Absorption of dyes from mixed fungi by cotton fabric with distinct mordants and dyeing pH

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Abstract. Cotton fabrics processed in dyes with different mordants and staining pH might alter colors variation and dye absorption. A recent study showed a mixture of Aspergillus and Paecilomyces can be used to dye cotton fabric using five different mordant chemicals, CuSO$_4$·5H$_2$O, FeSO$_4$·7H$_2$O, KAl(SO$_4$)$_2$·12H$_2$O, K$_2$Cr$_2$O$_7$, and MnSO$_4$·H$_2$O, and three distinctive dyeing pH (3, 7, and 11). Both fungi were collectively cultured on mineral salt glucose medium to a stationary stage in dark conditions for four weeks. The RHS color chart was used to determine the color of the filtrate and the spectrum of colors created on dyed materials. The results suggested that the color development and dye absorption of the fabrics were greatly affected by chemical compounds of mordant and the acidity degree of the dyeing process. The pH of the dyeing process has a greater impact on the absorption of fungal dyes by cloth than the mordant. Colors formed on cotton fabric can add colors variation to textile dyeing.

Keywords: absorption, coloring pH, cotton fabric, fungal dye (pigment), mordant.

1. Introduction

The expanding consumption of synthetic dyes in the textile industry produces wastes caused environmental problems. Not all of the dyes used to stain the fabric are fully absorbed into the fabric, leaving waste that will remain stable in nature. Amanuel et al. [1] reported that synthetic dyes are also known to contain chemical compounds that are carcinogens and are harmful to human health.

Natural dyes are often less harmful to the environment and offer several advantages over manufactured ones. Wang et al. [2] informed that natural dye beneficial properties, such as biodegradability and high environmental compatibility, are out of interest of current study in the use of dyes. Subramanian et al. [3] reported that the dyes are extracted from diverse natural origins such as animals, insects, microorganisms, minerals, and plants. Microbial pigments have increasingly become a research hotspot among natural dyes, according to Gong et al. [4], because of their diverse species, brief life cycle, and high output.

Ebrahim et al. [5] stated that fungi have been reported as a potential dyes producer. Various natural dyes from Aspergillus and Paecilomyces have been widely reported, such as brown dyes by Aspergillus nidulans [6] and A. niger (NRC 95) [7]; grey-purple dyes by Paecilomyces lilacinus and Paecilomyces sp. strain 542 [8]; melanin dyes by A. nidulans [6] and P. lilacinus [9]; orange dyes by Aspergillus isolates DUMB13 and DUMB14 [10]; purple dyes by A. sydowi A and E. qinxiangii [11]; orange-red by Aspergillus sp. strain R-2 [12] and Aspergillus sp. [13]; orange-white dyes by A. fumigatus [12]; red...
dyes by Aspergillus sp. strain 1 [14]; Isaria cicadae (formerly P. Sinclairii) [15; 13; 16]; and P. farinosus (I. farinosa) [15; 17]; and yellow dyes by A. chevalieri [18] and P. lilacinus [19].

Djufri [20] reported that the coloring process in the fabric is an interaction between the dyes and fabric fiber, and the movement of dyes to the internal part of fabric fiber. Johnson [21] informed that in general, the coloring process includes typically three stages that are: 1) dye transport to the fiber surface from the dyebath; 2) surface assimilation of the dye molecule at the fiber surface, and 3) diffusion of the dye from the surface to the inside of the fiber. Any of which can control the dyeing speed and the dyeing result.

In general, the pH of dye solution is critical in controlling dye adsorption or absorption capacity on textile materials. [22]. The impact of dyeing pH is connected to the relationship between pigment structure and textile materials [23]. Natural dyes are dyes yielded from a natural source and mostly non-substantive so they need chemicals called mordant in the form of metal salts that can increase the affinity between fabric (cotton, silk, and wool) and dyes [24]. The process of mordanting in principle is to condition the dyes that have been absorbed within a certain time so that a reaction occurs between the dye's material and the material used for mordanting.

