* then maintained on Potato Dextrose Agar (PDA) medium.

Figure 2. *Monascus purpureus* culture

1.2 Inoculation Process

Yam tuber and rice washed and dried, then crushed using a blender. Yam tuber smoothed then squeezed and taken the dregs. Yam tuber lees is dried in an oven at 50 °C for 2 days. 40 grams yam tuber lees and rice put into the different Erlenmeyer, then moisture content was adjusted to 50%. Yam tuber lees and rice then sterilized at 121oC for 20 minutes and cooled at room temperature. Both media were inoculated with Monascus purpureus suspension to form a permanent red color on a substrate. Erlenmeyer shaken every day. The fermented solid was dried for 48 hours at 50°C in the oven. The dried fermented solids then grind by using blender.

(a) (b) (c)

Figure 3. *Monascus purpureus* culture (a) yam tuber lees before fermentation (b) rice before fermentation (c) after fermentation

1.3 Dyes Characterization and Measurement

Each 1 gram of fermented yam tuber and rice mixed with 95% ethanol as much as 5 ml. The mixture is then rotated at 200 rpm for 1 hour, then filtered. Filtrates diluted with dilution factor 20. The optical density (OD) measured using Genesys UV-Vis Spectrophotometer at 400, 470, and 500 nm.

$$Unit\ OD = \frac{OD\ x\ solvent\ volume\ x\ dilution\ factor}{sample\ mass\ (g)} \quad (1)$$

Monascus dyes measured by using 25 ml extraction from previous dyes characterization. Monascus dyes extract dryed at 80^{o}C and solid content remained measured by analytical balance.

$$Dyes\ concentration = \frac{solid\ content\ (g)}{volume\ of\ extract\ (L)} \quad (2)$$

1.4 Analitical of Functional Group using Fourier Transform Infra Red Spectroscopy

FTIR spectroscopy testing done at the Laboratory of Analytical Chemistry ITB. Measurements carried out by a laboratory technician at the Laboratory of Analytical Chemistry, ITB.

1.5 Dyeing Process

4 grams of Monascus dyes from fermented rice and yam tuber extracted using water until the last extract obtained colorless solution. Silk was dyed with Monascus dyes extract in the range of pH 2-7 at intervals of 1 and liquor ratio 1 : 100. Dyeing process took place at room temperature using HT dyeing machine. After dyeing process, samples were washed with detergents then rinsed with cold water.

Figure 4. *Dyeing process*

1.6 Color Measurement

Dyed samples was measured using Premier scan SS 6200 Spectrophotometer. The data generated in the form of reflectance, K/S, and color coordinates refers to the CIE Lab. K/S expressed the value of color strength and determined using Kubelka Munk equation below.

$$K/S_{\text{of Dyes}} = K/S_{\text{after dye}} - K/S_{\text{before dye}} \quad (3)$$

1.7 Fastness Properties

Fastness properties of silk dyed tested refers to SNI standard methods, “SNI 0288:2008 - Kain - Cara uji tahan luntur warna – Gosokan” [12]. Color fastness to rubbing using a crockmeter then the discoloration evaluated by staining scale.

4. Result and Discussion

4.1. Dyes Characterization and Measurements

The optical density of dyes from Monascus through fermentation on yam tuber and rice can be seen at the Table 1.

Table 1. Optical Density of Yam Tuber and Rice Fermented

Wavelength	500
Yam tuber lees	4.66
Rice	22

Optical density of each fermentation medium extract showed dyes production. The higher the optical density, means higher dyes production. The concentration of the dye contained in each of the substrate measured by the following values. At 500 nm the red color substances formed at the end of the growth phase of the Monascus.

Table 2. Dyes Concentration in Yam Tuber Lees and Rice Fermented

Media	Concentration (%)
Yam tuber lees	9.24
Rice	43

Yield of Monascus dyes on fermented rice greater than fermented yam tuber lees. The substrate from yam tuber lees is a starch residual waste, so that the potential dye formed lower, due to nutritional deficiencies. Nonetheless, yam tuber still potential as a medium and capable of producing Monascus dyes.