The purpose of this study was to examine the dyeing pH and mordant effects on the absorption of dyes and colors of cotton fabrics dyed with the combination of fungi of Aspergillus and Paecilomyces.

2. Materials and Methods
2.1. Materials
The strains of Aspergillus and Paecilomyces utilized in this investigation were obtained from the soil at the Cibinong Science Center (CSC) in Indonesia. Because of its broad usage in consumer items and natural dyes research, Japanese cotton (bought from Bogor Market in Bogor, Indonesia) was chosen as the substrate. The research was carried out at the Environmental Microbiology Laboratory of the Research Center for Biology of the Indonesian Institute of Sciences (LIPI) in Cibinong. Analytical grade Merck chemicals were utilized, as well as technical grade KAl (SO₄)₂.12H₂O from the Bogor local market.

2.2. Methods
2.2.1. Inoculation process
The technique modified by Suciatmih et al. [25] was employed to inoculation mixed culture of Aspergillus and Paecilomyces, whereas the mineral salt glucose (MSG) medium was used for color synthesis [26]. Following the incubation time, the cultures were passed through five layers of cheesecloth to remove particles, and the filtrate was centrifuged (Kubota 6500, Japan) at 8500 rpm for 20 minutes [27]. The optical density of the filtrate was measured spectrophotometrically (Shimadzu, Japan) at 530 nm to quantify the dyes [25; 27]. The dyes' yield was estimated in OD units (UA530).

2.2.2. Dyeing procedure
Fabric dyeing with fungal dyes is carried out in two stages as follows:
1. Pre-mordanting
Fabric samples (4 cm x 4 cm or 0.24 g) were treated with or without pre-mordanting using 1.2 percent of each mordant (CuSO₄.5H₂O, K₂Cr₂O₇, MnSO₄.H₂O, alum, and FeSO₄.7H₂O) at a 1: 30 w/v (material: mordant) ratio at 90 °C for 30 minutes before the dyeing process. The cloth is then removed, squeezed, and air-dried at room temperature.
2. Dyeing
Various dyeing pH (3, 7, and 11) tests were carried out to determine the best dyeing pH. The inherent pH of the fungal dye solution was 7.41, which was altered to 3, 7, and 11 for dyeing using HCl and NaOH. Fabric samples were treated with dyes at different dyeing pH with the ratio of material to dyes being 1: 30.
The dyeing was done at 90 °C for 30 minutes and allowed to soak for 90 min. The stained cloth is then removed, rinsed with water, and dried at room temperature. The RHS color chart determines the color of the cloth after dyeing from each procedure [28]. Each treatment is repeated twice.

2.2.3. Absorption of dyes by fabric
The optical density of a dye solution sample at 530 nm was used to measure the proportion of dye absorption by the fabric [25; 27]. The following calculation is used to compute the percentage of dye absorption (%):

\[
\text{Percentage of dye absorption} = \left( \frac{\text{OD before dyeing} - \text{OD after dyeing}}{\text{OD before dyeing}} \right) \times 100
\]

3. Results and Discussion
On MSG medium, a mixture of Aspergillus and Paecilomyces developed a greyed-purple 187A dye with an absorbance of 4.67 UA/L (Figure 1). Suciatmih et al. [25] and Suciatmih [29] found that the same mixed fungus generated the same hue. The fungal dyes were included in the group of substantive dyes which produce a fast color just by boiling without mordant [30]. This result is obtained the same results of Suciatmih [29] on the same mixed fungus cultivated in the Backer and Tatum medium (1998) that yielded substantial dyes.

The dyeing process in this investigation was utilized in a variety of mordant treatments (Al\(^{3+}\), Cr\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), and Mn\(^{2+}\)) and dyeing pH levels of 3, 7, and 11. Based on 18 different treatments (6 mordant types and 3 dyeing pH), fourteen different colors on the fabric were obtained (Table 1). Mordant [31; 14] and dyeing pH [8] play a very important role in imparting color to textile materials.

Figure 1. Greyed-purple dyes from the mixed Aspergillus and Paecilomyces
1) Dyes from the mixed fungi, and 2) Mineral salt glucose medium
Table 1. Color variations of the cotton fabric dyed with mixed fungi dyes using different mordants and dyeing pH.

| Mordant/dyeing pH | Dyed cloth colors |
|-------------------|-------------------|
| Control (without mordant) | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| CuSO₄·5H₂O | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| K₂Cr₂O₇ | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| MnSO₄·H₂O | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| KAI (SO₄)₂·12H₂O | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
| FeSO₄·7H₂O | ![Image](image16.png) | ![Image](image17.png) | ![Image](image18.png) |

A single dye source mixed with variable dyeing pH results in a diversity of hues on the cloth. The fabric dyed with the dyes at an acidic pH (3) produced a 176D greyed-orange color; at a neutral pH (7) a violet 87A was obtained, and at an alkaline pH (11) showed an 89D violet-blue color. The findings of this investigation showed that fabric colored with dyes applied with varied dyeing pH generated diverse colors on the cloth. Suciatmih and Yuliar [8] found similar findings on woolen yarn colored with fungal dyes with varying dyeing pH (3, 6, and 9), as did Ren et al. [32] on wool fabric dyed with tea extract with different dyeing pH (3.5, 5.5, 7.5, and 9.5). Changing the pH of the dyes can change the color of the dyes of mixed Aspergillus and Paecilomyces [33] and tea polyphenols and tea pigments [32]. According to Wang et al. [2], the ionic nature of the dyes may allow for changes in the molecular structures depending on the prevailing pH values, resulting in varied hues at different pH levels.

Mordants type added to different dyes pH changed the color of the dyed fabric (Table 1). The addition of mordants (Al³⁺, Cu²⁺, Fe²⁺, K⁺, and Mn²⁺) to the dyes with a pH of 3 each changed the color of fabric that was originally 176D grayed-orange into 199C grey-brown, 89D violet-blue, 182D grey-red, 186C greyed-purple, and 94A violet-blue. Different mordants at a pH of 7 each changed the color of fabric that was originally colored 87A violet into 89D violet-blue, 87B violet, 87C violet, 87C violet, and 94A violet-blue. Different mordant applications added to the pH of dyes 11 each changed the color of fabric...
that was originally 89D violet-blue into 89C violet-blue, 94A-B violet-blue, 94B violet-blue, 94C violet-blue, and 94A violet-blue. This study showed that different mordants added to dyes pH 3, 7, and 11 changed the color of the fabric. This color changing is due to the reaction of diverse metal cations in the mordant namely Al\(^{3+}\) in KAl(SO\(_4\))\(_2\)·12H\(_2\)O, Ca\(^{2+}\) in CaCO\(_3\), Cr\(^{3+}\) in K\(_2\)Cr\(_2\)O\(_7\), Cu\(^{2+}\) in CuS\(_2\)O\(_4\)·5H\(_2\)O, Fe\(^{3+}\) in FeS\(_2\)O\(_4\)·7H\(_2\)O, and Mn\(^{2+}\) in MnS\(_2\)O\(_4\)·H\(_2\)O. The mordant type used during the dyeing process affects the characteristics of color shadings on the fabric [14].

PH and mordant each play a role in producing different colors on the fabric. Different mordants added to the dyes with pH 3 yield 6 fabric colors; with the pH dyes 7 was obtained 5 fabric colors, and with the pH dyes 11 showed 6 fabric colors. This study showed that different mordants applied to the pH of the dye of 3 and 11 produced more varied fabric colors (each 6) than pH 7 (5 colors). Except for Fe\(^{2+}\) (1 color, 94A violet-blue), the addition of other mordants, namely Al\(^{3+}\), Cu\(^{2+}\), K\(^{+}\), Mn\(^{2+}\), and control, to different dyeing pH (3, 7, and 11) each created three distinct colors on the fabric. This study indicated that the addition of various mordants to different dyeing pH created more variegated colors on the cloth, except for Fe\(^{2+}\). According to Haar et al. [34], the type of mordant affects the fiber-dyes association.

Metal ions from mordants would work as electron acceptors to create coordination bonds with dye molecules as electron donors, to produce new colors, and increase dye solubility, color depth, and colorfastness in fabric [35].