4.2. Analitical of Functional Group using Fourier Transform Infra Red Spectroscopy
Infrared spectra is a simple absorption spectra that can identify functional groups. Test sample analyzed shot through the infrared radiation that whenever energy is equivalent to a particular and specific wavelength is absorbed, then the intensity of the radiation that reaches the detector will decrease, and then recorded in the spectrum. Measurement of infrared spectra were recorded using a frequency wavelengths (cm-1) which is an inversion of the wavelength in centimeters (500-4000 cm-1). The energy required to excite vibrations of bond indicated by wavelength or frequency.

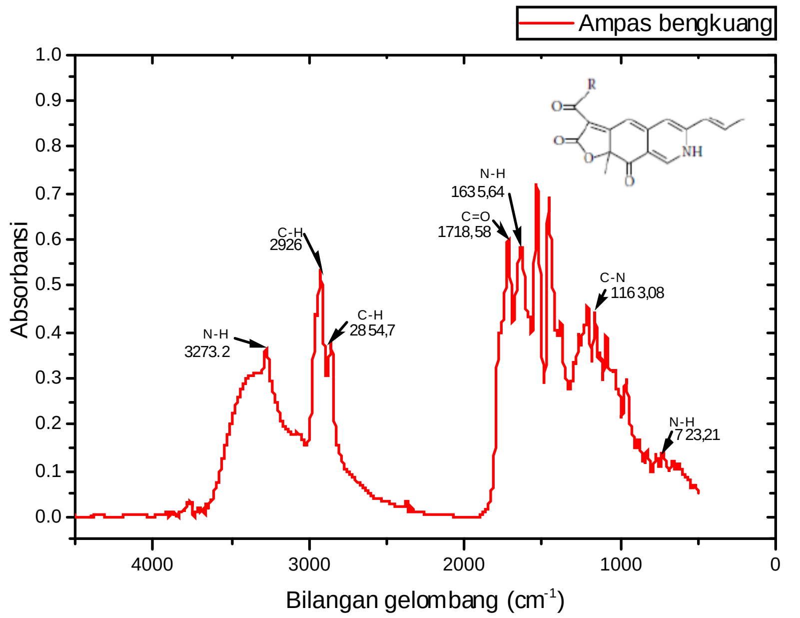

Figure 5. *FTIR spectrum of fermented yam tuber lees*

Based on the results of the FTIR spectra, both of extracts from fermented bengkoang and rice can be identified as Monascus dyes. The extracts has an aromatic compound with a ketone group, carboxylic, amines and other groups that are identical to the criteria of Monascus dyes.”

4.3. Dyeing Properties
The dyeing process was performed at room temperature for 45 minutes with pH ranges 2-7. Spectrophotometric measurements showed that the maximum wavelength which is owned by the results of dyeing both types of dye is in the area of 520 nm, except for yam tuber extract pH 6 and 7 shifts to the maximum wavelength 510 nm as shown at Fig.6 and Fig. 7.

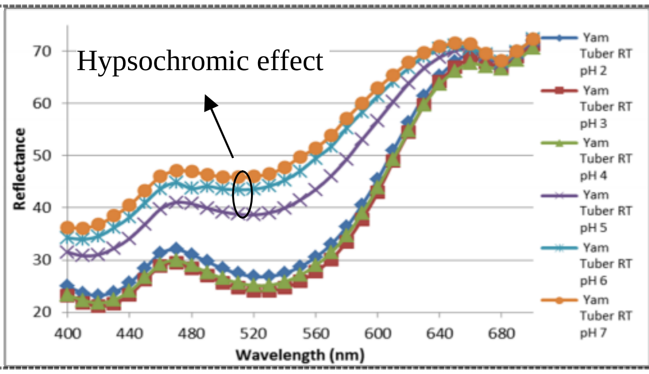

Figure 6. *Reflectance of each silk fibre using fermented yam tuber lees extract*

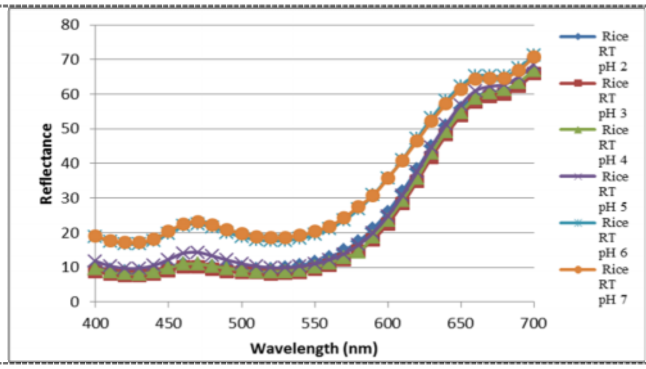

Figure 7. *Reflectance of each silk fibre using fermented rice extract*

Comparison of the results of dyeing silk using fermented rice extract and fermented yam tuber extract can be seen in Figure 8. The image shown that silk dyed by fermented rice has a darker color than fermented yam tuber extract.

Differences of dyebath pH causes a difference of lightness and hue of samples. Lightness and hue of each sample given in Table 3 and Table 4. While L* represents lightness, lower lightness value represent higher color yield. a* and b* represent of hue. a* positive represent redder, a* negative represent greenish, b* positive represent yellowish, and b* negative represent bluish.

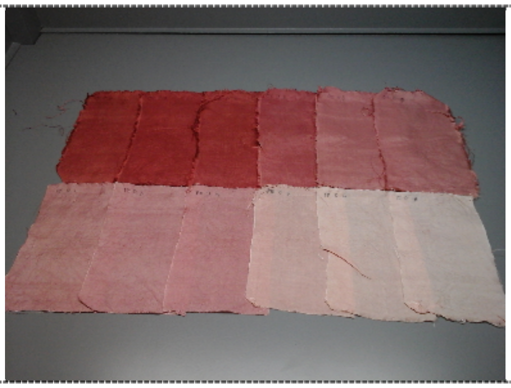

Figure 8. *Comparison of red silk dyed using fermented rice extract (above) and fermented yam tuber extract (below)*

Table 3. Color coordinates of fermented yam tuber lees

Media	L*	a*	b*
Yam tuber lees pH 2	65.344	18.806	9.272
Yam tuber lees pH 3	63.239	20.598	9.383
Yam tuber lees pH 4	63.927	19.747	9.821
Yam tuber lees pH 5	73.184	12.562	11.047
Yam tuber lees pH 6	76.215	10.535	11.643
Yam tuber lees pH 7	77.943	9.306	10.729

Table 4. Color coordinates of fermented rice

Media	L*	a*	b*
Rice pH 2	46.781	30.575	17.041
Rice pH 3	43.538	32.131	15.239
Rice pH 4	45.677	30.594	14.946
Rice pH 5	47.583	29.767	11.048
Rice pH 6	57.131	24.215	10.257
Rice pH 7	57.416	22.36	10.082

Based on lightness values in Tables 3 and 4 shows that the lightness obtained on silk dyed with fermented rice lower than bengkoang fermentation. Hue of silk dyed was seen that all the results of dyeing using the two extracts have a yellowish red color direction. From the color coordinates listed and maximum absorption at wavelength area of 510 – 520 nm, very obvious that the dyes are red. Effect of pH during the dyeing process can be seen in Fig. 8. In this figure shows that the color strength increasing in the acidic condition to a pH of 3, whereas at pH 2 color strength declined again. Silk dyed with fermented yam tuber extracts at pH 6 and 7 were not included in the chart, because of the hypsochromic effect causing discoloration. Wavelength shift that occurs at pH 6 and 7 resulted into different colors produced by the other sample. This is what underlies the second sample can not be compared in terms of color strength. Color strength can only compared to the conditions the same maximum wavelength

Table 5. Color coordinates of fermented rice

K/S After dyeing			**K/S of Dyes**		
Wave length (nm)	510	520	Wave length (nm)	510	520
Rice RT pH 2	5.185	5.190	Rice RT pH 2	4.831	4.840
Rice RT pH 3	5.879	6.190	Rice RT pH 3	5.525	5.840
Rice RT pH 4	5.623	5.667	Rice RT pH 4	5.270	5.318
Rice RT pH 5	4.785	4.984	Rice RT pH 5	4.431	4.635
Rice RT pH 6	2.694	2.752	Rice RT pH 6	2.341	2.402
Rice RT pH 7	2.547	2.594	Rice RT pH 7	2.194	2.245