Dyeing pH has a significant effect on the dye absorption process. The effect of dyeing pH is presented in Table 2. The dyes absorption by fabrics with the dyeing pH of acid (3) (20.772 ± 0.017) and alkaline (11) (43.596 ± 0.011) was greater than the pH of neutral dyeing (7) (9.783 ± 0.021). The same phenomenon also occurs when dyeing pH is combined with mordant. The absorption of dyes by fabric added with different mordants in the pH of acid and alkaline dyeing was also greater than the pH of neutral dyeing. For example, the absorption of the dye by fabric with dyeing pH of acid (3) combined with alum (51.622 ± 0.023) and alkaline (11) combined with alum (34.700 ± 0.012) was also greater than the combination between the pH of neutral dyeing (7) and alum (3.923 ± 0.022). The results showed that the absorption of dyes without or with different mordants in acid and alkaline dyeing pH was greater than neutral dyeing pH. In other words, dyeing pH has a significant effect on the absorption of the dye by fabric than mordant. Higher dye absorption also tends to result in a wider range of colors on the cloth (Table 1 & 2). A similar result was reported by Mukherjee and Kanakaraja [36], Velmurugan et al. [23], and Jabar et al. [37] on the higher dye uptake of cotton materials in acidic pH.

According to Jabar et al. [37], the high dye absorption of cotton materials in dyeing pH of acid (3) could be due to dye molecules migrating from solution into fabric matrices as a low molecular weight compound, which then underwent an acid-catalyzed in-situ polymerization reaction when the dyeing temperature was raised to 90°C. According to Jabar et al. [37], the high dye absorption of cotton materials in dyeing pH of acid (3) could be due to dye molecules migrating from solution into fabrics matrices as low molecular weight compounds, which later underwent acid-catalyzed in-situ polymerization reaction as dyeing temperature was raised to 90°C. The dye molecules in the fabric matrix became larger to leach out of the colored materials' pore locations.

Hossain et al. [38] observed a similar result on dye absorption on cellulose fiber, which increased with increasing pH value, however, the difference was not significant when using a higher pH than 10.5. The addition of sodium hydroxide overcomes the potential barrier by increasing the pH and decreasing the repulsion between the charged fiber surface and colored dye anions by imparting oppositely charged ions with the charged dye anion. This procedure enhances dyeability [39].
Table 2. Absorption of dyes from mixed fungi by cotton fabric using different mordants and dyeing pH.

| Mordant/dyeing pH | % Absorption of dyes by cotton fabric |
|-------------------|-------------------------------------|
|                   | 3        | 7        | 11       |
| Control (without mordant) | 20.772 ± 0.017 | 9.783 ± 0.021 | 43.596 ± 0.011 |
| CuSO₄·5H₂O        | 45.285 ± 0.010 | 9.690 ± 0.011 | 37.328 ± 0.025 |
| K₂Cr₂O₇          | 49.459 ± 0.014 | 6.650 ± 0.029 | 7.951 ± 0.022 |
| MnSO₄·H₂O         | 44.111 ± 0.019 | 5.816 ± 0.031 | 34.007 ± 0.014 |
| KAI (SO₄)₂·12H₂O | 51.622 ± 0.023 | 3.923 ± 0.022 | 34.700 ± 0.012 |
| FeSO₄·7H₂O        | 44.729 ± 0.026 | 4.126 ± 0.020 | 18.844 ± 0.028 |

4. Conclusion
Mixed fungi from *Aspergillus* and *Paecilomyces* produce dyes that can stain textiles. Fabric dyed with different dyeing pH conditions produces different colors. Different mordants added to different dyes' pH can change the color of the fabric. Different mordants applied to the pH of the dye of 3 and 11 produced more varied fabric colors (each 6) than pH 7 (5 colors). Except for Fe²⁺, the addition of other mordants to different dyeing pH produced more varied colors on the fabric. Absorption of the dyes without or added with different mordants in the pH of acid and alkaline dyeing was greater than the pH of neutral dyeing.

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