Table 6. Color coordinates of fermented rice

K/S After dyeing			**K/S of Dyes**		
Wave length (nm)	510	520	Wave length (nm)	510	520
Yam tuber RT pH 2	1.686	1.731	Yam tuber RT pH 2	1.332	1.381
Yam tuber RT pH 3	1.903	1.959	Yam tuber RT pH 3	1.550	1.610
Yam tuber RT pH 4	1.824	1.865	Yam tuber RT pH 4	1.471	1.515
Yam tuber RT pH 5	1.095	1.100	Yam tuber RT pH 5	0.742	0.751
Yam tuber RT pH 6	0.932	0.930	Yam tuber RT pH 6	0.579	0.580
Yam tuber RT pH 7	0.861	0.857	Yam tuber RT pH 7	0.507	0.508

Improved results of color strength dyeing extracts fermented yam tuber and rice occurs due to the acidic conditions an increase in the number of positive charge of the fibers. Under acid conditions amino groups in the protein fibers are protonated to form NH_3^+ groups. Silk which has the amine group ionized to form positive charges that interact via ionic bonds with the negatively charged dye.

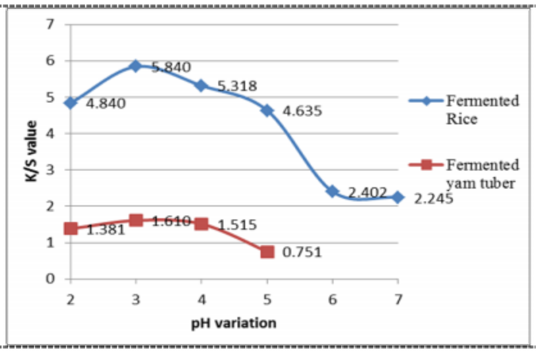

Figure 9. *Color strength of silk on various dye bath pH condition*

4.4. Fastness Properties

Color fastness to rubbing is done in dry and wet conditions to determine the response of individual fibers to rub against different conditions. Staining scale for each sample are given in Table 7and Table 8.

Table 7. Color fastness to rubbing of fermented rice

	Color fastness to rubbing	
	Dry	Wet
Rice pH 2	5	4/5
Rice pH 3	5	4/5
Rice pH 4	5	4/5
Rice pH 5	5	4
Rice pH 6	5	4
Rice pH 7	5	4

Table 8. Color fastness to rubbing of fermented yam tuber lees

	Color fastness to rubbing	
	Dry	Wet
Yam Tuber pH 2	5	4
Yam Tuber pH 3	5	4
Yam Tuber pH 4	5	4
Yam Tuber pH 5	5	4/5
Yam Tuber pH 6	5	4/5
Yam Tuber pH 7	5	4/5

Table 7 and Table 8 shows that the results of color fastness to rubbing in dyeing silk with fermented rice and yam tuber in dry conditions does not give the staining of the upholstery (staining scale value 5-excellent), while the results of color fastness to rubbing in dyeing silk with fermented rice and yam tuber in wet conditions give a little staining on upholstery (staining scale value 4-good to 4/5-very good). It is informed that the dyes used to color silk has excellent ability to bind to the fibers. Fastness to rubbing lower in wet conditions, it occur because the dye is applied to the silk has a solubility in water, so that when in contact with water, then the abrasion happened on the surface of the fiber, the dye is initially retained in the fiber migration to the surface of the upholstery.

5. Conclusion

In this research, the dyeing properties of fermented rice and yam tuber lees colorants were studied. Dyeing silk with fermented yam tuber lees having color characteristics like rice fermented rice. The optimum color absorption at a wavelength of 520 nm for both, except on the results of dyeing using yam tuber fermented extract with pH 6 and pH 7. The maximum absorption is achieved at pH 3 with values dyeing K/S 5.840. Color fastness to rubbing are excellent (5 point) in dry rub, while the wet rub still good at the range of 4 to 4/5. Based on this study, the yam tuber can be used as an alternative substrate instead of rice in the production of natural dyes through fermentation by Monascus purpureus.

6. Acknowledgement
We would like to thank the Politeknik STTT Bandung (Sekolah Tinggi Teknologi Tekstil) for license usage of Analytical Instrumentation, for Microbiology Laboratory, Chemical Engineering, ITB for the provider of Monascus purpureus.ity and for Analytical Chemistry Laboratory, Chemistry Department, ITB.

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